Study of interfacial reaction between Cu and Pb-free solders and rapid temperature cycling methodology for reliability assessment

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**STUDY OF INTERFACIAL REACTION
BETWEEN CU AND PB-FREE SOLDERS AND
RAPID TEMPERATURE CYCLING
METHODOLOGY FOR RELIABILITY
ASSESSMENT**

Submitted by

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School of Materials Engineering

A thesis submitted to Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy in Materials Engineering

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TERMINOLOGY

ATC	-	Accelerated Temperature Cycling
BGA	-	Ball Grid Arrays
C4	-	Controlled Collapse Chip Connections
CDF	-	Cumulative Distribution Function
CSP	-	Chip Scale Package
CTE	-	Coefficient of Thermal Expansion
DSC	-	Differential Scanning Calorimetry
DUT	-	Device Under Test
EDS	-	Energy Dispersive x-ray Spectroscopy
HCF	-	High Cycle Fatigue
h. c. p.	-	hexagonal-close-packed
IMC	-	Intermetallic Compound
I/O	-	Input/Output
LCF	-	Low Cycle Fatigue
MDS	-	Mechanical Deflection System
MTTF	-	Mean Time To Failure
NFM	-	Nonlinear (elastic-plastic) Fracture Mechanics
QFP	-	Quad Flat Packages
PCB	-	Printed Circuit Board
PDF	-	Probability Density Function
PTH	-	Pin-Through-Hole
PWB	-	Printed Wiring Boards
RTC	-	Rapid Temperature Cycling
SEM	-	Scanning Electron Microscopy
SMT	-	Surface Mount Technology
SRP	-	Strain Range Partitioning
TBGA	-	Tape Ball Grid Array
TEC	-	Thermoelectric Cooler
TPB	-	Three-Point Bending
UTS	-	Ultimate Tensile Strength
XRD	-	X-ray Diffraction

Abstract

With environmental, legislative and commercial concerns, lead-free solders have been increasingly used to replace the Pb-containing solders. Common features of the popular lead-free solders are that all of them contain high percentage of Sn and their melting temperatures are higher than eutectic Sn-Pb solder. Typical reliability issues with these high Sn content solders are the rapid consumption of the main element Cu and excessive growth of intermetallic compound (IMC) at solder/Cu interface, leading to the poor joint reliability.

The global objective of this research endeavor is to inhibit the excessive growth of IMC and improve the properties of Sn-Ag-Cu lead-free solder alloy by adding small amount of Sb. The overall properties of Sn-Ag-Cu-xSb solder alloys have been studied. It includes the formation of IMCs in the solder joints during reflow and ageing processes, the growth kinetics and microstructural evolution of the solder joint, and the mechanical properties of the solder joints. The effects of Sb additives on IMC growth during reflow, and ageing process and effect on mechanical testing have been analyzed in detail. Effect of testing conditions, such as strain rate, temperature, and thermal ageing on the strength and fracture behavior of solder alloy and solder joints formed by Sn-bearing solders with Cu substrate have also been discussed.

The influence of Sb on the growth kinetics of IMC and interaction between Sn-3.5Ag-0.7Cu-xSb ($x = 0, 0.2, 0.5, 1.0, 1.5, \text{ and } 2.0$) lead-free solders and Cu during reflow is investigated firstly. Results show that some of the Sb particles are dissolved in the β -Sn matrix (Sn-rich phase), some of them participate in the formation of $\text{Ag}_3(\text{Sn}, \text{Sb})$ and the rest dissolves in the Cu_6Sn_5 IMC layer. Both thickness and grain size of IMC decrease when Sb is added into the Sn-Ag-Cu solder system, and there is a significant drop at the composition of about 1.0 wt%. The growth exponents of IMC suggest that the growth of IMC is mainly controlled by grain ripening, slightly influenced by interdiffusion and chemical reaction. The data also show that Sn-3.5Ag-0.7Cu with about 1.0 wt% Sb solder system exhibits the smallest growth rate and gives the most prominent effect in retarding IMC growth and refining IMC grain size. Based on the

phase diagram analysis and the observation of the microstructural evolution of the solder joints, a heterogeneous nucleation mechanism for retarding the IMC growth due to Sb addition is proposed.

To investigate the solid-solid interaction and growth kinetics of IMC formation in Sn-3.5Ag-0.7Cu-xSb ($x = 0, 0.2, 0.5, 0.8, 1.0, 1.5,$ and 2.0) solder joint, isothermal ageing is performed at temperatures of 100°C , 150°C , and 190°C respectively. The thickness of IMC decreases when Sb is added into solder system. There is a significant drop in IMC thickness when Sb percentage reaches 0.8 wt%. Results reveal that adding Sb in Sn-3.5Ag-0.7Cu solder system can increase the activation energy, and thus reduce the atomic diffusion rate, so as to inhibit the excessive growth of the IMC. Compared with Cu_6Sn_5 IMC layer, Cu_3Sn layer has much higher activation energy. Based on the observation of the microstructural evolution of the solder joints, a grain boundary pinning mechanism for inhibition of the IMC growth due to Sb addition is proposed.

Tensile tests of Sn-3.5Ag-0.7Cu-xSb ($x = 0.0, 1.0$ and 2.0) solder alloy and Sn-3.5Ag-0.7Cu-xSb ($x = 0.0, 0.8$ and 2.0) solder joint were also carried out in this work. The ultimate tensile strength (UTS) of Sn-3.5Ag-0.7Cu-xSb solder alloys has a logarithmically linear increase relation with strain rate and has a linear decrease with temperature. The effect of strain rate on the tensile strength can be explained by dislocation multiplication and dislocation-dislocation interaction. Tensile strength of solder joints drops with the ageing time. IMC growth leads to the ductile failure mode transferring to brittle failure at solder/IMC interface with increase in ageing time. Sb-containing solder alloys and solder joints have higher UTS than Sb-free solder alloy and solder joints due to solid solution hardening and particle hardening.

In this study, a thermoelectric cooler-based rapid temperature cycling (RTC) testing method was established and applied to assess the long time reliability of solder joints in tape ball grid array (TBGA) assembly. This RTC testing methodology can significantly reduce the time required to determine the reliability of electronic packaging components. A three-parameter Weibull analysis characterized with a parameter of failure free time was used for assembly reliability assessment. It was found that the RTC not only speedily assesses the long-term reliability of solder joints

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within days, but also has the similar failure mode and failure mechanisms observed in accelerated temperature cycling (ATC) test. Based on the RTC and ATC reliability experiments and the modified Coffin-Manson equation, the solder joint fatigue predictive life can be obtained. The simulation results are in good agreement with the test results from the RTC. As a result, a new reliability assessment methodology was established as a possible alternative to ATC for the evaluation of long-term reliability of electronic packages.

Chapter 1 Introduction

1.1 Background and motivation

The electronic industry widely uses solder alloy as interconnect materials in electronic packaging. As a joining material, solder provides electrical, thermal and mechanical continuity in electronic assemblies. The performance and quality of the solder are crucial to the integrity of a solder joint, which in turn is vital to the overall functionality of the assembly. With the rapid development of surface mount technology and the growing interest of flip chip and other advanced packaging technologies driven by the demands on high performance, small size, and low cost, the soldering of components to the boards becomes challenging and the reliability of the joint is being questioned. The failure of only a single solder joint can render a device, or an entire electrical system useless. Therefore, reliability of solder joints has become a critical aspect of electronic circuit reliability.

Since the advent of electronics, solders composed of Pb and Sn have been widely used throughout the industry. For many years, different compositions of Sn-Pb solders have been utilized practically in all various types and levels of microelectronic packages. Some of these applications include controlled collapse chip connections (C4), ball grid arrays (BGA), quad flat packages (QFP), plated pin through holes, and more. The most widely used Sn-Pb solder is the eutectic in composition, which is primarily due to the merits of good soldering properties, adequate melting temperature range, proper mechanical metallurgical and fatigue resistance properties. These factors, combined with Sn and Pb being readily available and low cost metals, make eutectic Sn-Pb an ideal soldering alloy for industrial applications. The soldering system that is mainly based on eutectic and near eutectic Sn-Pb alloys has been well developed and refined with many years of experience. A relatively well-established knowledge base about the physical metallurgy, mechanical properties, flux chemistries, manufacturing processes and reliability of eutectic Sn-Pb solders exists [1].

However, emerging environmental regulations worldwide, most notably in Europe and Japan, have targeted the elimination of Pb usage in electronic assemblies, due to the inherent toxicity of Pb. This has made the search for suitable “Pb-free” solders an important issue for microelectronics assembly [1]. Major solder paste vendors have research programs targeted at developing new alloys that can be “drop in” replacements for eutectic Sn-Pb. The favored Pb-free solder alternatives vary from region to region. Sn-Au, Sn-In, Sn-Bi, Sn-Ag, Sn-Cu, and Sn-Ag-Cu solder systems have been in use in the electronics industry for special applications. Recently, much more researches have been focused on Sn-Ag, Sn-Cu, Sn-Ag-Cu and various versions of those alloys with small amount of additions of other elements. However, the information regarding the characteristics of these alloys is frequently proprietary; there is relatively little information available in the open literature. Until now, no Pb-free candidate can fully replace eutectic Sn-Pb; some reliability issues must be resolved before the lead-free solder alloys can be put into common application.

One of the important issue in implementation of lead-free soldering is the excessive growth of intermetallic layer at the interconnects. Research results show that ternary Sn-Ag-Cu alloys comprise a family of lead-free alternatives that show highest promise among lead-free replacements. Sources of supply are sufficient and the alloys exhibit good wetting, fatigue resistance and good overall joint strength. However, A few researchers have reported that the growth rate of the intermetallic layer for Sn-Ag-Cu alloy is higher than that for Sn-37Pb alloy [2-8]. Comparing with the eutectic Sn-Pb solder alloy, the possible reasons of IMC excessive growth in Sn-Ag-Cu solder systems are: (1) The solder alloy has higher tin composition; it consumes more Cu during reflow, and forms the thicker IMC at the solder/Cu interface; (2) the reflow temperature of Sn-Ag-Cu is more than 30°C higher than that of Sn-37Pb, so that the reaction rate is higher; (3) In Sn-Pb solder alloy, when Sn atom reacts with Cu atom, a thin lead-rich layer appears at the solder/IMC interface, which reduces the rate at which substrates are dissolved by Sn.

The long-term integrity of a solder joint very much depends on the IMCs that are formed during the soldering process. When soldering to copper or nickel, formation of intermetallic compounds is necessary to achieve a good joint. However if this layer becomes too thick, the base metal or finish may be consumed by the formation of

IMC and this leads to poor joint reliability. IMC existing at the interface between solder and metallization also decreases fatigue strength due to the brittleness especially if this layer is thick [9].

IMCs such as Cu_3Sn and Cu_6Sn_5 form and grow during both soldering operation and system operation. For the solder interconnects, solders with enhanced mechanical properties are required for high reliability. One approach is to add metallic elements to the solder. If the added particles have superior mechanical properties compared to the matrix, the composite solder is expected to be stronger and more creep resistant than the solder alone [10]. It is reported that adding some elements such as Sb, Bi, and In will improve the mechanical properties and reliabilities [11-15]. However, the effects of elements addition on the microstructure evolution and IMC formation are seldom reported. According to the phenomenon of precipitate in liquid reaction [16-18], adding impurities might be a good way to inhibit IMC growth and improve the overall properties.

The kinetics of interfacial reactions of Sn-bearing solders with Cu is still not fully understood. A number of studies gave useful information about the growth kinetics of IMC. It is reported that the growth exponents of IMC range between 0.21-0.25 for the temperatures 187 – 300 °C [19-20]. Kim and Tu analyzed the kinetics of the ripening of scallop-like growth in eutectic Sn-Pb solder system, and reported that the ripening is considered to be non-conservative. The total volume of the Cu_6Sn_5 IMC increases with increasing reflow time and the grain size is proportional to $t^{1/3}$ [21-22]. So far, the growth kinetic parameter of IMC layer in wetting reaction is seldom reported for lead-free solder study. Discussions on the reaction mechanisms are still quite limited and incomplete.

Since solder joints are usually subjected to thermomechanical stresses at operating temperatures as high as 0.5 to 0.8 times of T_m (melting temperature) of the alloy, a significant amount of deformation is introduced by plasticity and creep throughout the strain cycle. The thermal and mechanical reliability of solder joints is one of the major issues that hinder the development of packages towards small print and high density connections with robust reliability. For reliability analysis of solder joints, it is necessary and important to understand the mechanical properties of solder alloys. In

the past decade, much research has been carried out to study the mechanical properties of solder alloys [23-27]. However, two problems have been noted in the publication. Firstly, the experimental results obtained by different researchers were found to differ considerably even for the same solder alloys. For example, the ultimate tensile strength (UTS) of Sn-Ag-Cu solder can vary from a minimum of 10 MPa [28] to a maximum of 80 MPa [29]. Thus, it is necessary to understand the apparently large discrepancies in order to use these data. Secondly, the temperature ramp rates of accelerated thermal cycling (ATC) tests, carried out at different laboratories, can vary from 8 °C/min to 20 °C/min [30], while temperature ramp rate can be as high as 50 °C/min in a thermal shock test, which is used to assess package resistance to sudden temperature change [31]. Therefore, it is desirable to know the mechanical properties over a wide range of temperatures and strain rates to interpret the results in these acceleration tests. Unfortunately, the past studies in this area mostly focused on the effect of temperature. There are rare investigations on the effect of strain rate [32-33].

For accelerated reliability testing of surface mount solder attachments, the most common reliability threat comes from stress-relaxation based (thermal) fatigue damage. The fatigue is caused by cyclic differential thermal expansion/contraction between the board, the component, and the solder itself. A temperature cycling test with conditions reflecting the intended use environment coupled with an acceleration factor provoking the right type of failures could provide valuable information. However, it normally takes several months to complete a test and this is very time-consuming and expensive, especially, if it takes more than half a year to evaluate lead-free components. The electronics packaging industry is motivated to shorten product development cycle time while maintaining desirable levels of quality and reliability. Hence, a highly accelerated testing method that reduces the cycle time and can mimic true operating environments is greatly sought after for the understanding of wear-out reliability characteristics of packages.

1.2 Objectives

Based on the above research background, this thesis reports several soldering related issues of Sn-3.5Ag-0.7Cu-xSb solder alloys and solder joints. In order to inhibit the excessive growth of IMC and improve the properties of Sn-Ag-Cu alloy system, Sb element is added in this alloy system. The study covers IMC growth in both liquid state and solid state reactions, the effect of Sb on the formation and growth of IMCs, and the growth kinetics of IMCs in reflow and thermal ageing processes.

The thesis aims to provide a systematic understanding of the correlation of the microstructure and the mechanical properties of these Sb-containing solder joints. The effects of testing parameters on the mechanical property have been studied as well. Such studies would provide guidance to understand the mechanical behavior of lead-free solder joints from the microstructural point of view. Finally, a new rapid reliability testing system is set up to shorten the time of reliability test and to try to replace traditional ATC. The work covers five separate but inter-related sub-topics as detailed below.

1.2.1 IMC growth and kinetics in as-soldered Sn-3.5Ag-0.7Cu-xSb solder joints

The objective of this part is to study the formation and growth of IMCs during reflow. The thickness of the intermetallic compounds (IMCs), in different Sn-3.5Ag-0.7Cu-xSb solder joints are measured and the IMC growth kinetics are investigated. Effect of Sb on the phase constituents and growth kinetics of the IMC formed at solder/Cu interface during liquid state reaction is also studied.

1.2.2 IMC growth and kinetics in Sn-3.5Ag-0.7Cu-xSb solder joints during ageing

In this part of study, the solid-state interaction of various Sn-3.5Ag-0.7Cu-xSb solder joints in thermal ageing is compared. The objectives are to determine the IMC growth rate and activation energy in different solder systems, compare the effects of the addition amount on the IMC growth and explore the mechanisms of inhibition of the IMC growth.

Since Sb additive affects IMC growth in different layers, the growth kinetics of two IMC layers is studied separately to further understand the inhibition effect of Sb on IMCs growth.

1.2.3 Effect of testing parameters on mechanical properties of Sn-3.5Ag-0.7Cu-xSb solder alloys and solder joints

The objective of this part is to study the mechanical behavior of the Sn-Ag-Cu-Sb lead-free solder alloys and solder joints under different testing parameters, to understand the correlation between microstructure and the mechanical performance of the solder joint, to evaluate the additive effects on the mechanical properties of the solder joint, and to chose the best-fit additive to the Sn-Ag-Cu solder system.

1.2.4 New methodology of reliability assessment of solder interconnects

The main aim of this part is to develop a rapid temperature cycling (RTC) testing methodology and apply it to advanced package for long-term reliability assessment. ATC test is conducted as a basis of comparison for the results from the RTC methodology. RTC numerical approach is further developed for the understanding the failure mechanism. Finally, a new and quick reliability assessment methodology is established as a possible alternative to ATC.

1.3 Organization of thesis

This thesis is logically divided into 8 chapters:

Chapter 2 discusses contemporary and relevant literature that relates to various topics pertaining to this research. These topics include current status of lead-free solder systems, the present understanding and unsolved issues of interfacial reaction between Cu pad and Sn-bearing solders, such as morphology and growth kinetics of intermetallic compounds, reaction mechanisms in both liquid state reaction and solid state reaction. And the main mechanical properties and reliability issues of Pb-free solders are also reviewed.

Chapter 3 gives short descriptions of the experimental procedures and techniques used for analysis.

Chapter 4 is devoted to detailed experimental investigation on IMC growth of Sn-3.5Ag-0.7Cu-xSb ($x = 0.0, 0.2, 0.5, 1.0, 1.5$ and 2.0) solder joints during reflow process. The formation and growth kinetics of IMC in several systems are compared. Sn-Ag-Cu-Sb phase diagrams are analyzed and the possible components in the liquid-solid state reaction are summarized. The effect of adding Sb is explored and a grain refinement mechanism is suggested.

Chapter 5 presents the growth of IMC bilayers in Sn-3.5Ag-0.7Cu-xSb ($x = 0.0, 0.2, 0.5, 0.8, 1.0, 1.5$ and 2.0) solder joints during ageing. Cu_6Sn_5 and Cu_3Sn layers are considered as a single system and separated layers respectively. The growth rate and activation energy of IMC are calculated. The effect of Sb additive on the growth kinetics of the IMC layers is investigated as well.

Chapter 6 discusses the tensile testing of Sn-3.5Ag-0.7Cu-xSb ($x = 0.0, 0.8$ or 1.0 , and 2.0) solder alloys and solder joints. The effect of testing parameters such as strain rate and temperature on the tensile strength of solder alloy are presented. Tensile strength is measured on specially prepared samples of solder joints under different thermal aging temperature. Failure mechanism of solder joints is studied. Effect of solder composition on fracture behavior of these three types of solder joints is discussed as well.

A rapid temperature cycling (RTC) testing system for evaluation of the long-term reliability of TBGA eutectic solder package is explored in chapter 7. A three-parameter Weibull distribution is used to evaluate the reliability of the TBGA package. The correlation of RTC and common accelerated temperature reliability assessment methodologies is also studied.

Chapter 8 wraps up the thesis with the conclusions and the proposal of some future work related to reliability of lead-free interconnects.

Chapter 2

Literature Review

2.1 Soldering in electronic packaging

Electronic packaging is the science and art of establishing interconnections to make a suitable operating environment for electronic circuits. A package generally contains a number of circuit components combined into a functional unit or module. Individual circuits must also be connected with each other to form functional units through an input/output (I/O) system of interconnects. Furthermore, the chip and its embedded circuitry require the package to carry and protect it. As a general rule, there are three levels of packaging from chip-level (first level) to module (second level), and boards –level (third level) [34]. The three-level packaging hierarchy is illustrated in Fig. 2-1. The major functions of the electronic package are: (1) to provide an electrical current to power the circuits on a chip, (2) to distribute the electrical signals, (3) to dissipate the heat generated by the circuit, and (4) to support and protect the chip from hostile environments.

Solder interconnections in the microelectronics packaging plays a crucial role. As a joining material, solder provides electrical, thermal and mechanical continuity in electronics assemblies. The performance and quality of the solder are crucial to the integrity of a solder joint, which in turn is vital to the overall functioning of the assembly. Solders are used in different levels of the electronic assembly sequence. As a die bonding material in first level packaging, the solder provides the electrical and mechanical connection between the silicon die and the bonding pad. It also serves as a path for dissipation of the heat generated by the semiconductor. While the predominant method of providing electrical connection to the silicon chip is by using solder bumps on the surface of the Si die, instead of wire bonding, has been gaining acceptance in recent years, due to the higher number of input/output terminals that can be attached to a given area. Solder is the primary means of interconnect in level 2 packaging. Practically microelectronic devices are mounted on printed wiring boards

(PWBs) using solders. There are two primary means of attaching electronic components to PWBs: pin-through-hole (PTH) or surface mount technology (SMT). Surface mounted electronic components can be leaded, leadless, or have solder balls that are called ball grid arrays (BGAs) [1].

Fig. 2-1 Packaging hierarchy

With the development of electronic communication, the design trend of electronic transmission equipment is improved toward miniaturization, thin and lightweight electrical products. The solder joint reliability is, therefore, a critical issue for the quality of electronic joints, which has experienced a long-term severe temperature excursion [35]. The reliability of solder joints is dependent on solder composition, soldering condition, and joint geometry. With appropriate joint design, the use of solder alloys with excellent properties, and the employment of a better process, reliable joints are obtained.

2.2 Lead-containing solders

Sn-Pb solders have had the longest history of usage in the soldering of electronic components. With a melting eutectic temperature of 183 °C, the Sn-37Pb (wt.%)

eutectic solder has been the alloy of choice in the electronics and interconnect industry for several decades [36]. Some of the advantages of the Sn-Pb solders include abundant and relatively inexpensive raw materials, low refining and production costs, excellent corrosion and chemical attack resistance. In addition, the eutectic Sn-37Pb has good wetting and electrical characteristics and offers reasonable thermal fatigue resistance [37]. Addition of Pb to Sn offers the following advantages:

1. Pb reduces the surface tension of pure tin, which is 550 mN/m at 232°C, and the lower surface tension of Sn-37Pb solder (470 mN/m at 280°C) facilitates wetting [38].
2. As an impurity in tin, even at levels as low as 0.1 wt.%, Pb prevents the transformation of white or β tin to gray or α tin upon cooling past 13°C [38]. The transformation, if it occurs, results in a 26% increase in volume and causes loss of structural integrity to the tin [39].
3. Pb serves as a solvent metal, enabling the other joint constituents such as Sn and Cu to form intermetallic bonds rapidly by diffusing in the liquid state.

These factors make it an ideal alloying element with tin. However, there are environmental and health issues concerning the toxicity of Pb in the Sn-Pb solder alloys. The lead is a heavy-metal toxin that can damage the kidneys, liver, blood, and central nervous system [4]. Depending on the level of exposure, Pb ingestion can:

1. Cause hypertension.
2. Cause cognitive and behavioral changes.
3. Delay neurological and physical development.
4. Cause nervous and reproductive system disorders.

The concern about the toxicity of lead has led to an increase in controls and legislation on the use of lead. In the early 1990s, U.S. Congress published a bill to ban Pb from a wide variety of uses, including electronic solders [1]. The European Union has recently delivered the WEE (Waste in Electronic Equipment) directive that proposes ban Pb usage in electronic products by 2008 [40]. Now the implementation of Pb-free soldering is coming to the center stage in electronic industry. For these

reasons there has recently been a great deal of research to find suitable Pb-free replacement solder alloys and to study their reliability [7, 41-42].

2.3 Lead-free solders

The issue of lead-free soldering has piqued a great deal of interest in the electronics assembly industry as of late. Various Sn based binary eutectic alloys such as Sn-Bi, Sn-In, and Sn-Ag, ternary and quaternary alloy systems that include Cu, Ag, Sb, In, and Bi as additives to Sn-based solders are being investigated as replacements to the conventional Sn-Pb solders. Melting point, wettability, resistivity and mechanical properties were a few of the essential parameters that need to be satisfactorily matched in order for a solder to replace the Sn-Pb solders omnipresent in the electronics industry [43].

The melting temperatures of such lead-free solder alloys are lower or higher than that of tin-lead eutectic. In theory, many solder alloys could meet these requirements and replace eutectic or near-eutectic Sn-Pb solder in surface mount assembly. Sn-Bi, Sn-In, and Sn-Ag eutectic and near-eutectic alloys are already used in some applications because of specific advantages they offer over eutectic Sn-Pb, such as lower process temperature, compatibility with particular substrates, or superior reliability under certain conditions [44-45]. However, these alloys may not be suitable substitutes because of issues about processing, reliability, or the cost, availability, or toxicity of the raw materials. These alloys can only achieve parts of the supreme properties of eutectic tin-lead alloy. Some applications of lead-free solders have been made for thermal sensitive electronic components. Nevertheless, these solders are susceptible to damage at high operating temperatures. Other lead-free solders, such as Sn-Cu solders, have high melting points. These types of solders cannot be applied to thermal sensitive electronic components, but they can provide strong joints [46]. In general, high tin alloys are preferred, including Sn-Ag, Sn-Cu, Sn-Ag-Cu, Sn-Ag-Bi. Sn-Ag-Bi systems are used in some Japanese products already. Normally, Sn-Ag-Cu systems are more tolerant toward Pb contamination than Bi-containing systems [47-48]. And also, minor additions to the eutectic systems of Ni (to improve mechanical properties), Sb (potentially to improve wetting properties), or Bi (to reduce melting point) were

also considered [49]. For example, Sn-Ag-Cu-Sb solder systems are reported to have greater mechanical performance than eutectic Sn-Pb solder alloy [9, 47].

2.3.1 Sn-Ag (Cu) based lead-free solders

After much research, the Sn-Ag-(Cu) families of lead-free alloys have demonstrated the most promise for lead-free applications. These alloys possess the various desirable attributes. Indeed, it appears that the industry is moving in the direction of embracing these alloys. Following is a summary of the benefits of each of the aforementioned elements:

- 1) Sn — relatively low melting point; long history as a solder constituent.
- 2) Cu — plenty supply; soluble in tin; works well in low percentages.
- 3) Ag — plenty supply; less cost prohibitive than other lead-free alloys when used in a minimum quantity.

2.3.1.1 Sn-Ag alloy

The eutectic composition for the Sn-Ag binary system occurs at Sn-3.5Ag. The eutectic temperature is 221 °C. It is one possible replacement of the Sn-Pb. This is because it is less toxic than Pb containing solders. It has good ductility and better creep and thermal resistance than those of the Sn-Pb solder. Although Sn-Ag eutectic solder melts at 221 °C compared to the 183 °C melting point of Sn-Pb eutectic solder, this may be acceptable for general applications.

According to Sn-Ag phase diagram, an alloy with the composition of 3.5 wt% Ag in Sn should have a microstructure consisting of eutectic mixture in the as solidified condition. However, in actual practice, as the cooling conditions are seldom close to equilibrium conditions, the microstructure deviates from the eutectic mixture: dendrites of primary Sn rich solid solution (almost pure Sn) with the interdendritic space being filled by an eutectic mixture of Ag₃Sn lamellae in a Sn rich solid solution matrix [43].

The Sn-Ag system has limited solid solubility of Ag in Sn, making it more resistant to coarsening. As a result, the Sn-3.5Ag alloy forms a more stable, uniform microstructure that is potentially more reliable. Compared with Sn-37Pb, however,

the Sn-3.5Ag has the poorest wetting for reflow soldering among high Sn alloys [50]. The poor wettability is caused by high interfacial tension between solder and flux that is probably related to the high surface tension of Ag. And comparing with other Pb-free solder, the growth rate of IMC is higher, which strong affects the reliability of the solder joint [47].

2.3.1.2 Sn-Cu alloy

Eutectic Sn-0.7Cu has a melting point of 227 °C. It has better mechanical properties than Sn-37Pb, but there are reliability fall-outs due to the high soldering temperatures that can cause printed board warpage, a problem that becomes more severe when multiplayer boards are used [51]. Preferably used for wave soldering because low material cost and inserting of waves not costly.

2.3.1.3 Sn-Ag-Cu alloy

The Sn-Ag-Cu alloy is one of the promising lead-free alloys currently because of excellent overall characteristics. These alloy have good strength, fatigue resistance and plasticity [49, 2, 52-56].

Ternary eutectic temperature is about 217°C, although the exact composition is to be clarified. Kim et al. [57] reported the large endothermic peaks of Sn-3.0Ag-0.5Cu, Sn-3.5Ag-0.7Cu and Sn-3.9Ag-0.6Cu alloys appear at 217.6, 217.5 and 217.4 °C, respectively. Additional endothermic reactions in a higher temperature range were observed for Sn-3.0Ag-0.5Cu and for Sn-3.9Ag-0.6Cu while Sn-3.5Ag-0.7Cu did not show any other significant reaction. Sn-3.5Ag-0.7Cu alloy may be the eutectic solder alloy [58-59].

Cu is added to Sn-Ag in order to slow the Cu dissolution, lower the melting temperature, and improve wettability, creep and thermal fatigue characteristics. The composition with 3.0 to 4.7 percent Ag and 0.5 to 1.7 percent Cu generally possess a higher tensile strength than Sn-37Pb [60]. Within this range of compositions, it is found that an increase in Ag content from 3.0 percent to a higher level (up to 4.7 percent) does not offer any enhancement in fatigue resistance. When both Cu and Ag

are in higher dosages, the plasticity suffers. The composition of Sn-3.1Ag-1.5Cu performs significantly better than Sn-37Pb in both strength and fatigue. Among the compositions, the alloy with a lower Ag content (Sn-3.1Ag-0.5~1.5Cu) exhibited the best balance of all desirable properties-melting temperature, strength, plasticity, creep resistance and fatigue life. Many research results show that Sn-Ag-Cu alloys are most promising lead-free solders.

2.3.2 IMC growth problems in Sn-(Ag)-X systems

For the Sn-contained solders with Cu substrate, because Sn is the reactive species, Sn and eutectic Sn-Ag, Sn-Cu, and Sn-Ag-Cu all form the same intermetallic compounds at the solder/substrate interface as eutectic Sn-Pb on Cu (Cu_6Sn_5 and Cu_3Sn) [61]. From the phase diagram for Cu-Sn, shown in Fig. 2-2, the intermetallic phases, ε and η phases are stable below 300°C. The ε phase has a composition range between 25.7 and 27.1 wt.% Sn, and corresponds very closely to the composition Cu_3Sn . The η phase has Sn concentration of between 44.8 and 45.5 wt.%, and corresponds to the composition Cu_6Sn_5 . The Cu_6Sn_5 layer forms adjacent to the solder side and the Cu_3Sn layer next to the Cu substrate. The Cu_6Sn_5 crystals are of the hexagonal-close-packed (hcp) order. The Cu_3Sn phase is normally only found on the copper surface and is orthorhombic. The interface between these two layers can shift with time of exposure and soldering temperature. The Cu_6Sn_5 layer is normally the thicker one, and its properties dominate the joint.

Fig. 2-2 Cu-Sn binary phase diagram

In the Sn-Ag, Sn-Ag-Cu alloys system, it was found that the η growth involved inclusion of Ag_3Sn . As the η layer grew into the solder during ageing, Ag_3Sn particles located near the solder/IMC layer interface became incorporated into the η phase. EDX showed that η and ϵ IMC layers in annealed solder joints did not appear to have dissolved Ag within them.

Many reports have showed Sn-Ag, Sn-Cu and Sn-Ag-Cu alloy systems are the most promising lead-free alloys [62-64], however intermetallics growth is a problem for the use of the alloy systems. Salam [2] reported the thickness of the intermetallic layer for Sn-4.0Ag-0.5Cu alloy after ageing was higher than that of the Sn-37Pb alloy, as seen in Fig. 2-3.

Figure 2-3 Intermetallic compound thicknesses ageing at 120°C

Lee et al. [3] compared the activation energy of Cu consumption, compound growth of eutectic Sn-Pb and those of Sn-Ag, Sn-Cu, and Sn-Ag-Cu lead-free alloys, the IMC growth rates of lead-free solders are larger than that of Sn-Pb solder.

Because of its brittle nature and microstructural mismatch between solder and copper, too thick a Cu-Sn IMC layer at the solder /Cu interface causes the interface in the solder joint to be more sensitive to stress [65]. Also, if the IMC becomes a significant fraction of the solder joint, it can act as a site for crack initiation and propagation when the joint is deformed. The results of most researches indicate that the growth of IMC layer plays a degrading role in the mechanical strength of solder joints. It is found that the mechanical strength decreases with the increase in the amount of IMC at the interface [66-68]. Tu [69] reported the lifetime and thickness could be described as a monotonically decreasing curve. The rapid decrease of lifetime is over the thickness range up to 1.4 μm , for further increase in IMC thickness the lifetime decreases more slowly.

Obviously, the IMC layer plays a negative role on the reliability of solder joint if it is too thick. Inhibiting the excessive IMC growth will improve the mechanical properties and reliability of solder joint.

Miric [9] discovered that the Sn-Ag and Sn-Ag-Cu alloys dissolve the copper very fast compared with eutectic Sn-Pb solder, but the dissolution rate slows down after the Sb, Bi elements addition, as the reason is unknown. Seelig [41] also reported that doping of Sb in Sn-Ag-Cu resists the formation of IMC; the mechanism is not clear and needs to be investigated. It is supposed that the elements addition can suppress the IMC growth.

2.3.3 Effects of additives in lead-free solders

In the last section we have shown many metal elements are available for lead-free solder alloys. However, only Sn, Ag, and Cu are considered as base materials for the conventional surface mount applications. This is because the left metals have some application disadvantages:

- 1) Sb — reduce the overall solderability of solders if its concentration is above 0.12 %; at high levels of Sb tends to raise the melting points of solders;
- 2) Bi — potential supply problems; embrittlement problems; poor thermal and electric conductor;
- 3) In — supply problems; too costly; corrosion and oxidation problems;
- 4) Ga — supply problems; too costly; embrittlement problems;
- 5) Zn — oxidation and embrittlement problems.
- 6) Ca — toxicity issue;

Nevertheless, a small amount of these metals could be added in lead-free solders to achieve specific properties.

a) Bismuth

There are many studies on the Bi addition into eutectic Sn-Ag solder alloy. Addition of less than 5 % Bi lowers the melting point and improves wettability of Sn-Ag systems [9]. Yoshiharu and Masahisa [13] found the Sn-3.5Ag fatigue life dramatically decreases with increasing contents of Bi and adding this element over 2 % made fatigue life shorter than that of Sn-Pb eutectic alloy. Tensile strength of the alloy significantly increased with an increase in Bi contents due to solid solution

hardening (less than 5 % Bi) or dispersion strengthening of fine Bi particles, while ductility of this system dramatically decreased with increasing Bi contents.

Kariya et al. reported the reduction of ductility is caused by Bi additions to Sn-Ag alloys [15, 70]. This has been shown to reduce the fatigue life at room temperature when the alloy is driven into plastic deformation and the authors suggested 2 per cent limit on Bi to avoid this problem [49].

Bi has the same approximate cost as Sn. Unfortunately Bi in soldering alloys tends to create embrittlement. Bi alloys also are prone to failure in peel strength tests due to poor fatigue resistance. It is suggested that 5 per cent Bi is the maximum solubility level in Sn to avoid the risk of forming the Bi-Sn (Ag) eutectic with its 139(137) °C melting point. In alloy with more than ~2.5 per cent Bi, Bi precipitates could form by prolonged low temperature exposure. At worst, these precipitates could form as a grain boundary film that could be disastrous on sudden heating to above 138 °C [71-73].

b) Indium

Lee [14] suggested that In-containing systems are more promising in terms of solder mechanical properties and soldering performance, although the price of In may be a concern.

Tensile strength of Sn-3.5Ag-In increases but its ductility decreases with increasing In content. The microstructural observation suggests that indium atoms are dissolved in solid phase of β - Sn. Thus, the increase in tensile strength through In addition is probably caused by solid solution hardening mechanism. Furthermore, this alloy also contains coarse and plate like phases of Ag_3Sn similar to those in Bi-containing alloy. The loss of ductility in Sn-3.5Ag-In alloy should also be ascribed to the irregularly shaped second phase Ag_3Sn [15].

The content of In at 5 percent in Sn-Cu-In effectively depressed the alloy melting temperature of 99.3Sn-0.7Cu from 227 °C to 217 °C. It increases the tensile yield strength together with a reduction in plasticity [74-75].

In-based lead-free solders are best used with temperature sensitive components that do not require high joint strength and will not be exposed to harsh or high-stress environments.

c) Zinc

People have expressed strong interest in the Sn-Zn system because of its relatively low eutectic temperature (198.5°C) comparing to several other investigated Pb-free solders. Sn-Zn solder also exhibits good mechanical strength and low cost [76]. In the mid 90s, alloys based on Sn-Zn were investigated for wave soldering, but were discarded because the zinc content gave poor corrosion properties, and the stability of zinc oxide make it necessary to use the highly active fluxes. This character renders Sn-Zn alloy to poor wettability. It is important to improve oxidation resistance of the Sn-Zn solder system in order to practically apply it in electronic packaging. By adopting proper flux chemistry, the oxidation problem of Zn could be avoided [77].

McCormack [78] found that with the addition of Zn to eutectic Sn-Ag, the Zn is incorporated into the Ag_3Sn precipitates. It refines the microstructure and trends to suppress the formation of Sn dendrites, which making the Ag_3Sn precipitate finer and more spherical. Zn has some solid solubility in Sn, so it can be expected to have some strengthening effect on the Sn matrix.

d) Antimony

Sb has several forms, the most common of which is a hard, silver-white crystalline solid. Sb has an atomic weight of 121.75, a melting point of 630.5°C, and a boiling point of 1635°C [79].

Sb can be added into Sn-Ag, Sn-Cu, Sn-Ag-Cu and Sn-Pb solder systems. Adding Sb has the following advantages:

Sb addition leads to several material property enhancements in the solder joints, including improved solder strength, better thermal resistance and a longer fatigue life [56, 11]. The Sb addition in the solder alloys improves both room temperature and the

high temperature strengths [80]. Karl et al. dopes Sb in Sn-Ag-Cu solder alloy to improve the thermal fatigue properties of this alloy [41]. Vianco [81] reported the addition of Sb as a ternary trace element in Sn-Pb alloy imparts better mechanical properties-tensile and creep strengths as well as ductility and fracture toughness. The Sb-contained solders were all much superior to their non-Sb equivalents both at room temperature and at 80°C.

The addition of Sb appears to have a beneficial effect on the thermal properties of the Sn-based solders. Vianco suggested that a 0.25 wt% addition of Sb to the Sn-Ag-Cu solder reduced its coefficient of thermal expansion, but a 0.5 wt% addition increased it [80].

It is recommended the Sb composition cannot higher than 7 wt% (the solubility limit of Sb in Sn) in order to prevent the formation of Sn-Sb intermetallic compounds, which can severely impact the fluidity of the molten solder or reduce the ductility of the solidified joint [80, 12].

Research has shown that adding elements can improve the earlier-mentioned properties of solder alloys. However, the kinetics and mechanism involved in the strengthening of the solder alloy is not well understood because of complexities involving diffusivity and liquid-solid reactions. The understanding is necessary in order for industrial application. Therefore, the need to investigate and characterize the influence of additives on the mechanical properties of lead-free solder alloys arises.

2.4 IMCs formation and growth

Two kinds of IMC growth kinetics in solder joints will be reviewed in this section: solder wetting reaction and solid-state ageing. A reaction above the melting point of the solder is defined as a wetting reaction. Below the melting point, it is defined as solid-state ageing [82]. During reflow, when molten Sn-based solder is in contact with a clean metal surface to be jointed, complex wetting reactions are expected. These include dissolution of the base metal into the molten solder, formation of intermetallic compounds at the interface as well as in the interior of the solder joint, growth or ripening of intermetallics grains, interdiffusion across the interface, and so forth.

Grains ripening are dominant growth mechanism in wetting reaction. Once the solder has solidified, a very slow but steady solid-state diffusion of the elements continues. In reality, the additional diffusion growth at room ambient is negligible over the life of the average assembly. As the operating temperature of a device nears the melting point of the solder, the diffusion rate also increases. Under those conditions, the additional solid-state IMC formation can become a major longevity issue.

The major difference between wetting reaction and solid-state ageing is the amount of reaction time and the morphology of the reaction products. In the wetting reaction, it is about 1 minute, yet in solid-state ageing, it is over hundreds of hours. During solid-state ageing, the scallop type Cu-Sn IMCs will change into layer type due to minimization of interfacial and grain boundary energies [3, 83].

2.4.1 IMC formation and growth during reflow

For different Sn-based solder alloys, the chemical reactions are different. Tu etc. have been done many studies on Sn-Pb solders with thick and thin Cu foils [82-84, 86]. They found that a scallop-type IMC morphology is common in solder reactions. Besides the reaction between eutectic Sn-Pb and Cu, it has been observed in wetting reaction between eutectic Sn-Pb and Ni, between eutectic Sn-Ag and Cu, and also between eutectic Sn-Bi and Cu [82]. Their nonconsecutive ripening theory will be briefly recapped here.

During reflow, the solder alloy melts when temperature is higher than its melting point. Only Cu dissolves into the molten solder and no diffusion of the components of the solders into the Cu are assumed [84-85]. At the solder interface, interfacial reaction forms two Cu-Sn compounds: a scallop-like Cu_6Sn_5 phase and a thin-layered Cu_3Sn phase. The morphologies of IMCs are shown in Fig. 2-4 [82]. Normally the first intermetallic compound forming at the solder/Cu interface is η - Cu_6Sn_5 phase because η - Cu_6Sn_5 has lower activation energy comparing to ε - Cu_3Sn phase [21]. However, the η phase is thermodynamically unstable with Cu, the ε phase will form between them. Experimentally, both η and ε have been found [7].

The growth mechanism of IMC during reflow is complex and involves chemical reaction of elements, atomic diffusion and grains ripening. Atomic diffusion is necessary for atomic transport of Sn and Cu through the intermetallic layer, and reaction processes at the solder/intermetallic interfaces actually generate the intermetallic compound compositions. Chemical reaction and interdiffusion during IMC growth are common to both reflow and ageing processes. A lot of studies have been reported on grain ripening of solder joint during reflow [7, 21, 84, 86]. Tu et al. [82] has reported these scallops grow bigger but the number of the scallops become fewer in the same area if the reflow time prolonged. It is non-conservative ripening, since the total volume of the scallops has increased over time.

Fig. 2-4 Cross-sectional SEM image of scallop type IMC formation at Sn-based solder/ Cu interface

Fig. 2-5 A schematic diagram of the cross-section of two scallops of Cu_6Sn_5 grown between molten eutectic Sn-Pb solder and Cu ($r_1 > r_2$).

A schematic diagram of the cross-section of the growth is shown in Fig. 2-5 [21]. The two arrows represent the two fluxes to be considered in the growth. In between the Cu_6Sn_5 and Cu, there is a very thin layer of Cu_3Sn . It is assumed that Cu can diffuse

through the thin Cu_3Sn quickly but not the bulk of Cu_6Sn_5 . Between the Cu_6Sn_5 grains, there are molten solder channels extending all the way to the $\text{Cu}_3\text{Sn}/\text{Cu}$ interface. Since the Cu_3Sn compound layer is so thin, these channels serve as fast diffusion and dissolution paths of Cu in the solder [21]. This flux is represented by the vertical arrow. The Cu atoms diffuse very rapidly in the molten solder to reach the growth front of the Cu_6Sn_5 , where it can react with Sn to add to the compound. At the same time, there is a ripening reaction among the scallops, so there are Cu fluxes going between the scallops, as represented by the horizontal arrow. By combining these two fluxes, the growth equation of an average size scallop has been given as [21]:

$$r^3 = \int \left(\frac{\gamma \Omega^2 D C_0}{3 N_A L R T} + \frac{\rho A \Omega v(t)}{4 \pi m N_p(t)} \right) dt \quad (2-1)$$

where r is the radius of an average size scallop, γ the surface energy of the scallop, Ω the average atomic volume, D the atomic diffusivity in the molten solder, N_A the Avogadro's number, L the numerical factor relating the mean separation between scallops and the mean scallop radius, RT has the usual thermodynamic meaning, ρ the density of Cu, A the total area of the solder/Cu interface, $v (= dh/dt$, where h and t are thickness of Cu and time, respectively) is the consumption rate of Cu in the reaction, m the atomic mass of Cu, and N_p is the total number of scallops at the interface. In the equation, the first term on the right-hand side is the ripening term, and the second term is the interfacial reaction term.

In the kinetic analysis of growth of Cu_6Sn_5 , it was found that the ripening flux is about 10 times greater than the flux of Cu being supplied from the substrate. So the ripening process dominates the growth of Cu_6Sn_5 . The growth kinetics of Cu_6Sn_5 has been measured to have a $t^{1/3}$ dependence on time [7]. As the average scallops become bigger and bigger, the total number of scallops at the interface, N_p , becomes smaller and smaller, the second term in the right-hand side will become comparable to the first term. Then the kinetics will not be dominated by ripening, and the growth of the scallops will slow down [72].

During the wetting reaction, the neighboring scallops will not join together to form grain boundaries. Therefore, they can only grow bigger by ripening. On the other hand, the scallops cannot keep on growing to become very big. This is because the bigger the scallops, the lesser the channels per unit area of the interface. Since channels are the short circuit paths for Cu atoms to reach the molten solder, the scallop-type growth will slow down when the channels are reduced [7].

Since there are always channels between the compound grains, the ripening of grains occurs simultaneously with the diffusion of Cu into liquid solder through the channels and the reaction between Cu and Sn. Therefore, the ripening is not a constant volume process due to the accompanying interfacial reaction and diffusion [84]. However, the ripening affects the rate of interfacial reaction. The reduction of the channel area by ripening growth might control the consumption rate of Cu during the reflow; it decreases with the time of reflow.

Furthermore, since the growth of IMC during soldering is very complex, some authors reported that, the time dependence of the IMC growth rate is often described by $L = (Dt)^n$ with varying n which is determined by curve-fitting methods, where D represents the diffusion coefficient and L is the average thickness of the IMC layer [66, 87].

2.4.2 Diffusion controlled growth during ageing

This section summarizes the recent research results on the solid-state growth of the interfacial Cu-Sn IMC under prolonged ageing at elevated temperature.

The growth kinetics of IMC during solid-state ageing is simpler than that during reflow and it only involves chemical reaction and atomic diffusion. Normally after reflowing, the η layer, at the interface between IMCs and solder, is rather wavy. When the ageing time is extended, the η layer smoothened and another layer of IMC, ε layer is observed in between the η layer and Cu substrate. The solid-state growth of the η -phase is attributed to grain boundary diffusion, and interdiffusion of the

microscopic constitutive species, which react to form the IMC while the growth of ε - Cu_3Sn phase consumes η -phase Cu_6Sn_5 .

During ageing, the morphology of Cu_6Sn_5 changed from scallop-type to layer-type. This change requires the growth of IMC in the valleys between the scallops. In other words, in the initial stage of the solid-state aging the IMC growth is faster in the valley than at the peak of scallops.

Figure 2-6 A schematic diagram of Cu diffusion paths during solid-state ageing.

Fig. 2-6 shows a schematic diagram of this growth where the arrows show the Cu flux. The arrow (path 1) from the peak of a scallop to the valley is driven by the curvature effect. The arrow (path 2) from Cu to the solder is driven by the interfacial reaction between Cu and solder to form the IMC. They combine to form a layer-type Cu_6Sn_5 . In solid-state aging, the solubility and diffusivity of Cu in Sn are much less than those in the molten solder; hence, the rate of IMC growth is much slower. This is more so when the IMC layer becomes a diffusion barrier and the growth becomes diffusion controlled by path 2.

Formation and growth of an intermetallic compound (IMC) phase in solder joints during ageing has been intensively studied experimentally and theoretically [10, 19, 88-93]. Most of these analytical studies are based on the one-dimensional (1-D) Fick's law. Bulk diffusion dominates as the major mechanism of mass transport. The relationship between the thickness of IMC layer and aging time is generally considered to have the usual form

$$L = (Dt)^{1/2} \quad (2-2)$$

where L is the layer thickness, D is the diffusion coefficient and t is the ageing time. Layer growth is faster for higher ageing temperature with the interdiffusion coefficient being given by the Arrhenius equation

$$D = D_0 \exp^{-(Q/RT)} \quad (2-3)$$

Where D_0 is the diffusion constant, Q is activation energy for the growth of interfacial Cu-Sn IMC layer, R is the gas constant, and T is the absolute temperature.

Many reports have reveals that the growth kinetics of total IMC layer of Sn-Pb solder joints followed diffusion law during ageing. However, as we know, the η -phase (Cu_6Sn_5) layer formed during reflow continues to grow and an additional layer of ϵ -phase (Cu_3Sn) forms at the η -Cu interface during ageing. There is not many studies to report the growth kinetics for these two phases individually. Prakash [94] reported that the thickness results fit a power law relationship against time with average exponents 0.69 and 0.44 for η -phase and ϵ -phase in Sn-Pb solder joint respectively. As to Pb-free solder joints, the growth kinetics of these two layers of IMC has not been reported.

2.5 Mechanical properties of lead-free solders

When an electronic device is in operation, the solder connections are subjected to mechanical stresses and strains. The primary cause of these stresses and strains arises from the fact that the electronic component and the board have different coefficients of thermal expansion. An example of how these stresses are generated, between the silicon die and the substrate, is shown in Fig. 2-7 [1]. If room temperature represents the unstrained conditions, then as the temperature of the system rises, the board expands more than the component, resulting in the solder ball connection being subjected to shear strain. As the system is switched “on” and “off”, it is subjected to thermal cycling, resulting in the solder connection being subjected to cyclic shear stresses. The resultant shear strain will be determined by the shear modulus of the particular solder material.

The solder connections are thus subjected to cyclic loading, and depending upon its fatigue life, the number of cycles before fatigue failure begins can be determined. Plastic deformation of the solder connection is also possible, if the shear strain due to differential thermal expansion exceeds the shear strain for yielding.

The solder joint can also be subjected to tensile loading, typically when the board or substrate is bent, as shown schematically in Fig. 2-8 [1]. This can happen during mechanical handling of the product, and sometimes when the finished product is clamped in the test fixtures for testing after assembly. The tensile properties such as yield strength, ultimate tensile strength (UTS) and elastic modulus are therefore necessary to determine the extent of tensile deformation the solder connection can withstand without failure.

Fig. 2-7 Solder joints subjected to shear strain during thermal cycling due to CTE mismatch between the Die (α_1), the solder (α_2) and the substrate (α_3).

Fig. 2-8 Solder joints subjected to tensile loading due to substrate bending during handling of the assembly.

When a device is actually operating, the differential thermal expansion can result in a constant static loading being applied on the solder connection. Since even room temperature represents a homologous temperature that is higher than $0.6 T_m$ where T_m is the melting point of solders in degrees Kelvin, this result in the solder connection being loaded under conditions where it can be susceptible to creep, i.e. exposure to constant load at elevated temperatures [1].

2.5.1 Tension and Shear properties – time-independent monotonic deformation

In tensile or shear tests, displacement is imposed at a steady rate. On this time scale, if the displacement is held constant, the material ceases to deform further. The initial deformation is elastic and the strain is entirely reversible. Subsequent deformation is plastic and the material is permanently deformed [95].

In most applications, solder joints are not under pure shear or pure tensile loading. A relationship between shear and tensile deformation is needed to account for multiaxial stress states. Assuming that the von Mises yield criterion applies [96], (i.e. that yielding occurs at the specific equivalent stress), the relationship is

$$\sigma = \sqrt{3}\tau \quad (2-4)$$

$$\varepsilon = \gamma / \sqrt{3} \quad (2-5)$$

where σ and ε are the true tensile stress and strain, and τ and γ are the true shear stress and strain [33]. Another important design parameter in finite element models of solder joint stresses and strains is Young's modulus, which relates the stress and the elastic portion of the strain [33, 95].

The UTS is the maximum engineering stress a material can withstand in tension. For solders, the scatter in values is quite large because of the strong dependence of the UTS on both microstructure (including ageing time after solidification) and temperature. For different compositions of Sn-Ag-Cu solder alloys, the UTS varies from 29.7 to 52.8 MPa [97-98]. Shown in Fig. 2-9, for Sn-3.5~3.8Ag-0.7Cu solder alloy, the higher the testing temperature, the lower the UTS [28, 33]. Furthermore, UTS is dependent on strain rate. The UTS data for Sn-3.5Ag are ranging from 35 – 55

MN m⁻² with different strain rate [97]. Shi et al. revealed that at lower temperature (-40 °C), the relationships between yield stress, UTS and strain rate of Sn-37Pb solder alloy are approximately linear on the log-log plot and become increasingly non-linear as the temperature is increased to 125 °C [33]. No systematic data were found for different temperatures and strain rates for Pb-free solder alloy. Systematical research work is needed to study the temperature and strain rate dependent mechanical properties for lead-free solder alloys.

Fig. 2-9 UTS for Sn-Ag-Cu solder alloy

2.5.2 Creep Resistance - time-dependent monotonic deformation

Creep refers to deformation that takes place over a period of time that relaxes a fixed imposed stress or displacement. Creep involves deformation mechanisms, such as grain boundary sliding, vacancy diffusion, etc., which requires thermally driven diffusion processes. Therefore, creep deformation plays an important role only when the temperature exceeds half the melting temperature (degrees in Kelvin) of the material. For the solders of interest here, room temperature is well above half of the melting temperature, consequently, creep is an very important deformation mechanism of solder [95].

Fig. 2-10 Typical creep curve showing the three stages of creep. Curve A is constant-load test; curve B, constant-stress test.

A typical creep curve is shown in Fig. 2-10 [101]. The curve can be ideally divided into three regions; primary, secondary and tertiary creep. The creep rate given by $d\varepsilon/dt$ decreases rapidly with time initially during primary creep and is approximately constant in the secondary creep region. Primary creep is dominated by transient creep while secondary creep is dominated by steady-state creep. For low temperature and stresses, primary creep is the predominant creep process. The steady-state secondary creep region is the most relevant because it has the simplest and most reproducible behavior and deformation mechanisms that have great engineering significance [102]. Tertiary creep is often associated with microstructural changes in the phases that are present [103].

Representation of the secondary creep deformation by a mathematical equation commonly uses the Dorn equation [101], which is given by:

$$\frac{d\gamma_s}{dt} = \frac{C G b}{RT} (b/d)^p (\tau/G)^n D_0 \exp(-Q/RT) \quad (2-7)$$

where, $d\gamma_s/dt$ is the steady state creep rate, G is the shear modulus, b is the Burger's vector, R is universal gas constant, T is the absolute temperature in kelvin, d is the grain size, τ is the applied stress, D_0 is a frequency factor, Q is the activation energy for the deformation process, n is the strain exponent, p is the grain size exponent and C is a constant characteristic of the underlying mechanism.

Darveaux etc. developed constitutive relations, which describe the behavior of solder joints under a wide range of conditions. At intermediate stresses, the strain rate depends on stress to the power, n . At high stresses, the strain rate is an exponential function of stress. The power law breakdown region can be described by a single expression [104-105]:

$$\frac{d\gamma_s}{dt} = C_4 \frac{G}{T} \left[\sinh\left(\alpha \frac{\tau}{G}\right) \right]^n \exp\left(\frac{-Q}{RT}\right) \quad (2-8)$$

where α prescribes the stress level at which the power law dependence breaks down, and C_4 is a constant characteristic of the underlying micromechanism.

To obtain the true activation energy, the temperature dependence of the shear modulus must be incorporated

$$G = G_0 - G_1 T' (^{\circ}C) \quad (2-9)$$

where G_0 is the modulus at 0 $^{\circ}C$, G_1 give the temperature dependence, and T' is the temperature in $^{\circ}C$.

Creep seems to be the dominant deformation process as one reaches temperatures greater than 0.5 T_m . Igoshev et. al [106] show that accumulation of grain boundary defects starts early during creep. Depending on the stress states during creep at high temperatures, failure can take place via transcrystalline (at lower stresses) or inter-crystalline (at higher stresses) cracking. Darvaeux and Banerji [104] have shown that dislocation climb is the main factor contributing to creep deformation.

2.5.3 Fatigue Resistance - cyclic deformation

Fatigue, a measure of resistance to failure due to cyclic loading, can be isothermal or “thermal”. Isothermal fatigue is where imposed cyclic displacement occurs at a constant temperature. Thermal fatigue, on the other hand, is a condition where cyclic displacement occurs due to a change in temperature, because of the joining of two materials with dissimilar coefficients of thermal expansion. Fatigue in solder joints leads to crack initiation and crack propagation; the fatigue life of a solder joint is determined by the number of stress cycles it endures before a crack is initiated and propagates. Even when the cyclic stress is well below the yield stress of the material, fatigue failure can occur due to defects and irregularities in the microstructure that may serve as crack initiation sites. Defects in the microstructure of a material serve as stress concentration sites that promote inhomogeneous deformation resulting in rapid growth of cracks [1, 95].

An accelerated temperature cycling (ATC) test is the most commonly used testing method to determine the effect of solder fatigue on product lifetime. During the ATC test, the units are subjected to alternating temperatures with a given ramp rate and dwell time at low and high temperature extremes.

For many years, the Coffin-Manson [107] equation has been widely and successfully used in estimating the fatigue life under plastic deformation. It correlates the fatigue life to the plastic strain range through a power law function. The empirical Coffin-Manson relationship shows as [108].

$$\frac{\Delta \varepsilon_p}{2} = \varepsilon_f' (2N_f)^c \quad (2-10)$$

where $\Delta \varepsilon_p / 2$ = plastic strain amplitude

ε_f' = fatigue ductility coefficient

c = fatigue ductility exponent

$2N_f$ = stress reversals to failure (1 cycle = 2 reversals).

The equation represented a major breakthrough in the field of low cycle fatigue. It is therefore not surprising that this is the model most often seen in the solder fatigue literature. However, in most electronics packaging applications it is not a single high-stress event that breaks a component solder joint; rather it is repeated or prolonged load applications that result in fatigue or creep failure of the solder joints. It has long been recognized in the aerospace establishment that the Coffin-Manson equation is inadequate for modeling in-service thermal fatigue conditions in high temperature alloys. Thermal fatigue involves a combination of creep and plastic strains, and each can have a different effect on the component life. The Coffin-Manson equation does not allow differentiation between these two strains, resulting in inaccurate life predictions [24].

2.5.4 Solder creep-fatigue interactions with surface mount components

There are many models to study the creep-fatigue interactions and predict fatigue life in solder interconnections. The presence of competing failure mechanisms makes the selection of a particular methodology or model to be the “cure-all” for failure predictions almost impossible and therefore it is necessary to classify the models or methods according to their potential applications. The methods are classified into five categories [109]:

1) Stress based approach

The stress-life approach relates the stress amplitude to cycles-to-failure in a power law form with the help of two temperature-dependent material constants (fatigue strength coefficient and fatigue damage exponent) that are usually determined empirically. In 1910, Basquin proposed that the fatigue life was a function of the stress [110]:

$$N_f = \sigma'_f (\sigma_a)^b \quad (2-11)$$

Where σ_a is the stress amplitude, σ'_f is the fatigue strength coefficient, N_f the number of cycles to failure, and b is the fatigue strength exponent.

This approach uses force or stress as the control parameter and measures the resulting deformation or strain. It works well for products or designs with long fatigue lives, typically referred to as high cycle fatigue (HCF), and involving constant amplitude, completely reversed cyclic loading. The analysis and estimation of material constants for this approach are quite simple and allow for quick “back of the envelope” life calculations. It is not quite suitable for solder life predictions under thermal cycling loads wherein solder experiences elastic and inelastic deformations (including time-independent “plastic deformation” and time-dependent “creep” deformation) and exhibits shorter lives, typically referred to as low cycle fatigue (LCF).

2) Strain based approach

- Total strain approach

In this approach, the Coffin-Manson equation is combined with Basquin’s equation:

$$\frac{\Delta \varepsilon}{2} = \frac{\sigma'_f}{E} (2N_f)^b + \varepsilon'_f (2N_f)^c \quad (2-12)$$

where $\Delta \varepsilon / 2$ is the total strain amplitude, b and c are Basquin’s fatigue strength exponents and Coffin-Manson’s fatigue strength exponents respectively. This model is displayed graphically in Fig. 2-11. At large strain amplitudes the total strain model reduces to Coffin-Manson model and at small strains reduces to Basquin’s model [24]. Further modifications [111] have enabled the strain-life model to be sensitive to mean stresses when the loading is not completely reversed. The main limitation of the strain based approach is its inadequacy to account for time-dependent effects (i.e. different ramp rates, strain rates, frequency of loading, hold times etc.) especially at elevated temperatures [112]. Its use is appropriate only for constant amplitude, completely reversed cyclic loading [113].

Fig. 2-11 Schematic of total strain versus life equation

- Frequency-modified Coffin-Manson model

The frequency-modified version of this approach [114] empirically incorporates effect of cycling frequency in the total strain range model.

$$\frac{\Delta \varepsilon_p}{2} = \varepsilon'_f (2N_f \times \nu^{k-1})^c \quad (2-13)$$

where $\Delta \varepsilon$ is inelastic strain range, ν is the cycling frequency, k is a material parameter.

Recently, in order to predict the fatigue-creep life of components, some variations of the model have been reported. Shi et al. [115] proposed a modified Coffin-Manson model for eutectic tin-lead solder, given by

$$[N_f \nu^{(k-1)}]^m \Delta \varepsilon = C \quad (2-14)$$

where

$$v^{(k-1)} = \begin{cases} v^{(k_1-1)} & \text{for } 1\text{Hz} \geq v \geq 10^{-3}\text{ Hz} \\ \left[\frac{v}{10^{-3}} \right]^{(k_2-1)} (10^{-3})^{(k_1-1)} & \text{for } 10^{-3}\text{ Hz} > v \geq 10^{-4}\text{ Hz} \end{cases}$$

$$\text{where } k_1 = 0.919 - 1.765 \times 10^{-4} T - 8.634 \times 10^{-7} T^2 \quad (2-14a)$$

$$k_2 = 0.437 - 3.753 \times 10^{-4} T - 8.04 \times 10^{-7} T^2 \quad (2-14b)$$

$$m = 0.731 - 1.63 \times 10^{-4} T + 1.392 \times 10^{-6} T^2 - 1.151 \times 10^{-8} T^3 \quad (2-14c)$$

$$C = 2.122 - 3.57 \times 10^{-3} T + 1.329 \times 10^{-5} T^2 - 2.502 \times 10^{-7} T^3 \quad (2-14d)$$

The frequency-modification approach is good for situations in which the in-service loading is uniform for all cycles and is a sinusoidal wave of constant frequency.

- Strain range partitioning (SRP) approach

The SPR model accounts for different types of strains causing different amounts of damage [24]. In this model, the cyclic stress-strain hysteresis loop is partitioned into four categories: the plastic strain in tension and compression (PP), the creep strain in tension and compression (CC), the creep strain in tension-plastic strain in compression (CP) and the plastic strain in tension-creep strain in compression (PC). The damage due to each of these four loading components, evaluated from four separate strain-life curves, is linearly superposed to obtain the total damage.

$$\frac{1}{N_f} = \frac{F_{pp}}{N_{pp}} + \frac{F_{cc}}{N_{cc}} + \frac{F_{pc}}{N_{pc}} + \frac{F_{cp}}{N_{cp}} \quad (2-15)$$

where N_{ij} is the cycles to failure for the material if the total inelastic strain range of the hysteresis loop were of type ij , where ij is either PP, CC, PC, or CP, F_{ij} is the fraction of the total inelastic strain range of the hysteresis loop.

The SRP approach requires special care in planning experiments and conducting analysis [116]. The main disadvantage of strain-based approach is its inability to adequately account for creep and stress relaxation during hold times with complex

load histories. However, the simplicity and availability of extensive experimental data for solder makes this approach very attractive.

3) Energy based approach

- Energy life approach

It correlates the fatigue life to the mechanical hysteresis energy in a power law form [117].

$$N_f = 7860 \Delta W^k \quad (2-16)$$

where ΔW is the viscoplastic strain energy density per cycle, k is a material constant.

- Energy partitioning approach

Analogous to SRP model, the need for strain rate (or failure mechanism) dependent energy life curves resulted in the development of the energy partitioning model [118]:

$$W_{tot} = W^e + W^p + W^c \quad (2-17)$$

The energy-partitioning model is a generalized creep-fatigue model that partitions the area under the stress-strain hysteresis loop into three components-elastic energy, plastic work and creep work. The total energy per cycle is defined as the sum of the stored elastic energy, the plastic work dissipated, and the creep work dissipated. Each quantity is related to fatigue life by a power law relationship and total damage is obtained by linear superposition of individual damages.

- Frequency-modified energy based approach

Shi et. al [119] proposed a frequency-modified energy based approach to predict the fatigue life at different frequencies. This model also introduced the flow stress into the frequency-modified energy model to account for influence of temperature on the fatigue life. It is shown as

$$\left[N_f \nu^{(k-1)} \right]^m \frac{W_p}{2\sigma_f} = C \quad (2-18)$$

$$\text{where } \nu^{(k-1)} = \begin{cases} \nu^{(k_1-1)} & \text{for } 1\text{Hz} \geq \nu \geq 10^{-3} \text{ Hz} \\ \left[\frac{\nu}{10^{-3}} \right]^{(k_2-1)} (10^{-3})^{(k_1-1)} & \text{for } 10^{-3} \text{ Hz} > \nu \geq 10^{-4} \text{ Hz} \end{cases}$$

where σ_f is the flow stress of the material.

However none of the energy-based models (including the energy partitioning model) are sensitive to mean stress effects when the loading is not completely reversed. This is particularly important for creep deformations where hydrostatic mean stresses can play a significant role in damage accumulation. Ongoing research is directed towards incorporating microstructural influences, mean stress effects and experimentally estimating the energy partitioning model constants for a variety of solder compositions [109].

4) Fracture mechanics approach

This approach is based on quantitative analysis of structures with pre-existing flaws or cracks. Approaches based on nonlinear (elastic-plastic) fracture mechanics (NFM) theory have been successfully applied to solder to understand the crack propagating process [116, 120-121]. The main shortcoming of this approach is the experimental difficulty in acquiring crack related measurements for small specimens such as solder.

$$\frac{dA_c}{dN} = B(\Delta W_p)^b \quad (2-19)$$

where $\frac{dA_c}{dN}$ is the crack area growth rate and ΔW_p is the plastic work per cycle. B and b are material constants.

5) Continuum damage mechanics approach

The damage mechanics approach involves the use of internal state variables to track the material degradation in presence of micro-voids or cracks under continuous load application [122-123]. The relative difficulty in applying these models arises from complex stress analysis that involves the use of several empirical constants that represent dynamically changing material state.

In summary, based on the application and failure mechanism of interest, there are a variety of approaches (stress, strain, energy, fracture mechanics, continuum damage) that can be used to characterize the damage in a material. The most popular solution is to accumulate damage throughout the life cycle using an appropriate damage superposition scheme. Normally, the fatigue-dominated process is generally modeled by Coffin-Manson type relationship modified to account for any creep strain and its dependence on cycle frequency and temperature [103]. Empirical relationships, most commonly Coffin-Manson rule in conjunction with complex nonlinear finite element analysis is used extensively at the present time to access the fatigue life of solder joints. This is largely due to the simplicity of the empirical models when compared to non-empirical, physics-based models (based on fracture or damage mechanics), whose computational expense is often prohibitive. Empirical models differ in their nature, but the most widely used criteria are strain range and total strain energy [124].

2.6 Reliability testing and methodology of lead-free solders

There are many ways to define reliability; the most simplistic approach is to define the product life as the length of time over which a product will function in its desired manner. Reliability is a generically used term in the electronics industry that has many possible meanings or definitions depending on the application. For example, reliability may refer to the thermal cycle fatigue resistance or it may be related to the number of on and off or power cycles as component chip may experience before becoming non-functional. Thermal reliability of the package assembly is one of the main areas of electronics packaging reliability [125].

Thermal reliability is typically a measure of the ability of a device to survive either cyclic environmental temperature changes or variations in the internal component or

die temperature. External or environmental thermal excursions are due to changes in the ambient temperature that the device is operating in. For example, in automotive under the hood applications, the electronics may experience a rapid change in temperature when the vehicle is started or turned off. Realistic temperature for under the hood applications is on the order of $-20/-30\text{ }^{\circ}\text{C}$ to well in excess of $100\text{ }^{\circ}\text{C}$ during operation. Internal temperature variations are due to the changes in the power consumption for an integrated circuit (IC) during operation. Additionally, as the device is turned on and off, the IC will heat from room temperature to its operating temperature in a short period of time (seconds). In power cycling, there is a significant temperature gradient across the die and within the package since regions of the IC heat and cool faster than other regions. The temperature gradient will cause the solder joints to be at different temperatures within the solder joint array depending on the location of the bump compared to the die. Solder bumps used for heat and ground connections underneath the die may be at a higher temperature compared to those at the component corners during package use [27].

2.6.1 Reliability testing methods

An accelerated test needs to be well designed to accelerate the same deformation mechanisms for reliable prediction of lifetime in field use condition. The ideal condition for an acceleration test is one with maximum acceleration factor, keeping the same deformation mechanisms as in field use.

One common test procedure for determining the characteristic thermal cycle reliability of an assembly is the performance of ATC testing. In ATC, components are assembled onto a PCB and then exposed to two extreme conditions in a thermally controlled chamber. The assembly is subjected to a “cold” temperature for an extended dwell period and then the assembly is exposed to a “hot” temperature dwell. Typically, testing is carried out between -40°C and 125°C [126]. The time that the sample takes to heat or cool to the extreme conditions is the ramp time. The ramp is the time /temperature change in $^{\circ}\text{C}/\text{second}$. The time of exposure at each extreme is the dwell time. In ATC, the assembly is exposed to isothermal dwell temperature. Ideally, in this testing, all the solder joints reach the same dwell temperatures.

As the devices are continually cycled between these two temperature extremes, stress builds up in critical areas of the device due to a mismatch of the coefficients of thermal expansion (CTE) of the different materials and an accumulation of plastic stress in the device. This mismatch results in mechanical stress within the device, some of which is dissipated during the dwell time. However, the stress continually builds up in the critical areas of the solder bump, until a crack begins to initiate. As the stress continues to increase, the crack will begin to propagate through the solder ball. In the context of a Level 2 reliability test, crack initiation typically occurs at the corner of a solder joint and can be detected through some type of external sensor, typically by measuring the electrical resistance of a series of solder bumps interconnected in a daisy-chain configuration. As the crack propagates through the bump, the resistance increases until finally, when the bump cracks entirely, the resistance becomes immeasurably large.

ATC testing is typically performed once a product is established and package construction is fixed by the manufacturer. Development of new packages, and changes in package variables, such as pad design, require shorter duration tests to minimize the product development cycle [125]. However, ATC normally takes several months to complete a test and this is very time-consuming and expensive. The electronics packaging industry is motivated to shorten product development cycle time while maintaining desirable levels of quality and reliability. Moreover, due to the non-uniform temperature distribution in high power device and optoelectronics packaging, ATC testing is inappropriate for the accelerated testing of this kind of packaging. Hence, a highly accelerated testing method that reduces the cycle time and can mimic true operating environments is greatly sought after for the understanding of wear-out reliability characteristics of packages.

Different accelerated isothermal mechanical cycling approaches were developed as alternatives to ATC. Lau and Pao [27] established a three-point bending (TPB) methodology. The PCB was supported at both ends and mechanical loading was applied at the center of the PCB assembly. Load versus deflection graph was then plotted to determine the load where solder joint failure occurs. Since the failure mechanism is overstress and not wear-out, this method is more applicable to simulate manufacturing, handling, shipping, and rework conditions. Some research efforts

[127-128] have been tried to develop the accelerated vibration method. However, the creep response of solder alloy under the high frequency excitation loading is quite different from that obtained under the low frequency ambient temperature loading. Another mechanical deflection system (MDS) test is to use torsion loading as reported by Zubelciewicz [129] and Pang et al [130-131]. The MDS is capable of accelerating solder joints failures to within days instead of months. In addition, MDS is meant to mimic solder joint failure mechanisms similar to those from the ATC tests. Recently, power cycling testing was chosen to determine the, e loadinif $T_c (e)T_j^{0.028} T_c^{2.347} T_8 (AT)T_j^0 T_c$

instantaneous failure rate $h(t)$ represents the instantaneous rate of failure for units of a population that have survived to time t and is defined as follows:

$$h(t) = \frac{f(t)}{R(t)} \quad (2-21)$$

Equation is typically represented by the bathtub curve shown in Fig. 2-12 [27]. Three distinct regions that exist in the bathtub curve are: 1) infant mortality failure, 2) random failure, and 3) wear-out failure. Infant mortality failures occur early in the life cycle and have decreasing failure rates while wear out failures have increasing failure rates. Infant mortality and random failures need to be separated from the wear out failure distribution when analyzing life test data. Environmental stress testing [43] is used to screen poor quality assemblies that would be prone to infant mortality and random failure in service. Process control corrective measures ensure that SM assemblies that are shipped are of high enough quality and do not fail in the field until the wear out threshold is reached. Failure rate in the wear-out regions for solder joints can be described using Weibull statistical analysis [133].

Fig. 2-12 Bath-tub reliability curve

2.6.3 Weibull life distribution

One of the most important issues with solder joint accelerated life test models is the choice of a statistical distribution of time to failure that fits the early part of the wear

out failure distribution. The cumulative failure of the solder joints is usually modeled using two or three-parameter Weibull distribution. The rule for the probability density function (PDF) of the three-parameters Weibull plot (when $\gamma = 0$, it is two parameters weibull plot) is [134]:

$$f(t) = \frac{\beta}{\eta^\beta} (t - \gamma)^{\beta-1} \exp\left[-\left(\frac{t - \gamma}{\eta}\right)^\beta\right] \quad (2-22)$$

And the cumulative distribution function (CDF) for the three-parameter weibull distribution is [133]:

$$\text{For } t < \gamma : F(t) = 0 \quad (2-23)$$

$$\text{For } t > \gamma : F(t) = 1 - e^{-\left(\frac{t - \gamma}{\eta}\right)^\beta}$$

Where the three independent parameters are:

- The minimum life or failure-free time, γ , prior to which no failures are expected.
- The characteristic life, η , or time to a CDF of 63.2%.
- The shape parameter, β , given by the slope of the failure distribution on Weibull paper with the origin of the time axis shifted to γ .

Therefore, the failure rate function is presented as:

$$h(x) = \frac{f(x)}{R(x)} \quad (2-24)$$

Where $R(x)$ is the reliability function, defined as $1 - F(x)$.

For better accuracy, a median ranking approach was used to estimate the cumulative density function:

$$F(t) = \frac{i - 0.3}{j + 0.4} \quad (2-25)$$

where i is the failure number and j is the sample size.

The mean time to failure (MTTF) is then calculated by [133]:

$$MTTF = \gamma + \eta * \Gamma(1 + \frac{1}{\beta}) \quad (2-26)$$

where $\Gamma(x)$ denotes the gamma function.

Two-parameter Weibull analysis is widely used in the evaluation of reliability of electronic packaging; however, some researchers reported that three-parameter Weibull analysis better fits the testing data than two-parameter Weibull analysis [133, 135].

2.7 Summary

The transition to lead-free has necessitated the replacement of the widely used eutectic Sn-Pb solder in electronic assemblies. Considerable research has been carried out to identify a suitable replacement for the eutectic Sn-Pb solder. Sn-Ag-Cu solder alloy has emerged as one of the possible replacements. Literature has shown that the excessive growth of IMC in Sn-Ag-Cu solder joints has a negative affect on the mechanical properties and reliability of this solder alloy. Based on the literature review, the presence of the fourth element, such as Sb, will improve the mechanical properties and reliability of Sn-Ag-Cu solder joint. However, how this additive and its amount affect IMC formation and microstructural evolution, which causes continuous change in mechanical properties, is unknown. It is necessary to investigate the effect of Sb on IMC growth, so as to improve the performance of Sn-Ag-Cu solders. In addition, the growth kinetics of IMC layers, mechanical properties of lead-free solder joints is necessary to be understand for further application of lead-free replacements.

The mechanical properties of solder joints are known to be sensitive to the testing conditions, solder alloy, and microstructure of the solder joint as reviewed in literature survey. Thus it is considered that microstructural evolution due to ageing, the strain rate and temperature variations will affect the mechanical properties of solder

materials. The tensile testing of different strain rate and temperature in solder alloy, unaged and aged Sn-Ag-Cu solder joints should be done to investigate the effect of additive and testing parameters on tension properties.

Another issue about solder reliability is the accelerated testing. In order to shorten the testing time of reliability evaluation, much effort should be investigated to develop new testing approaches for replacement of traditional ATC test.

Chapter 3

Materials, Processes, and Testing

This chapter aims to give a brief description of the materials, processes, testing, and all experimental and analytical techniques used for the studies. The purpose, theoretical background (where applicable) and conditions for each technique will be presented.

3.1 Materials

3.1.1 Substrate

Copper substrates (20mm × 12mm × 2mm) for the study of IMC formation were made from 2 mm thick Cu strip of commercial purity (99.99%). The surface of the Cu piece was ground on a series of silicon carbide papers and then polished with 0.25 μm diamond paste to produce a mirror surface. Immediately prior to reflow, the surface was dipped in a solution of 50% nitric acid (HNO₃) in water for several seconds to remove any copper oxide and then rinsed in acetone.

3.1.2 Solder and additives

Sn-3.5Ag-0.7Cu-xSb (x = 0, 0.2, 0.5, 0.8, 1.0, 1.5, and 2.0) solder pastes were used in this project. The Sb-containing solders were prepared primarily by mechanically dispersing the Sb powders into the Sn-3.5Ag-0.7Cu solder paste. The mixture was then blended manually for sufficient time to ensure uniform distribution of the Sb powders. The purity of Sb powder is 99.995%. Its particle size is about 5 - 20 microns.

3.1.3 Printed Circuit Board (PCB) and Ball Grid Array Packages

Double side high T_g flame retardancy (FR4) PCBs were used in study of the correlation of ATC and RTC tests. The dimension of PCB is 212mm x 150mm x 1.60mm, 2 layers. Surface finishing is immersion Au. The under bump metallization (UBM) is 3 – 10 μm Ni.

304 I/O tape ball grid array (TBGA) was mounted onto PCB as a test vehicle: It has 1.27 mm pitch between solder joints. It consists of polyimide substrate, Sn-Pb eutectic solder, copper pad, epoxy overmold, silicon die and copper stiffener. The dimension of the TBGA304 is given in Table 3-1.

Table 3-1 Dimensions of the TBGA assembly

Material	Length (mm)	Width (mm)	Height (mm)
Solder ball	$\varnothing=0.75$		0.60
Copper pad	$\varnothing=0.53$		0.025
Epoxy	18.5	18.5	0.78 max. / 0.43 min.
Polyimide	20.66	20.66	0.15
Silicon die	8.90	8.90	0.32
Heat sink	31.8	31.8	0.46 max. / 0.15min

3.2 Solder reflow processes

The primary purpose of the reflowing process is to melt the solder paste, wet the surface to be jointed and allow the solder to solidify and form a strong metallurgical bond. Six different Sb-containing Sn-3.5Ag-0.7Cu-xSb solders ($x = 0, 0.2, 0.5, 1.0, 1.5,$ and 2.0) were printed on the well-prepared Cu substrates using stencil printing and solder joints with the printing size of 5 mm $\times$ 5 mm were formed by means of a standard infrared reflow oven. As the amount of solder paste used would affect the formation of the IMC, care was taken to ensure a uniform layer of solder was applied onto each Cu substrate and the solder paste thickness was measured to be within 180 – 200 μm . For the study of liquid-solid reaction, the specimens were reflowed at a peak temperature of 250°C. The heating times above liquidus temperature were 2s,

12s, 48s, 240s, 1 hour, and 2 hours respectively. The longer reflow times of 240s, 1 hour, and 2 hours in this work were specially designed to study the effects of Sb addition on the IMC growth kinetics of the soldering reaction. The typical reflow temperature profile is shown in Fig. 3-1.

Fig. 3-1 Reflow temperature profile at above liquidus for different times

3.3 Isothermal Accelerated Testing

Sample ageing is done to study the solid-solid reaction. All ageing of samples were done in a non-vacuum Blinder M115 ageing oven.

Seven different compositions of the Sb-containing solder Sn-3.5Ag-0.7Cu-xSb ($x = 0, 0.2, 0.5, 0.8, 1.0, 1.5, \text{ and } 2.0$) were printed on the Cu substrates and solder joints were formed by means of reflow oven. To study the effects of Sb addition on the formation and the growth kinetics of IMC layer between Sn-3.5Ag-0.7Cu-xSb lead-free solder and Cu substrate, the specimens prepared by the same approach in section 3.2 were reflowed above liquidus but the peak temperature not beyond 250°C for 60 seconds, and then aged at temperatures of 100, 150, and 190°C for 1, 10, 50, 100, 200, 400, and 600 hours respectively. The typical reflow temperature profile is shown in Fig. 3-2.

Fig. 3-2 Reflow temperature profile at above liquidus for 60 seconds at peak temperature

3.4 Differential Scanning Calorimetry (DSC) test

DSC was used in the study to determine the melting characteristics of Sn-3.5Ag-0.7Cu-xSb solder alloys. The solders are put into an aluminum pan (weight ~ 5 mg) and then put in a Thermal Analysis (TA) Instruments 2010 DSC with an inert nitrogen atmosphere purging the sample cell. Thermal scan is carried out at a 5 °C/min heating rate ranging from room temperature to 250 °C.

3.5 Tensile test

Two kinds of tensile tests were executed in this project. One is to test the strength of solder alloy itself; the other is to test the strength of solder joints.

3.5.1 Tensile test of solder alloy

For tensile test of solder alloy, samples with dimensions of 15 x 1.5 x 0.3 mm were

fabricated using a custom-made mold, as shown in Fig. 3-3. Solder paste with compositions of Sn-3.5Ag-0.7Cu-xSb ($x = 0.0, 1.0$ and 2.0) was printed into the mold. The mold was then passed through a Forced-convection Reflow Oven, using temperature reflow profile as shown in Fig. 3-2. The profile peaked at $250\text{ }^{\circ}\text{C}$ and remained above solidus temperature for 60 seconds. Prior to tensile test, the samples were further ground down to $10 \times 1.5 \times 0.2\text{ mm}$ using 1200 grit silicon carbide paper. The quadrate-shaped bulk solder specimen for the uniaxial tensile test is shown in Fig. 3-4. The specimens were aged for 24 hours at 60°C in vacuum to eliminate the surface residual stresses.

Fig. 3-3 Mold used for the fabrication of the tensile samples

Fig. 3-4 the specimen configuration used for tensile testing of solder alloy (unit: mm)

The tensile tests were carried out on a MTS micro-force tester at three different temperatures (25°C , 75°C and 125°C). At each test temperature, three different strain rates ($1 \times 10^{-4}\text{ s}^{-1}$, $1 \times 10^{-3}\text{ s}^{-1}$, and $1 \times 10^{-2}\text{ s}^{-1}$) were used. Four samples per test condition were used and the results were averaged to reduce the experimental error. In

order to perform testing ranging from 25°C to 125°C, the tensile tester was fitted with a thermally insulated chamber. A computer with data acquisition software was used to collect data.

Specially designed specimen grips with sawteeth were used to grip the samples during testing. When the specimen grips and the heating chamber have reached thermal equilibrium of the set temperature, the specimen is placed into the chamber. In order to ensure that there is no slippage of the sample during testing, super glue is applied to the ends of the sample to enhance the grip.

3.5.2 Tensile test of solder joint

Joint strength was evaluated by a joint tensile test. To consider the strength of the solder and the Cu pad, the Cu/solder/Cu joints were used as test specimen. Fig. 3-5 shows the schematic drawing of the fixture that holds the Cu strips to be soldered together. Metal plate (D) was used to prevent defect formation on the specimen surface when securing the specimen.

Fig. 3-5 Schematic diagram of approaches to fix solder joint. Description of labels in the figure: A – Ceramic holder, B – Sn-3.5Ag-0.7Cu-xSb ($x = 0.0, 1.0$ and 2.0 wt%) solder paste, C – Cu strips, D – Metal plate, E – Clamping plate, F – Screws, and G – Screws.

The procedures to form the tensile testing specimens are as follows. Firstly, two pieces of polished and cleaned Cu strips were fixed in the holder, as shown in Fig. 3-5, which maintains the opposite ends parallel to each other with a 1.0 mm space between the plates. The Sn-3.5Ag-0.7Cu-xSb ($x = 0.0, 1.0, \text{ and } 2.0 \text{ wt\%}$) solder paste was filled into the space then. Care was taken to supply sufficient amount of solder for the joining. The specimen holder was sent into a reflow oven and reflowed at 250°C with 60 seconds dwell time above liquidus. The specimen holder was finally taken out of the oven and cooled in air. Excessive solder flowed out of the solder joint area was carefully ground away. The as-soldered specimens were cut into small pieces with rectangular cross section in the dimension about $1.6 \times 2.6 \text{ mm}$ using a diamond cut-off saw, ground and polished to be the uniform dimensions of $1.5 \times 2.5 \text{ mm}$. The schematic of the tensile testing specimen is shown in Fig. 3-6.

Fig. 3-6 the specimen configuration used for tensile testing of solder joint (unit: mm)

The as-soldered Sn-3.5Ag-0.7Cu-xSb ($x = 0.0, 1.0 \text{ and } 2.0 \text{ wt\%}$) tensile testing specimens were aged at 150°C for 0, 200, 400, 600, 800, and 1000 hours respectively.

Tensile tests were carried out on an Instron 5548 tensile tester at a strain rate of $1 \times 10^{-3} \text{ s}^{-1}$ at 298K in order to obtain data on tensile strength. For each condition, four samples were tested.

3.6 PCB Assembly

TBGA components were pre-baked in oven for 24 hours at 120°C to eliminate the moisture present in the package prior to being assembled onto the PCB for ATC and

RTC test. Solder paste were printed on the PCB by semi-automated solder printing machine using 8 mils thick stencil. 12 TBGA (for ATC test) or 4 TBGA (for RTC test) components were placed onto a printed PCB one by one using Pick and Place machine. The PCBs were then sent for reflow in a Convectional Reflow Oven, using optimum reflow profile shown in Fig. 3-7. After assembly, the PCBs were inspected using X-ray to ensure proper joint were formed between the components and PCB.

Fig. 3-7 Reflow temperature profile at above liquidus for about 100 seconds

3.7 Temperature Cycling Testing

3.7.1 Accelerated Temperature Cycling Test

TBGA devices were subjected to ATC test which was ramped between -40 and 125°C. Each cycle lasted 60 minutes with 15 minutes rise and drop times, and 15 minutes hold times at either temperature extreme. The temperature loading profile of ATC is shown in Fig. 3-8. The temperature loading profile was controlled by a personal computer. A software package was developed to handle all data acquisition and control tasks. In this study, solder joint failure was defined as a complete cracked joint with resistance reaching 300Ω with reference to the initial resistance of 1.5Ω.

Fig. 3-8 Temperature loading profile for ATC test

3.7.2 Rapid Temperature Cycling Test

A custom instrumentation setup was developed in order to carry out the rapid temperature cycling (RTC) test, as illustrated in Fig. 3-9 (a) and (b). It consists of thermoelectric coolers (TECs), TEC controllers, heat exchanger, data acquisition unit, thermistors, and personal computer. Each TEC was connected to the TEC control unit and was in direct mechanical contact with a single device to heat and cool the device. The heat exchanger used to extract heat from the TEC to the environment. A layer of thermal grease was used to ensure good thermal contact between the TECs and the heat exchanger. Thermistors were placed near the TEC/device under test (DUT) interface to monitor the temperature of the DUT. The testing printed circuit board (PCB) was connected to a data acquisition unit along with each of the thermistors. The temperature loading profile was controlled by a personal computer. A custom software package was developed to handle all data acquisition and control tasks.

A brief description is given here to describe TECs themselves and the details of how they are controlled.

Thermoelectric coolers work on the so-called Peltier effect first discovered in 1834 by scientists Thomas Seebeck and Jean Peltier. Peltier's discovery that heat could be emitted or absorbed when current flowed through two dissimilar electrical conductors

formed the basis for modern thermoelectrics. However, it wasn't until the mid-20th century that their application became practical, due to advances in semiconductor technology. Basically, the TEC can be thought of as a compact, solid-state heat pump. The devices contain a number of p- and n-type semiconductor pairs typically composed of heavily doped bismuth telluride. When connected to a DC power source, heat can be moved from one side of the TEC to the other. This has the effect of creating one hot side and one cold side of the TEC. By reversing the direction of the current, the hot side and cold side can be switched. By placing the TEC in contact with one side of DUT, the temperature of the DUT can be controlled by regulating the amount and sense of current that flows to the TEC.

It should be noted that the TEC is merely a heat transportation device, being able to move heat from one place to another. However, in order to heat and especially to cool the system, the heat exchanger (air cooled) must be used. Because semiconductors are poor thermal conductors, TECs consequently have very low heat capacities, and are therefore able to create very large temperature gradients in a short period of time, which makes them ideal for rapidly cycling and precisely controlling the temperature of a DUT.

Fig. 3-9 RTC experimental setup (a) Overview of RTC set up; (b) Top view of experimental setup of TECs and heat exchanger.

TBGA devices were subjected to RTC which was ramped between 0 and 100°C. The temperature loading profile of RTC is shown in Fig. 3-10. Each cycle lasted 6 minutes with 1.5 minutes rise and drop times, and 1.5 minutes hold times at either temperature extreme.

Fig. 3-10 Temperature loading profile for RTC test

3.8 Sample Observation and Characterization

For metallographic observations, both specimens with Cu substrate and components subjected to PCB were cut and mounted in Klarmount and cross-sectioned perpendicularly to the solder joint. They were then successively ground down to 1000 grit with a silicon carbide paper cooled with flowing water. Polishing was performed using 5 μm Al_2O_3 suspension followed by 0.25 μm diamond paste. The specimens used for IMC cross-sectional view were then etched in a dilute solution of 2 % concentrated Hydrochloric Acid (HCl), 6 % concentrated HNO_3 and 92 % H_2O for about 30 seconds. This process would provide the contrast between Cu_6Sn_5 and solder matrix. They were then coated with gold. Those specimens for failure site observation, were directly coated with gold after polishing.

To observe the microstructural evolution of the intermetallic grains and confirm the IMC phases with X-ray diffraction (XRD), the solder alloys on the top of the IMCs of the specimens with Cu substrate were chemically etched by using 13% (by volume) nitric acid. Scanning electron microscopy (SEM) was used to study the microstructural morphology of IMCs. Energy dispersive x-ray spectroscopy (EDS)

and XRD were used to characterize the composition of the IMCs. The mean thickness measurement of the IMCs was performed using SEM and image analysis. In order to determine the IMC thickness, two samples were prepared for each testing condition. Five to eight SEM photographs were taken at different positions for each sample. Software named “Image tool” was used to measure the area and the length of IMC for each photograph. The area divided by length is defined as the thickness of IMC. More than ten thickness data were used to get an average thickness for one testing condition.

Chapter 4

IMC growth and kinetics of as-soldered Sn-3.5Ag-0.7Cu-xSb solder joints

4.1 Introduction

Nowadays solder joints with higher reliability are demanded because the trend in electronic packages is to make products smaller and faster. The higher reliability of solder joint is directly dependent on the quality of the bond formed between the solder and the Cu substrate. Formation and growth of IMCs in reflow process is a crucial issue for the reliability of solder joints. During reflow, molten solder comes into contact and reacts with the Cu substrate. The nature of this interaction is dependent on the composition of the solder, and how each of the constituents interacts with the Cu substrate. In this work, the fourth element Sb is added to Sn-3.5Ag-0.7Cu solder alloy to investigate the properties and microstructure of the solder joints.

The interfacial reaction between Cu and solders, either eutectic Sn-Pb or lead-free, in the solder reflow process has been a topic of many studies. Most of the studies were concentrated on reactions during relatively short time frames that correspond well to the reflow time employed in the packaging industry. However only a few work gave useful information about the growth kinetics of IMC. Bader et al. [19] investigated the growth of Cu_6Sn_5 in diffusion couples consisting of a 5 μm thick layer of pure Sn sandwiched in-between two Cu substrates, and reported the growth exponents of $n = 0.21$ and 0.25 for the temperatures of 240 and 300°C , respectively. Schaefer [20] found the IMC layer growth between molten solder and copper followed a 0.25 power factor dependence on time in Sn-36Pb-2Ag solder in the temperature range from 187 to 258°C . Kim and Tu analyzed the kinetics of the ripening of scallop-like growth in eutectic Sn-Pb solder system, and reported that the ripening is considered non-conservative. The total volume of the Cu_6Sn_5 IMC increases with the increasing reflow time and the grain size is proportional to $t^{1/3}$ [21-22]. So far, the growth kinetic parameter of IMC layer in wetting reaction has seldom been reported for lead-free

solders. Another part of this work focus on the study of the effect of Sb on the IMC formation, and growth kinetics of the Sn-Ag-Cu alloy. The interaction time of molten Sn-3.5Ag-0.8Cu-xSb solder with Cu substrate was extended from the conventional short time to as long as several hours.

4.2 Thermal properties of Sb-containing solder alloys

Differential Scanning Calorimetry (DSC) testing was used to investigate the effects of Sb addition on the melting point of Sn-3.5Ag-0.7Cu solder alloy. Fig. 4-1 shows the heat flow (exothermic) versus temperature curves of these solders. The melting point in the DSC curves is typically determined by first identifying the steepest portion of the low temperature side of the heat absorption well, determining the slope at that point, and then extrapolating this line of slope to the temperature at the axis of constant differential heat flow [136].

Shown in Fig. 4-2, the melting temperatures change slightly with the addition of Sb elements. It can be seen that the melting temperature of Sn-3.5Ag-0.7Cu is 217.52 °C. It is similar to other studies [57, 137-138]. The melting point decreases when Sb composition was less than 0.5 wt%, the melting point of 0.5 wt% Sb-containing solder alloy reaches the lowest point of 216.90 °C. However, it increases with the increase of Sb proportion when Sb proportion is over 0.5 %. When 2.0 % Sb was added, the melting point of Sn-3.5Ag-0.7Cu solder increases by more than 3.5 °C.

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Fig. 4-1 DSC profiles of Sn-3.5Ag-0.7Cu-xSb for (a) x = 0.0, (b) x = 0.2, (c) x = 0.5, (d) x = 0.8, (e) x = 1.0, (f) x = 1.5, and (g) x = 2.0

Fig. 4-2 Relationship between melting point and Sb proportion of Sn-3.5Ag-0.7Cu-xSb solder alloys

4.3 Phases formation during liquid-solid reaction in Sb-containing solder joints

Until now, no phase diagram on Sn-Ag-Cu-Sb quaternary alloy can be found in publications. However it can be divided into four ternary systems to analyze the IMC phases [12, 139-140]. Since Sn is the major element in Sn-3.5Ag-0.7Cu-xSb solder alloys, three ternary diagrams Sn-Ag-Cu, Sn-Ag-Sb, and Sn-Cu-Sb are analyzed in details to understand the possible phases of IMC formation.

From the ternary Sn-Ag-Cu phase diagram, shown in Fig. 4-3, the alloy composition of 3.5 wt% Ag and 0.7 wt% Cu is near eutectic [139].

Figure 4-3 Projection of liquidus surface in Sn-rich portion of Sn-Ag-Cu system

When the reflow temperature approaches the eutectic melting point of 217°C in this quasi-eutectic Sn-Ag-Cu solder system, the copper atoms of the substrate react with the molten solder and the Cu₆Sn₅ IMC nucleate at the solder/Cu interface. The wetting reaction is as follows [139]:

Sn-Ag-Sb phase diagram is shown in Fig. 4-4. Table 4-1 shows the composition of phases at invariant temperature. From the ternary phase diagram, the nominal equations for the invariant reactions are [12]:

Ag₃(Sn, Sb) and SnSb phases are stable phases in the Sn-Ag-Sb system when temperature is higher than 234.8 °C. Masson [12] indicated the uniform distribution of the Ag₃(Sn, Sb) compound from the Ag-Sn side to the Ag-Sb side in the Sn-Ag-Sb ternary phase diagram, thereby demonstrating the chemical stability of the ε - Ag₃ (Sn, Sb) compound at room

temperature. [11].

Metallurgically, the Sn-Cu-Sb alloy has three terminal phases at 25°C [138]. Those phases are the β -Sn matrix phase that is essentially pure Sn, the SnSb phase and the Cu₆Sn₅ intermetallic.

Figure 4-4 Liquid projection of the Sn-Ag-Sb system.

Table 4-1 Composition of phase at invariant temperature

Invariant Reaction	Phase	Composition		
		Sn	Ag	Sb
$L + (Sb) \Leftrightarrow Ag_3(Sn, Sb) + SnSb$ 378.5°C	Liquid	34	14	52
	(Sb)	11	0*	89
	Ag ₃ (Sn,Sb)	18	72	10
	SbSn	36	0*	64
$L + SbSn \Leftrightarrow Ag_3(Sn, Sb) + (Sn)$ 234.8°C	Liquid	89	5	6
	SbSn	57	0*	43
	Ag ₃ (Sn,Sb)	27	72	1
	(Sn)	92	0*	8

Integrating these ternary systems together, the Sn-3.8Ag-0.7Cu-xSb (x is less than 8.0) alloy solidification can be analyzed as follows:

$\text{Ag}_3(\text{Sn}, \text{Sb})$ primarily precipitates when temperature is higher than 234.8°C . Since the Sb additive is less, and Sn can dissolve up to 6% or 7% Sb, the experimental alloy will not fall within the (Sn)- $\text{Ag}_3(\text{Sn}, \text{Sb})$ -SnSb triangle [141], the entire SnSb primary phase transforms into Sn-rich phase (Sb) and $\text{Ag}_3(\text{Sn}, \text{Sb})$. As the Sb exhaust, Ag_3Sn begins to precipitate. At 217°C , Cu_6Sn_5 begin to form. When the liquefied solder alloy is cooled to the Sn-Ag-Cu eutectic point, the Cu_6Sn_5 , Ag_3Sn and pure Sn precipitate at the same time. In short, the as-solidified Sn-Ag-Cu-Sb alloy may consist of primary Sn-rich phase (Sb), Ag_3Sn eutectic structures, ε - $\text{Ag}_3(\text{Sn}, \text{Sb})$ compound, and Cu_6Sn_5 eutectic structures.

4.4 Microstructural Evolution

Figures 4-5 to 4-8 show the typical SEM micrographs of the cross-sectional view of the Sn-3.5Ag-0.7Cu-xSb ($x = 0, 0.2, 0.5, 1.0, 1.5$, and 2.0) solder joints for the reflow dwell times of 2, 48 seconds, 1 hour, and 2 hours respectively at above liquidus. The IMC grows thicker with the increase of reflow time. It is clearly shown that the Cu_6Sn_5 phase grows as scallop-like grain into the molten solder, and results in a very rough interfacial morphology between the IMC and the solder. After forming the layer structure of Cu_6Sn_5 phase between the solder and Cu substrate, a thin layer of the Cu_3Sn compound will generally be grown at the interface between the Cu_6Sn_5 and Cu. However, the growth of Cu_3Sn phase is limited by short diffusion time, and the layer structure only can be observed by SEM under higher resolution.

Fig. 4-5 SEM micrographs of cross-sectional view of Sn-3.5Ag-0.7Cu-xSb solder joints reflowed for 2 seconds. (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.5$, (d) $x = 1.0$, (e) $x = 1.5$, and (f) $x = 2.0$ wt%.

Fig. 4-6 SEM micrographs of cross-sectional view of Sn-3.5Ag-0.7Cu-xSb solder joints reflowed for 48 seconds. (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.5$, (d) $x = 1.0$, (e) $x = 1.5$, and (f) $x = 2.0$ wt%.

Fig. 4-7 SEM micrographs of cross-sectional view of Sn-3.5Ag-0.7Cu-xSb solder joints reflowed for 1 hour. (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.5$, (d) $x = 1.0$, (e) $x = 1.5$, and (f) $x = 2.0$ wt%.

Fig. 4-8 SEM micrographs of cross-sectional view of Sn-3.5Ag-0.7Cu-xSb solder joints reflowed for 2 hours. (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.5$, (d) $x = 1.0$, (e) $x = 1.5$, and (f) $x = 2.0$ wt%.

A column chart shown in Fig. 4-9 summarizes the IMC thicknesses in solder joints reflowed for different dwell time. The thicknesses of IMC in Sb-containing and Sb-free solder joints only show a little difference for the short reflow dwell times (less than 48 seconds). For the longer reflow dwell times, the IMC layer of the Sb-containing samples is obviously thinner than that of the Sb-free samples. When the reflow dwell time prolongs to 2 hours, the IMC thickness drops from 11.7 μ m to 9.5 μ m for the solder with 1.0 % Sb. The results also reveal that for the same reflow time, IMC thickness decreases with the increase of Sb proportion, and the downward trend persists until the weight percentage of Sb approaches to about 1.0%. Beyond this amount, however, the IMC thickness increases slightly, but is still thinner than that of the Sb-free solder joints. This result reveals that adding Sb could inhibit the growth of IMC in liquid-solid reaction. But, it is not very suitable for the industry application (reflow time less than 100 seconds).

Fig. 4-9 IMC thickness vs reflow time for different Sb proportions.

Fig. 4-10 SEM micrographs of top view of IMC layer of Sn-3.5Ag-0.7Cu-xSb solder joints reflowed for 2 seconds. (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.5$, (d) $x = 1.0$, (e) $x = 1.5$, and (f) $x = 2.0$ wt%.

Fig. 4-11 SEM micrographs of top view of IMC layer of Sn-3.5Ag-0.7Cu-xSb solder joints reflowed for 48 seconds. (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.5$, (d) $x = 1.0$, (e) $x = 1.5$, and (f) $x = 2.0$ wt%.

Fig. 4-12 SEM micrographs of top view of IMC layer of Sn-3.5Ag-0.7Cu-xSb solder joints reflowed for 1 hour. (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.5$, (d) $x = 1.0$, (e) $x = 1.5$, and (f) $x = 2.0$ wt%.

Fig. 4-13 SEM micrographs of top view of IMC layer of Sn-3.5Ag-0.7Cu-xSb solder joints reflowed for 2 hours. (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.5$, (d) $x = 1.0$, (e) $x = 1.5$, and (f) $x = 2.0$ wt%.

SEM micrographs of the top view of IMC layer in three types of Sn-3.5Ag-0.7Cu-xSb ($x = 0, 1.0$ and 2.0 wt%) solder joints reflowed for 2, 48 seconds, 1 hour and 2 hours are shown in Fig. 4-10 to Fig. 4-13, respectively. It can be seen that the grains grow in solid-liquid reaction by consuming smaller grains and decrease in number. This observation is agreement with other researchers [21-22, 142]. The trace of grain ripening and shrinking can be found in Fig. 4-13. According to Ostwald ripening mechanism [142], the difference of the radius between neighboring grains of the IMC will cause the solder flux to diffuse to the bigger grain and away from the smaller one, thus shrinking the smaller grains while enlarging the bigger grains. The bigger the difference between the radii of the IMC grains, the higher the ripening rate. As shown in these figures, the IMC grains in Sb-containing solder joint are more uniform and evenly distributed than those in Sb-free solder joints. This conclusion is further supported by the information on the IMC grain size distributions and standard deviations of the measurement for different Sb compositions as shown in Fig. 4-14. The results clearly show that the standard deviation of the grain size measurement in Sb-free solder joint is larger than that in Sb-containing solder joints.

Fig. 4-14 IMC grain size distributions for different Sb compositions reflowed for (a) 48s and (b) 2 hours.

The column chart of the grain size versus different reflow dwell time with various Sb percentages is shown in Fig. 4-15. As expected, the grain size increases with the increase in reflow time and the effect of Sb addition on grain size shows a similar trend as the IMC thickness study. For reflow times shorter than 48 seconds, the average grain size of Sb-

containing and Sb-free solder joints is very close. For the reflow times longer than 48 seconds, the average grain size in different solder alloys starts diverging from one another. Under isochronal conditions, for the samples reflowed at above liquidus for 2 hours, the average grain size in Sb-free solder joints is $14.2\mu\text{m}$, while in 1.0 wt% Sb-containing solder joints it decreases to $11.9\mu\text{m}$. In terms of the experimental results, it can be concluded that the Sb additive may act as a grain refiner in IMC formation and growth. The results reveal that the grain refining effect is most prominent when the amount of Sb increases to about 1.0 wt%. A further increase in Sb proportion will cause the grain size to increase slightly.

Fig. 4-15 IMC grain size vs reflow time for different Sb proportions.

4.5 Growth kinetics of the IMC formation

The growth of the IMC layer is sophisticated for the liquid-solid reaction, and some researchers reported that the kinetics often does not follow Fick's diffusion law [8, 20, 143, 144]. To determine the time dependence of IMC growth, a general empirical equation, the power law, is employed to describe the relationship between IMC thickness and reflow time:

$$X = kt^b \quad (4-4)$$

where X is the average IMC thickness, t is the time, k is the growth constant, and b is the growth exponent of IMC layer. k and b are determined by analyzing the measured IMC thickness using curve-fitting. The aim of the fitting procedure is to find those values of the parameters which best describe the data. The standard way of defining the best fit is to choose the parameters so that Chi-Square, the sum of the squares of the deviations of the theoretical curve(s) from the experimental points for a range of independent variables, is at its minimum.

In this work, both IMC thickness and grain growth parameters are used to describe the kinetics of IMC growth because the IMC growth in reflow process involves two different growth kinetics processes. One is the IMC formation and growth controlled by atomic diffusion and interfacial reaction, and another is the grain ripening growth controlled by volume diffusion between the Cu_6Sn_5 scallops.

The curve fitting plots of the thickness and grain size of IMC are shown in Fig. 4-16 and Fig. 4-17. $X = kt^b$ fits the experimental data quite well. The entire R^2 are equal or higher than 0.980. As well known, the IMC growth related to both growth exponent and growth parameter. The k and b values shown in Fig. 4-18 reveal that 1.0wt % Sb solder joint gives the lowest growth exponent and lower growth parameter among all of the compositions. This implies adding 1.0wt % Sb effectively inhibits the growth of IMC - both thickening rate of IMC layer and ripening rate of IMC grain decrease.

Fig. 4-16 Curve fitting of the IMC thickness for Sn-3.5Ag-0.7Cu-xSb solder joints. (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.5$, (d) $x = 1.0$, (e) $x = 1.5$, and (f) $x = 2.0$.

Fig. 4-17 Curve fitting of the IMC grain size for Sn-3.5Ag-0.7Cu-xSb solder joints. (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.5$, (d) $x = 1.0$, (e) $x = 1.5$, and (f) $x = 2.0$.

Fig. 4-18 Curve fitting parameters for different Sb proportions solder systems. (a) Growth parameters of IMC thickness; and (b) Growth parameters of IMC grain

Generally, following atomic diffusion and interfacial reaction, the Cu_6Sn_5 grains form at the solder/Cu interface. In order to reduce free energy of the IMC growth, the large grains grow by the accumulation of elements that diffused from the small grains according to the Ostwald ripening theory [22, 142]. The grain ripening occurs once the IMC is formed and then atomic diffusion, chemical reaction and grain ripening become mutually dependent. The growth exponents ($b = 0.32\sim 0.35$ for IMC thickness and $b = 0.289\sim 0.316$ for grain size) for the growth of IMC layer indicate that the IMC growth is controlled by grain ripening. However, the growth exponents of IMC slightly deviate from the classical Ostwald ripening theory, i.e. $r \propto t^{1/3}$, which shows that the ripening growth is affected by atomic diffusion and interfacial reaction.

4.6 Sb additive effect - Heterogeneous nucleation

As well known, grain refinement is a well-established process resulting in enhanced metallurgical properties such as yield strength, toughness, ductility and surface finishing characteristics. As mentioned before, the Sb additives could play a role to retard the IMC layer growth and refine the IMC grains with the decrease in grain size of up to nearly 20 % for the reaction time of 2 hours. It indicates that adding Sb might improve mechanical

properties and long-term reliability of the solder joints. Hence, it is meaningful to understand the mechanism of the Sb additive effect on the growth of IMC.

From the Sn-Ag-Cu ternary phase diagram, the first IMC formation in the wetting reaction of Sn-Ag-Cu solder joints should be Cu_6Sn_5 . When the reflow temperature reaches the eutectic point, the solder alloy melts, and the Cu resolves into the melted solder and react with Sn quickly. When Cu_6Sn_5 comes into being, it begins by the formation of very small solid particles or nuclei. Additional samples of Sn-3.5Ag-0.7Cu solder joint were prepared to undergo reflow at 217°C for very short time. The SEM images shown in Fig. 4-19 were taken at magnification of 7500X, showing the nuclei formation during rapid liquid-solid reaction.

Fig. 4-19 IMC layer of Sn-3.5Ag-0.7Cu solder joints formed at very short reflow dwell time.
(a) dwell at 217 °C for zero second, and (b) dwell at 217 °C for 2 seconds

Based on the classical solidification theory [145], only those nuclei whose radius is larger than the critical nucleus size can grow up stably. The creation of a critical nucleus can be considered to be a thermally activated process, i.e. the nuclei must be able to cross the activation energy barrier ΔG^* before it becomes a stable nucleus. ΔG^* is given as

$$\Delta G^* = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_v^2} \right) \frac{1}{(\Delta T)^2} \quad (4-5)$$

where γ_{SL} is the solid/liquid interfacial free energy, T_m melting point of IMC, L_v the latent heat of fusion per unit volume and ΔT undercooling of IMC.

It can be seen from equation 4-5 that if nucleation is to be made easier, the interfacial energy

term must be reduced. This can be achieved by heterogeneous nucleation whereby the nucleus formed in contact with Cu substrate or any other nucleation sites (e.g. inclusions like foreign particles, excess vacancies etc) disperse in the liquid solder, which gives a well understanding the nucleus formed on the Cu substrate shown in Fig. 4-19.

Integrating Sn-Ag-Cu-Sb four ternary systems together, the Sn-3.5Ag-0.7Cu-xSb (x is less than 2.0) alloy may consist of several phases, that is, the primary Sn-rich phase [Sn(Sb), Sb is less than 7 wt%], the Ag_3Sn phase, $\epsilon\text{-Ag}_3$ (Sn, Sb) compound, Cu_6Sn_5 phase, and Cu_3Sn phase. Between 234.8 to 378.5 °C, the SnSb phase is a stable phase and exists in the form of small SnSb particles that finely disperse in the molten solder and often offer preferred sites for Cu_6Sn_5 nucleation. Consider a solid nucleus forming in contact with a perfect SnSb particle surface as depicted in Fig. 4-20.

Fig. 4-20 Heterogeneous nucleation of spherical cap on a flat SnSb particle surface

Assuming γ_{SL} is isotropic it can be shown that for a given volume of nuclei the total interfacial energy of the system is minimized. The nucleus has the shape of a spherical cap with a contact angle θ given by the condition that the interfacial tensions γ_{ML} , γ_{SM} and γ_{SL} balance. The activation energy barrier ΔG_a^* becomes [39]

$$\Delta G_a^* = S(\theta)\Delta G^* \quad (4-5)$$

$$S(\theta) = (2 + \cos\theta)(1 - \cos\theta)^2 / 4 \quad (4-6)$$

$S(\theta)$ has a numerical value less than 1 dependent only on θ , i.e. the shape of the nucleus. The activation energy barrier as Sb added ΔG_a^* is smaller than ΔG^* by the shape factor $S(\theta)$. Therefore, more nuclei can cross the energy barrier and grow up stably as Sb is added. The addition of Sb can increase the nucleation rate and decrease the IMC grain size.

From SEM micrographs of top view of the IMC layer in Sn-3.5Ag-0.7Cu-1.5Sb solder joint reflowed for 1 hour shown in Fig. 4-21. It can be observed that a very small amount of Cu_6Sn_5 particles are broken mechanically from the intermetallic/Cu interface, which was also reported by other researchers [146-147]. EDS analyses of these broken grains provide the evidence that SnSb may be the nucleating agent. The EDS results in areas A and B indicated in Fig. 4-21 are shown in Fig. 4-22 and Fig. 4-23. The results show that in area A, the Cu_6Sn_5 grain contains 2.8 wt% of Sb. In area B, on the surface of Cu_6Sn_5 grain, the Sb weight percentage is 1.68 %. The Sb concentration inside the Cu_6Sn_5 grain is higher than that on the Cu_6Sn_5 surface, which suggests that SnSb might be the nucleating agent acting as a heterogeneous inoculant for nucleation of Cu_6Sn_5 grains.

Fig. 4-21 SEM micrographs of top view of a broken Cu_6Sn_5 grain of Sn-3.5Ag-0.7Cu-1.5Sb solder joint reflowed for 1 hour.

Fig. 4-22 EDS analysis of the inside of Cu₆Sn₅ grain in Sn-3.5Ag-0.7Cu-1.5Sb solder joint reflowed for 1 hour.

Sb addition also affects the grain ripening of the IMC phase. Since Sb addition increases the rate of IMC nucleation, the difference between the IMC grain radius in Sb-containing solder joint should be smaller than that in Sb-free solder joint. As discussed previously, the IMC grain sizes in Sb-containing solder joint are more uniform than those in Sb-free solder joints, which is because the IMC grain ripening slows down due to Sb addition.

Fig. 4-24 SEM micrographs of cross-sectional view of Sn-3.5Ag-0.7Cu-xSb solder matrix reflowed for 240 seconds, (a) $x = 1.0$, (b) $x = 2.0$ wt%.

It was mentioned previously that the 1.0 wt% Sb-containing solder joint has the smallest average IMC grain size. Beyond this amount, the IMC grains become slightly larger. To explore the mechanism for this phenomenon, SEM pictures of solder matrix with 1.0 and 2.0 wt % Sb reflowed for 240 seconds have been taken, and are shown in Fig. 4-24 (a) and (b) respectively. It can be observed that the strip-like $\text{Ag}_3(\text{Sn}, \text{Sb})$ particles shown in Fig. 4-24(a) are thinner and shorter than the flake-like particles shown in Fig. 4-24(b) because high Sb proportion in solder matrix enable the $\text{Ag}_3(\text{Sn}, \text{Sb})$ particles to grow larger and become flake-like particles during reflow. Based on the theory of grain refinement, the grain refining behavior appears to be sensitive to the morphology and size distribution. The strip-like particles are probably the more efficient nucleating sites than flaky and petal-like particles [148]. When more than 1.0 wt % Sb is added, SnSb and $\text{Ag}_3(\text{Sn}, \text{Sb})$ phases become flake-like and distribute unevenly, which decreases the nucleation rate and leads to the decrease in grain refining efficiency of the IMC. This is a probable reason why the grain size of IMC increases a little as more than 1 wt % Sb is added.

The proposed mechanism for the effect of Sb on IMC formation can be summarized as follows: during the wetting reaction, SnSb particles may be initially formed and finely dispersed in the molten solder and then some of them precipitate on the top of the substrate and become the heterogeneous nucleation sites of Cu^nSn_m IMC grains. According to the

theory of heterogeneous nucleation, the Cu_6Sn_5 phase prefers to nucleate on the SnSb surface in order to reduce the thermodynamic barrier. With the increase of Sb proportion, more SnSb particles forms and more nucleation sites are produced. The increase in nucleation probability of Cu_6Sn_5 grains consequently leads to the refinement of the grains. As a result, the small and uniform grains obtained in the Sb-containing solder joint slow down the ripening rate, and the refinement effect is achieved. However, when excessive Sb is added, the grain refining inoculants coarsen and distribute unevenly, resulting in the degradation of the grain refinement effect.

4.7 Summary

The effect of Sb addition on IMC growth in Sn-Ag-Cu lead free solder joints in reflow process has been studied. DSC results show that less than 0.8 % Sb addition decrease the melting point of Sn-3.5Ag-0.7Cu solder alloy, further increase in the proportion of Sb increases the melting point of this alloy. SEM micrographs show that the IMC morphologies of Sn-3.5Ag-0.7Cu solder joints have been changed as a result of Sb addition. The IMC layer becomes thinner and the grain size becomes smaller with an increase in Sb proportion up to 1.0 wt%. The growth exponents for IMC layer and grains in solder joints suggest that the kinetics of the IMC formation for the soldering reaction does not simply obey the interfacial reaction-controlled growth or diffusion-controlled growth, but is a combination of both. The grains ripening rate is less than that of Ostwald ripening, which means that atomic diffusion and grain ripening occur simultaneously and their rate is mutually dependent. Comparing with different solder systems, the solder alloy with about 1.0 wt% Sb has the lowest growth exponent for the formation of the IMC and adding 1.0 wt% Sb inhibits the grain ripening most effectively. The effect of Sb addition on the IMC growth might be explained with heterogeneous nucleation theory. When Sb is added in the Sn-Ag-Cu solder alloy, SnSb particles precipitate from the molten solder and become the heterogeneous nucleation sites of Cu_6Sn_5 IMC during reflow. The free energy of the IMC phase ΔG_a^* decreases and the rate of Cu_6Sn_5 nucleation increases with an increase in Sb proportion up to 1.0 wt%. However, when excessive Sb is added, the grain refining inoculants coarsen and distribute unevenly, resulting in the degradation of the grain refinement effect. In contrast to Sb-free solder joint, adding Sb into Sn-Ag-Cu solder alloy could form a solder joint with finer and more uniform grains, and retard grain ripening and IMC growth.

Chapter 5

IMC growth and kinetics of Sn-3.5Ag-0.7Cu-xSb solder joints during ageing

5.1 Introduction

In application, all solder joints undergo ageing with time, which results in the alteration of the microstructure. Depending on the temperature to which the solder joint is exposed during service, the rate of ageing can differ. Higher temperatures naturally cause faster ageing. Solder joint in typical automotive under-the-hood service conditions are exposed to temperature of around 150°C, while those in computer related applications experience temperature of 50-80 °C. Such high temperature causes dynamic recrystallization and grain growth to occur within the solder microstructure. This change in the microstructure alters the properties of the solder joint and changes the way the solder material would respond to further deformation processes [101]. This chapter aims at exploring the effects of Sb additive on the microstructure evolution and the growth kinetics of the IMC layer in Sn-Ag-Cu lead-free solder joints during ageing. This chapter is divided into three parts. The first section discusses the growth kinetics of whole IMC layer, considering the Cu₆Sn₅ and Cu₃Sn layers as a single system. The second section discusses the growth kinetics of individual IMC layer, considering the Cu₆Sn₅ and Cu₃Sn layers separately. The last section explores the effect of Sb on the growth of IMC during ageing.

5.2 Growth of IMC bilayers: Cu_6Sn_5 and Cu_3Sn as a single entity

5.2.1 Microstructural Evolution

The experimental for solid-solid reactions between solder alloy and Cu substrate has been described in chapter 3. In this study, backscattered SEM model was used to observe the cross-sectional microstructural evolution of the solder joints as this model can show different IMC layers of Cu_6Sn_5 and Cu_3Sn clearly. Figures 5-1 to 5-3 show the typical SEM images of the solder/Cu interface of the Sn-3.5Ag-0.7Cu-xSb ($x = 0, 0.2, 0.5, 0.8, 1.0, 1.5$ and 2.0) solder joints aged at the temperature of 190°C for 1, 200, and 600 hours, respectively. The pictures reveal that the morphology of Cu_6Sn_5 phase gradually transforms from the scallop-type to layer-type during aging. Fig. 5-2 and Fig. 5-3 clearly show that layer structure of the Cu_6Sn_5 and Cu_3Sn phases exists at the interface and the layer of Cu_3Sn is less uneven than Cu_6Sn_5 . For the solder joint aged for 600 hours, the Cu_3Sn layer is almost as thick as the Cu_6Sn_5 layer.

All three figures show that the Sb-containing solder joints have thinner IMC layer compared with the Sb-free solder joints. As a single entity, the IMC thicknesses in solder joints aged at different ageing temperatures for different time are listed in Table 5-1. In determination of the average thickness of the IMC layer, the standard deviations were calculated for all cases and the ratio of the standard deviation to the thickness was found to be within 10 %. Results show that the growth rate of the IMC depends on the ageing temperature, ageing time, and Sb composition. The thicknesses of the IMC decrease a little bit for the as-soldered Sb-containing solder joints, which means that Sb addition only has slight influence on the IMC growth during reflow process. After ageing, the IMC thickness of the Sb-containing samples is apparently thinner than that of the Sb-free samples, regardless of the ageing temperature. For the same ageing temperature and time, IMC thickness decreases with the increase of Sb composition, and the downward trend persists until the weight percentage of Sb approaches 0.8-1.0 %. Beyond this amount, the IMC thickness increases slightly again, but is still thinner than that of the Sb-free solder system.

Fig. 5-1 Backscattered SEM micrographs of cross-sectional view of Sn-3.5Ag-0.7Cu-xSb solder joints aged at 190°C for 1 hour. (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.5$, (d) $x = 0.8$, (e) $x = 1.0$, (f) $x = 1.5$ and (f) $x = 2.0$ wt %.

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Fig. 5-2 Backscattered SEM micrographs of cross-sectional view of Sn-3.5Ag-0.7Cu-xSb solder joints aged at 190°C for 200 hours. (a) x = 0, (b) x = 0.2, (c) x = 0.5, (d) x = 0.8, (e) x = 1.0, (f) x = 1.5 and (g) x = 2.0 wt %.

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Fig. 5-3 Backscattered SEM micrographs of cross-sectional view of Sn-3.5Ag-0.7Cu-xSb solder joints aged at 190°C for 600 hours. (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.5$, (d) $x = 0.8$, (e) $x = 1.0$, (f) $x = 1.5$ and (f) $x = 2.0$ wt %.

Table 5-1 Average thickness (μm) of IMC in Sn-3.5Ag-0.7Cu-xSb solder joints after ageing

Temp. (°C)	Sb proportion (wt%)	Ageing time						
		0h	1h	10hs	100hs	200hs	400hs	600hs
100°C	0	3.56	4.15	3.65	4.80	5.23	5.54	5.81
	0.2	3.16	2.79	2.96	3.30	3.57	4.23	4.71
	0.5	3.11	3.19	3.24	3.62	3.32	3.67	4.04
	0.8	3.07	2.92	3.05	3.36	3.20	3.60	3.89
	1.0	3.35	3.46	3.09	3.36	3.51	3.99	4.51
	1.5	3.26	3.33	3.27	3.34	3.79	4.05	4.15
	2.0	3.23	3.24	3.35	3.29	3.56	4.00	4.22
150°C	0	3.56	4.40	4.33	5.88	5.98	7.47	8.08
	0.2	3.16	3.55	3.92	4.42	4.83	5.55	7.09
	0.5	3.11	3.32	3.56	3.75	4.15	4.84	5.71
	0.8	3.07	2.77	3.17	3.94	4.46	4.67	4.77
	1.0	3.35	3.61	3.74	4.33	4.41	5.67	6.15
	1.5	3.26	3.40	3.74	4.31	4.43	5.24	5.44
	2.0	3.23	3.44	3.58	3.84	3.94	5.09	5.74
190°C	0	3.56	4.23	5.27	8.21	10.69	11.02	14.84
	0.2	3.16	4.14	4.28	6.83	9.00	11.71	13.30
	0.5	3.11	3.69	3.95	6.28	8.05	9.65	11.51
	0.8	3.07	3.44	4.26	6.78	8.80	10.84	11.88
	1.0	3.35	3.95	4.09	6.29	8.26	10.23	11.06
	1.5	3.26	3.83	4.48	6.66	7.94	9.78	11.88
	2.0	3.23	3.95	4.15	6.35	8.26	10.47	12.04

SEM micrographs of the top view of three types of solder joints (Sn-3.5Ag-0.7Cu-xSb, $x=0.0$, 0.2 and 0.8 wt %) aged at 190°C for 1 hours, 200 hours and 600 hours are shown in Fig. 5-4 to Fig. 5-6 respectively. In three kinds of solder alloys, all Cu_6Sn_5 IMC grain size become coarse as the ageing time increases. After ageing for an hour, the surface of IMC is still rather rough. Many scallop-like grains extrude from the smaller grains. After 200 hours ageing, the Cu_6Sn_5 surface becomes more flat, and the grains connect together closely. When the ageing time is up to 600 hours, the grains coarse a lot, some small grains merge together to become a big grain. Fig. 5-6 clearly shows that some grains coalesce to become a big one, and the trace of the disappearing grain boundary can be clearly observed. This indicates that the big grain is formed from two or more small grains. Experimental results also reveal that the grain size of IMCs in Sb-containing solder joint is smaller than that in Sb-free solder joint. The grain size of IMC decreases as the Sb composition increases, which may indicate that adding Sb helps to refine the grain size of the IMC and hence may improve the mechanical properties of the solder joints. The mechanism will be discussed in detail later on.

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Fig. 5-4 SEM micrographs of top view of IMC layer of Sn-3.5Ag-0.7Cu-xSb solder joints aged at 190°C for 1 hour. (a) $x = 0$, (b) $x = 0.2$, and (c) $x = 0.8$ wt%.

Fig. 5-5 SEM micrographs of top view of IMC layer of Sn-3.5Ag-0.7Cu-xSb solder joints aged at 190°C for 200 hours. (a) $x = 0$, (b) $x = 0.2$, and (c) $x = 0.8$ wt%.

Fig. 5-6 SEM micrographs of top view of IMC layer of Sn-3.5Ag-0.7Cu-xSb solder joints aged at 190°C for 600 hours. (a) $x = 0$, (b) $x = 0.2$, and (c) $x = 0.8$ wt%. Some small grains coalesce to become a big one, and the trace of the disappearing grain boundary can be clearly observed.

5.2.2 Growth kinetics of the IMC formation

The relationship between the thickness of IMC layer and ageing time is generally considered to follow Fick's law, which is shown in Fig.5-7. The interdiffusion coefficient could be determined from a linear regression analysis of X vs $\sqrt{t}$, where the slope of the straight line is $\sqrt{D}$.

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Fig. 5-7 Relationship between IMC thickness and square root of ageing time in Sn-3.8Ag-0.7Cu-xSb solder joints. (a) x = 0, (b) x = 0.2, (c) x = 0.5, (d) x = 0.8, (e) x = 1.0, (f) x = 1.5, and (g) x = 2.0 wt %.

The relationships between IMC growth rate D and Sb composition in Sn-3.5Ag-0.7Cu-xSb solder alloys for the aging temperature of 100, 150, and 190°C are shown in Fig. 5-8. The results reveal that for three different ageing temperatures, the growth rates decrease quickly when 0.2 wt% Sb is added, and the lowest growth rate is located at the range of Sb compositions of 0.5-1.0 wt %. The results also show that further increase in Sb composition only has a little bit influence on the IMC growth rate. It is worth to note that the Sb compositions of the solder joint which has lowest growth rates for the aging temperature of 100, 150, and 190°C are different, and the turning points are located at 0.5, 0.8, and 1.0 wt % respectively. A possible explanation for this phenomenon is that the mutual solubility of Sn and Sb increases with increase in temperature leading to more fine particles precipitated on the grain boundary in reflow process to inhibit the diffusion of Sn and Cu atoms across the IMC layer.

Fig. 5-8 Growth rates of IMC vs Sb proportions for different aging temperature

In this study, Arrhenius relationship (Equation 2-3) is used to determine the activation energy for intermetallic growth, the plots are shown in Fig. 5-9. The interdiffusion coefficient obtained from the thickness measurements are used to determine the activation energy for the growth of the intermetallics. The activation energies of seven solder systems are given in Fig. 5-10. Results reveal that Sb-free solder joint has the lowest activation energy of 48.8 kJ/mol. When 0.2 wt % Sb is added, the activation energy raises to 57.1 kJ/mol. The activation energy continuously increases and reaches the highest value of 74.8 kJ/mol at 0.8 wt% Sb,

with the total increment of more than 50%. However, continuous increase in Sb to 1.0 wt% causes the activation energy to decrease to 64.0 kJ/mol. A further increase in Sb to 1.5 and 2.0 wt%, the activation energies only change a little bit and reach to 67.0, and 68.3 kJ/mol respectively. Nevertheless, the IMC formation in solder joints with 1.0-2.0 wt% Sb still possesses a higher activation energy compared to Sb-free solder joints. Correlating IMC growth rates and activation energies, it could be concluded that adding of Sb in Sn-3.5Ag-0.7Cu solder alloy can increase the activation energy, and thus reduce the atomic diffusion rate, so as to inhibit the excessive growth of IMC.

Fig. 5-9 Arrhenius plots for the formation of IMC at Sn-3.5Ag-0.7Cu-xSb solder joints

Fig. 5-10 Relationship between activation energy and Sb proportion

5.3 Growth of IMC bilayers: Cu_6Sn_5 and Cu_3Sn as independent entities

Previous section reveals that adding Sb into Sn-3.5Ag-0.7Cu solder alloy system can reduce the atomic interdiffusion rate, and thus inhibit the excessive growth of the IMC layers. However, the analysis and discussion was limited within the growth kinetics of the total IMC layer formation. In order to well understand the mechanism, this part of work aims at exploring the effects of Sb additive on the formation and growth kinetics of the individual Cu_6Sn_5 and Cu_3Sn IMC layers formed at the interface between lead-free solders and Cu substrate.

5.3.1 Microstructural Evolution

Figure 5-11 shows a typical SEM micrograph of the IMC formation in a Sn-3.5Ag-0.7Cu as-soldered joint. Generally, as reported, a thin layer of Cu_6Sn_5 (η phase) intermetallic compound is formed as soon as the eutectic solder is melt on a Cu substrate. Under high resolution of backscattered SEM, a duplex structure of intermetallic compounds at the solder/Cu interface can be observed. The EDS results shown in Fig. 5-12 reveal that the IMC phases are Cu_6Sn_5 and Cu_3Sn (ϵ phase) respectively. The layer in contact with the solder is the Cu_6Sn_5 phase, while the Cu_3Sn is a very thin layer and sandwiched between Cu_6Sn_5 layer and Cu substrate. Cu_3Sn layer was found in all seven solder alloys. Normally the first intermetallic compound forming at the solder/Cu interface is η - Cu_6Sn_5 phase because η - Cu_6Sn_5 has lower activation energy comparing to ϵ - Cu_3Sn phase [149]. However, the η phase is thermodynamically unstable with Cu. With the formation of η phase, the ϵ phase will form by consuming η phase [7]. The phase formation and evolution in an interfacial region involve the diffusion of Sn and Cu atoms. As described by Dayananda et al. [150], the elements only intrinsically diffuse into a direction in which their own chemical potentials are lowered. Since the change in composition can cause great changes in the component chemical potentials, the availability or mass supply of the components that are involved in the interfacial reaction plays a very important role in the phase evolution [85]. During reflow, because the melted solder has higher mobility than solid Cu, rich tin atoms could be available at the interface, which leads to accelerate the formation and growth of Cu_6Sn_5 (Sn-rich IMC phase) and inhibit the growth of Cu_3Sn (Cu-rich IMC phase). Therefore, the Cu_6Sn_5 phase grows as a

dominated phase and only a very thin Cu_3Sn layer can be observed in the as-soldered solder joints during reflow.

Fig. 5-11 Backscattered SEM micrograph of cross-sectional view of Sn-3.5Ag-0.7Cu as-soldered joint

Fig. 5-12 EDS analysis of IMC layer in Sn-3.5Ag-0.7Cu as-reflowed solder joint: (a) Cu_6Sn_5 layer and (b) Cu_3Sn layer.

Figure 5-13 is the typical SEM images of the solder/Cu interface in the Sn-3.5Ag-0.7Cu solder joints aged at the temperature of 100°C, 150°C, and 190°C for 600 hours, respectively. The images reveal that the Cu_6Sn_5 layer is less uniform than the Cu_3Sn layer. At low ageing temperature, Cu_6Sn_5 layer is always thicker than the Cu_3Sn layer, whereas for the solder joint aged at 190°C for 600 hours, the Cu_3Sn layer is almost as thick as the Cu_6Sn_5 layer. The results indicate that at lower temperatures Cu_6Sn_5 formation dominates, while at higher temperature the Cu_3Sn layer has a significant contribution to the growth of the total IMC layer. To understand the physics behind the problem, it is necessary to study the growth rate and kinetics of both IMC layers.

Fig. 5-13 Backscattered SEM micrographs of cross-sectional view of Sn-3.5Ag-0.7Cu solder joint aged for 600 hours: (a) aged at 100°C (x7500), (b) aged at 150°C (x3500), and (c) aged at 190°C (x2000).

5.3.2 Growth kinetics of the IMC formation

In order to study the mechanism that adding Sb in Sn-3.5Ag-0.7Cu solder alloy system could inhibit the IMC layer formation in the solder joints, the Cu_6Sn_5 and Cu_3Sn layers were individually characterized. Table 5-2 shows the average thicknesses of the individual IMC layer growth against the ageing time for different ageing temperatures. The curve-fitting graphs based on Equation 4-4 are shown in Fig. 5-14 and Fig. 5-15. Results display that the growth exponents n of the Cu_6Sn_5 and Cu_3Sn formation range from 0.42 to 0.83. The growth exponents depend not only on the ageing temperature and Sb concentration, but also on the IMC phases. For the Sb-contained solder joint, it can be seen that the higher the ageing temperature, the smaller the growth exponent. At higher ageing temperature, the growth exponent is quite close to the 0.5 for both Cu_6Sn_5 and Cu_3Sn IMC layer growth, which means that both Cu_6Sn_5 and Cu_3Sn IMC layer growth might be diffusion-controlled process. At ageing temperature of 100°C , the IMC growth exponents in Sb-contained solder joints significantly deviate from 0.5 but less than 0.83, which means that the IMC growth is not completely diffusion-controlled, but also affected by chemical reaction.

Table 5-2 Average thickness (μm) of IMC growth in Sn-3.5Ag-0.7Cu-xSb solder joints after ageing

Sb Composition (wt %)	Ageing time (h)	100°C		150°C		190°C	
		Cu ₆ Sn ₅	Cu ₃ Sn	Cu ₆ Sn ₅	Cu ₃ Sn	Cu ₆ Sn ₅	Cu ₃ Sn
0	1	3.54	0.31	3.61	0.36	3.78	0.57
	10	3.57	0.38	3.78	0.42	4.02	1.31
	100	4.41	0.43	4.70	1.28	5.26	2.95
	200	4.75	0.55	4.72	1.37	6.23	4.16
	400	4.70	0.64	5.68	1.99	6.44	4.98
	600	5.12	0.68	5.88	2.43	8.34	6.31
0.2	1	2.69	0.32	3.08	0.3	3.50	0.61
	10	2.65	0.32	3.18	0.42	3.60	1.14
	100	2.95	0.39	3.65	0.96	4.44	2.49
	200	3.09	0.48	3.77	1.16	5.65	3.17
	400	3.67	0.56	4.39	1.63	6.87	4.79
	600	4.06	0.65	4.93	2.18	7.37	6.03
0.5	1	2.65	0.28	2.79	0.43	3.10	0.52
	10	2.82	0.34	2.81	0.58	3.02	1.17
	100	2.95	0.39	2.96	0.92	4.05	2.54
	200	2.97	0.49	3.45	1.07	4.99	3.29
	400	3.51	0.55	3.68	1.51	5.43	4.32
	600	3.65	0.59	4.04	1.98	6.37	5.48
0.8	1	2.41	0.28	2.47	0.3	3.07	0.48
	10	2.68	0.37	2.70	0.47	3.10	1.11
	100	2.83	0.42	2.86	1.08	4.16	2.44
	200	2.76	0.39	3.25	1.14	3.93	3.18
	400	3.12	0.48	3.42	1.55	5.35	4.5
	600	3.23	0.63	3.51	1.98	6.08	5.23
1.0	1	2.95	0.33	3.18	0.29	3.45	0.41
	10	2.76	0.33	3.26	0.52	3.15	1.04
	100	2.96	0.40	3.40	1.02	3.96	2.47
	200	3.10	0.42	3.59	1.29	4.85	3.48
	400	3.28	0.55	4.04	1.76	5.77	4.19
	600	3.64	0.68	4.24	2.16	5.75	5.61
1.5	1	2.91	0.3	3.05	0.33	3.32	0.55
	10	2.92	0.35	3.25	0.48	3.46	1.09
	100	2.91	0.4	3.26	1.12	4.27	2.18
	200	3.35	0.45	3.61	1.33	4.32	3.91
	400	3.54	0.52	3.65	1.84	5.07	4.9
	600	3.48	0.67	3.84	2.03	6.37	5.51
2.0	1	2.84	0.33	3.02	0.36	3.42	0.52
	10	2.96	0.31	3.13	0.46	3.19	1.28
	100	2.87	0.39	3.17	0.91	4.22	2.37
	200	3.21	0.42	3.71	1.08	4.42	3.96
	400	3.57	0.50	3.77	1.64	5.31	4.67
	600	3.63	0.64	4.35	2.10	6.18	5.62

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Fig. 5-14 Thickness vs. ageing time for Cu_6Sn_5 IMC layer in Sn-3.5Ag-0.7Cu-xSb solder joint: (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.5$, (d) $x = 0.8$, (e) $x = 1.0$, (f) $x = 1.5$, and (g) $x = 2.0$ wt%.

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Fig. 5-15 Thickness vs. ageing time for Cu_3Sn IMC layer in Sn-3.5Ag-0.7Cu-xSb solder joint: (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.5$, (d) $x = 0.8$, (e) $x = 1.0$, (e) $x = 1.5$, and (g) $x = 2.0$ wt%.

It is worth to mention that the interdiffusion coefficient cannot be determined by the empirical Equation 2-3. In order to study the Sb additive effect on the individual IMC layer growth, the interdiffusion coefficients and activation energies are still estimated in light of diffusion-controlled mechanism. The growth rates of Cu_6Sn_5 and Cu_3Sn IMC layer formation are determined by curve fitting in terms of Equation 2-2 and the results are shown in Fig. 5-16. It can be seen that both Cu_3Sn and Cu_6Sn_5 layers have higher growth rate at ageing temperature of 190°C and the growth rate of Cu_3Sn is faster than that of Cu_6Sn_5 . However, at 100°C , the growth rates of the Cu_3Sn IMC layer are lower than that of the Cu_6Sn_5 layer. These results reveal that the Cu_3Sn phase has more contribution to the total IMC layer growth at higher temperature whereas less contribution at lower temperature. The results also show the evident effects of Sb addition on the IMC growth rates. For the Cu_6Sn_5 phase, the growth rates has a fast decrease at the Sb concentration range of 0 to 0.5%, and further increase in Sb percentage has very little influence on the IMC growth rate for three different aging temperatures. For the Cu_3Sn phase, it can be seen that the growth rates display a wave curve at ageing temperatures of 190°C and 150°C , and the lowest growth rate occurs at the range of 0.5-1.0 wt % Sb. However, the growth rate almost keeps unchanged and is about $10^{-15} \text{ cm}^2/\text{s}$ at 100°C .

Fig. 5-16 Growth rates of IMC vs Sb proportions for different aging temperature ($10^{-15} \text{ cm}^2/\text{s}$): (a) Cu_6Sn_5 layer and (b) Cu_3Sn layer.

The activation energies of seven solder systems for the Cu_6Sn_5 and Cu_3Sn intermetallic layers are determined in terms of Equation 2-3 and are shown in Fig. 5-17. The activation energies for the growth of the Cu_6Sn_5 and Cu_3Sn intermetallics in different alloys are in the range of 30 to 43, and 86 to 91 kJ/mol, respectively. The much lower activation energy of the Cu_6Sn_5 phase than Cu_3Sn could be used to explain why Cu_6Sn_5 forms earlier during reflow. These results are comparable with the results reported by Lee et al. [149], in which the activation energies are reported to be 48.54 and 89.06 kJ/mol for the growth of Cu_6Sn_5 and Cu_3Sn intermetallics formed between Sn-3.5Ag-0.7Cu solder and Cu substrate by solid-state isothermal aging, respectively. The activation energy of Cu_6Sn_5 being much lower than that of Cu_3Sn indicates that the growth rate of the Cu_6Sn_5 should be higher than that of Cu_3Sn . Comparing the results shown in Fig. 5-16 and Fig. 5-17, it seems accordant at low ageing temperature. However, at high ageing temperature, the growth rate of Cu_6Sn_5 is lower than that of Cu_3Sn . This is because the growth of Cu_3Sn is based upon the consumption of Cu_6Sn_5 compound. Generally, at higher temperature, the Sn and Cu atoms can easily obtain enough energy to overcome the energy barrier, leading to the fast growth of both phases. Nevertheless, since the high growth rate of Cu_3Sn usually accompanies a high consumption rate of the Cu_6Sn_5 phase, the growth rate of the Cu_3Sn phase may become higher than the difference between the real growth rate and the consumption rate of the Cu_6Sn_5 . The growth rate of Cu_6Sn_5 plotted in Fig. 5-16 is actually the result of real growth rate minus the consumption rate of Cu_6Sn_5 . At low temperature, as the growth rate of the Cu_3Sn phase is

very low, the difference of the real growth rate and the consumption rate for the Cu_6Sn_5 could keep being higher than the growth rate of the Cu_3Sn phase.

Compared with the activation energy of the total IMC layer growth in last section, the activation energies with different Sb percentage for the Cu_6Sn_5 layer show a similar trend, and Sb-free solder joint has the lowest activation energy (30.26 kJ/mol). When 0.2 wt% Sb is added, the activation energy rises to 33.18 kJ/mol. The activation energy continuously increases and reaches the highest value of 43.05 kJ/mol at 0.8 wt% Sb. However, a further increase in Sb to 1.0 wt% causes the activation energy to decrease to 41.54 kJ/mol. Further increase in Sb to 1.5 and 2.0 wt% results in a decrease of the activation energies to 40.07 and 37.33 kJ/mol, respectively. On the other hand, the activation energies of Cu_3Sn do not have significant change with the change of Sb proportion, ranging from 86.72 to its highest value of 90.91 kJ/mol at 0.8 wt% Sb.

Fig. 5-17 Relationship between activation energy and Sb proportion: (a) Cu_6Sn_5 layer and (b) Cu_3Sn layer.

5.4 Sb additive effect - grain boundary pinning mechanism

5.4.1 Sb additive effect on total IMC growth

The formation of IMC components have been shown in section 4.3, the Sn-3.5Ag-0.7Cu-xSb (x is less than 2.0) alloy may consist of the primary Sn-rich phase Sn(Sb), the Ag₃Sn phase, ϵ -Ag₃ (Sn, Sb) compound, Cu₆Sn₅ phase, and Cu₃Sn phase. The experimental results also

Fig. 5-19 EDS analysis of the top of IMC layer in Sn-3.5Ag-0.7Cu-1.0Sb solder joint aged at 190°C for 200 hours.

The x-ray mapping results of Sn, Ag and Cu in Sn-3.5Ag-0.7Cu-xSb solder joints are given in Fig. 5-20 to Fig. 5-22. The results of Ag mapping show that many Ag-rich phase appears and may be in forms of Ag_3Sn or $\text{Ag}_3(\text{Sn}, \text{Sb})$ after adding Sb in contrast of Sn mapping images. It has been reported by some researchers that some Ag_3Sn particles precipitates along the grain boundary of Cu_6Sn_5 IMC in Sn-Ag-Cu solder joints [11, 151], which may be an important factor that affects the growth of the interfacial IMC layer in solder joints. It is also found in this study that many fine particles pin along the grain boundary in both Sb-containing and Sb-free samples but the compositions of the particles in Sb-containing solder joints are somewhat different from that in Sb-free solder joints. It is worth to mention that the higher the percentage of Sb, the more the particles precipitate along the grain boundary. The higher magnification SEM micrograph of the top view of the IMC layer in Sn-3.5Ag-0.7Cu-1.0Sb solder joint aged at 190°C for an hour shown in Fig. 5-23 clearly reveals that the distinguishable particles pin along the grain boundaries of the IMC. Actually these small particles could precipitate in the channels between the IMC grains during reflow process. The EDS analyses show that there are two kinds of particles, particle A and B, indicated in Fig. 5-23. The EDS analysis of particle A presented in Fig. 5-24 suggests particle A may be the $\text{Ag}_3(\text{Sn}, \text{Sb})$ phase since Sn-Ag-Sb alloy system only have $\text{Ag}_3(\text{Sn}, \text{Sb})$ stable ternary phase at room temperature. The appearance of Cu element shown in Fig. 5-24 may come from Cu_6Sn_5 stable phase because of this small particle pinning on the Cu_6Sn_5 IMC matrix. Particle B is

confirmed to be $\text{Cu}_6(\text{Sn,Sb})_5$ phase and the proportion of Sb is 1-2 wt%, which is similar to the result in Fig. 5-19. XRD result from the top of the IMC layer, shown in Fig. 5-25, further reveals the existence of Cu_6Sn_5 , $\text{Ag}_3(\text{Sn, Sb})$ phases in IMC layer. According to the microstructural evolution and phase analysis of above results, Sb in the solder alloy may disperse or diffuse into the solder and IMC layer with three approaches. Some of the antimony powders dissolves in the β -Sn matrix (Sn-rich phase), some of the remainder participates in the formation of ϵ - $\text{Ag}_3(\text{Sn, Sb})$ component, and the rest dissolves in Cu_6Sn_5 IMC layer as impurities.

Figure 5-20 Backscattered SEM and X-ray mapping of the X2000 cross-section view of Sn-3.5Ag-0.7Cu solder joint aged at 190°C for 200 hours. (a) SEM view, (b) Ag mapping, (c) Cu mapping and (d) Sn mapping.

Figure 5-21 Backscattered SEM and X-ray mapping of the X2000 cross-section view of Sn-3.5Ag-0.7Cu-1.0Sb solder joint aged at 190°C for 200 hours. (a) SEM view, (b) Ag mapping, (c) Cu mapping and (d) Sn mapping.

Figure 5-22 Backscattered SEM and X-ray mapping of the X2000 cross-section view of 2.0 Sb contained sample aged at 190°C for 200 hours. (a) SEM view, (b) Ag mapping, (c) Cu mapping and (d) Sn mapping.

Fig. 5-23 Higher magnification image of particles pinning on the grain boundary for Sn-3.5Ag-0.7Cu-1.0Sb solder joint aged at 190°C for an hour.

Fig. 5-24 EDS analysis of a small $\text{Ag}_3(\text{Sn}, \text{Sb})$ particle pinning on the grain boundary shown in area A of Fig. 5-23.

Fig. 5-25 XRD spectra taken from the top of IMC layer in Sn-3.5Ag-0.7Cu-1.0Sb solder joint aged at 190°C for 1 hour

It is worth mentioning that after adding Sb, more particles precipitate, and IMC layers become thinner. There might have some correlation between the thickness of IMC and the amount of particles precipitated along the IMC grain boundary. As well known, grain boundary diffusion plays an important role in the growth kinetics of IMC in solder joints.

IMC growth is controlled by diffusion of the constituent atomic species through the IMC layer to the reaction sites located at the solder/ Cu_6Sn_5 interface and the $\text{Cu}_3\text{Sn}/\text{Cu}$ interface. Generally, elements diffuse through the grain boundaries more rapidly than through the grain to maintain continuous interfacial reaction [152-153]. The existence of $\text{Ag}_3(\text{Sn}, \text{Sb})$ and Cu_6Sn_5 (Sb) particles at the Cu_6Sn_5 grain boundary actually obstructs the grain boundary diffusion of Cu and Sn via the IMC layer leading to inhibit the growth of the IMC. This grain boundary pinning mechanism could explain why adding Sb in Sn-3.5Ag-0.7Cu solder decreases the growth rate of the IMC. Moreover, when Sb percentage is more than 0.8 wt%, the $\text{Ag}_3(\text{Sn}, \text{Sb})$ particles precipitating on the grain boundary become denser and denser and some of neighbors coalesce together and become elongated particles resulting in inability to precipitate in the channels between two grains of the IMC, which makes the elemental interdiffusion rate increases slightly again.

On the other hand, as mentioned earlier, the Sb addition refines the grain size of the IMC. It could also be explained with the proposed grain boundary pinning mechanism. Fig. 5-26 shows a SEM micrograph of a Sn-3.5Ag-0.7Cu-1.0Sb solder joint aged at 150°C for 600 hours. It can be observed from Fig. 5-26 that at region A, the big grain coalesces from two smaller grains as there are no particles pinning along the boundary and a light grain boundary trace can be clearly observed. However, at region B indicated in Fig. 5-26, two particles pinning along the grain boundary prevent the IMC grains from coalescing. Based on the grain coalescence theory by Li [154], the coalescence of two subgrains and the elimination of a subgrain boundary must result in a relative rotation of the two subgrains. The subgrains cannot coalesce if there is one or more small particles pinning along their grain boundary and obstructing the grain rotation. This may be the reason why adding of Sb has a function of refining the grain size of the IMC.

Fig. 5-26 Higher magnification image showing particles pinning on the grain boundary in Sn-3.5Ag-0.7Cu-1.0Sb solder joint aged at 150°C for 600 hours. At area A, grains coalesce and grain boundary disappears. At area B, two particles pin along the grain boundary and prevent the IMC grains from coalescing.

5.4.2 Sb additive effect on separated layers

According to the results of growth rates and activation energies, it can be found that adding Sb (up to 1.0 wt%) can effectively reduce the growth rate of Cu_6Sn_5 at any temperature, but has less effect on Cu_3Sn growth, especially at low temperature. To understand the mechanism, the previous results on the total IMC layer growth during reflow and ageing process can be helpful. Since Sb has higher affinity to the constituent element of Sn in Sn-Cu-Sb ternary system [12, 155] and Sb is next to Sn in the periodic table with the difference in atomic mass less than 15% [80], Sb atoms trend to replace some of the Sn atoms in Sn-based compounds and hence readily dissolves in the β -Sn matrix (Sn-rich phase) or in the Cu_6Sn_5 , or forms Ag_3Sb that precipitates simultaneously with Ag_3Sn . EDS results of Fig. 5-27 illuminate that more Sb atoms diffuse into Cu_6Sn_5 layer than those into Cu_3Sn layer due to the shorter diffusion path. As well known, the crystal structures of both Ag_3Sb and Ag_3Sn are orthorhombic [156]. XRD result shown in Fig. 5-25 indicates that the Ag_3Sb has similar lattice spacing as Ag_3Sn . Therefore, these two phases may precipitate simultaneously during cooling. As shown in Fig. 5-26, the small ϵ - $\text{Ag}_3(\text{Sn}, \text{Sb})$ or $\text{Cu}_6(\text{Sn}, \text{Sb})_5$ particles precipitating

and pinning along the grain boundary of Cu_6Sn_5 layer obstruct Cu and Sn diffusing through grain boundaries and thus inhibit the formation of the IMC in the solder joint. Since the $\varepsilon\text{-Ag}_3(\text{Sn}, \text{Sb})$ particles precipitate on top of Cu_6Sn_5 layer during reflow, many of them pinn along the Cu_6Sn_5 grain boundary and effectively inhibit the grain boundary diffusion, and thus affect the growth rate of the Cu_6Sn_5 layer. On the other hand, small mount of Sb atoms diffused into Cu_3Sn layer by replacing Sn atoms has less effect on the layer growth of Cu_3Sn layer than Cu_6Sn_5 . The study of activation energies for the two IMC layers further supports this postulation. The activation energy of Cu_6Sn_5 significantly increases with the increase in Sb proportion up to 0.8 wt%, whereas the activation energies of Cu_3Sn changes smoothly although there is a similar changing trend with the Cu_6Sn_5 .

Fig. 5-27 EDS analysis of IMC layer in Sn-3.5Ag-0.7Cu-1.0Sb solder joint aged for 100 hours: (a) Cu_6Sn_5 layer and (b) Cu_3Sn layer.

5.5 Summary

The effect of Sb addition on IMC growth in Sn-3.5Ag-0.7Cu solder joints during ageing has been studied in this work. SEM micrographs show that Cu_3Sn IMC layer presents in the as-soldered Sn-3.5Ag-0.7Cu-xSb solder joints. The Cu_3Sn layer grows faster than Cu_6Sn_5 layer at higher ageing temperatures, while Cu_6Sn_5 layer grows faster than Cu_3Sn layer at low ageing temperatures. The IMC morphologies of Sn-3.5Ag-0.7Cu solder joints have been changed as a result of the Sb addition. The IMC layer becomes thinner and the grain size becomes smaller with an increase in Sb proportion. It is also observed that the fine particles precipitating increases the IMC layer with an increase in Sb proportion during reflow. Sb addition can increase the activation energy of Sn-3.5Ag-0.7Cu solder alloy system, and reduce the atomic diffusion rate, so as to inhibit the excessive growth of the IMC layers. It is found that the solder alloy with about 0.8 wt% Sb has the highest activation energy and lowest interdiffusion coefficient for the growth of total IMCs, Cu_6Sn_5 and Cu_3Sn IMC layers. Sb addition mainly affects the growth of Cu_6Sn_5 rather than Cu_3Sn . The effect of Sb addition on the IMC growth may be explained with grain boundary pinning mechanism. The small particles precipitating and pinning along the grain boundary obstruct Cu and Sn diffusion through grain boundaries and thus inhibit the formation of the IMC in the solder joint. The small particles pinning at the grain boundary also have the function to block the coalescence of the grains, which may be the reason why adding of Sb elements can refine the grain size of the IMC.

Chapter 6

Effect of Sb composition and Testing Parameters on Tensile Strength of Sn-3.5Ag-0.7Cu Solder Alloys and Solder Joints

6.1 Introduction

The solder joints connect the electronic components to the board electrically as well as mechanically. Failure of solder joints could occur by mechanical shock during manufacture and transportation, high-cycle fatigue (vibration during in-service condition) and thermomechanical fatigue (environmental temperature changes, change in temperature during power on/off cycles, etc.). Of them, the life under thermomechanical fatigue is an important reliability indicator. Shear testing is a common quality control test to assess the mechanical integrity of the joint, which is an indirect indicator of the electrical connection as well, particularly in ball grid arrays. This test is easy and quick to use on real components but is not valuable when one is investigating the failure mechanism. The results are difficult to interpret in terms of fundamental strength properties because the prevailing stress conditions are not known accurately, and the friction between the shearing surfaces also contributes to the failure load. Further, the frictional damage impairs fracture surface investigations. Thus, lap shear and tensile tests are preferred by researchers. In addition, tensile fracture surfaces are better preserved and could lead more evidence towards the failure mechanism. In tensile tests the stress is more uniform across the section and is the same on all the constituents namely the solder, the substrate and the interfaces. As a result the failure should occur at the weakest constituent of the joint. Hence, tensile testing is selected to assess the joint strength in this study.

In the past decade, much research has been carried out to study the mechanical properties of solder alloys [23-27]. However, the mechanical properties of the Sb-containing solder alloys are not reported. In addition, the experimental results

obtained by different researchers vary widely, depending on the test condition, for nominally the same solder alloy type. It is believed that the apparently large discrepancies among the different studies are mainly due to differences in the test temperatures and strain rates employed in different laboratories. Hence, it is necessary to investigate the effects of temperature and strain rate on the mechanical properties systematically.

In this chapter, tensile tests of Sn-3.5Ag-0.7Cu-xSb ($x = 0.0, 1.0$ and 2.0) solder alloys and Sn-3.5Ag-0.7Cu-xSb ($x = 0.0, 0.8$ and 2.0) solder joints were carried out. The tensile tests of solder alloys were executed at various strain rates from $1.0 \times 10^{-4} \text{ s}^{-1}$ to $1.0 \times 10^{-2} \text{ s}^{-1}$, and different temperatures from 25°C to 125°C , to investigate the effects of test temperature and strain rate on the mechanical properties. The tensile tests of solder joints aged for different times were carried out to explore the effects of ageing time on the mechanical properties.

6.2 Tension properties of Sb-containing solder alloys

6.2.1 Microstructure analysis of tensile testing specimens

The samples for tensile test and microstructure analysis were prepared by the method described in chapter 3. Figure 6-1(a) is the typical SEM photograph of the as-soldered ternary Sn-3.5Ag-0.7Cu untested solder specimen. It consists mainly of Sn-rich phase, Ag_3Sn and Cu_6Sn_5 intermetallics. The composition of Sn-rich phase is shown in Fig. 6-2. Results show that 2.68 wt % Ag is dissolved in the β -Sn matrix. The proportion of Ag varies in different area and is about 2-5 wt %. Ag_3Sn intermetallics exist in needle and disk shapes, and are embedded within the Sn-rich phase. By adding Sb, another laminated Sn-rich phase (with Sb) appears, as shown in Fig. 6-1(b) and 6-1(c). The EDS results of Sn-rich (with Sb) phases in Sn-3.5Ag-0.7Cu-1.0Sb and Sn-3.5Ag-0.7Cu-2.0Sb are given in Fig. 6-3 and Fig. 6-4 respectively. It seems to show that the higher Sb proportions, the thinner the laminated plates. In addition, the size of Ag_3Sn seems to increase with an increase of Sb proportion, which is in accordance with the results shown in section 4.6.

Fig. 6-1 SEM micrographs of Sn-3.5Ag-0.7Cu-xSb untested specimens. (a) $x = 0.0$, (b) $x = 1.0$, and (c) $x = 2.0$. A: Sn-rich phase with Ag; B: Ag_3Sn phase and C: Sn-rich phase with Sb;

Fig. 6-2 EDS analysis of Sn-rich phase (with Ag) in untested Sn-3.5Ag-0.7Cu solder alloy.

Fig. 6-3 EDS analysis of Sn-rich phase in untested Sn-3.5Ag-0.7Cu-1.0Sb solder alloy. (a) with Sb area and (b) with Ag area shown in Fig. 6-1(b).

Fig. 6-4 EDS analysis of Sn-rich phase in untested Sn-3.5Ag-0.7Cu-2.0Sb solder alloy. (a) with Sb area and (b) with Ag area shown in Fig. 6-1(c).

6.2.2 Effect of strain rate on the tensile strength of Sb-containing solder alloys

The tensile tests of Sn-3.5Ag-0.7Cu-xSb ($x = 0.0, 1.0$ and 2.0) solder alloys were carried out at different strain rate and temperature. The tensile curves generated from the Instron data, yielded a good measure of reproducibility and consistency for each alloy tested at each test condition. By plotting the stress-strain curves under isothermal condition into one graph, the effect of strain rate on the Sn-3.5Ag-0.7Cu tensile properties could be evaluated and compared. The typical stress-strain curve at a constant temperature of $75\text{ }^{\circ}\text{C}$ is shown in Fig. 6-5. It is noted that the UTS of Sn-3.5Ag-0.7Cu-xSb ($x = 0.0, 1.0$ and 2.0) solder alloys are strongly dependent on the strain rate.

Fig. 6-5 Stress–strain curve of eutectic Sn-3.5Ag-0.7Cu alloy at 298 K for different strain rate.

The effect of strain rate on the UTS for different solders at temperatures of 25, 75, 125°C respectively is presented by logarithmically plotting the UTS versus strain rate as shown in Fig. 6-6. Clearly, the UTS of three solder alloys increases as the deformation rate increases. The same result has been reported by Li [44]. Increase in the strain rate from 10^{-4} s^{-1} to 10^{-2} s^{-1} approximately increases the UTS one-third at room temperature.

Fig. 6-6 Effect of strain rate on UTS at different testing temperature: (a) 25 °C, (b) 75 °C, and (c) 125 °C.

The plots show approximately straight lines with a constant slope for any given temperature. This is expected as the UTS has a linear function of logarithmic strain rate.

The relationship between strain rate and UTS obeys [157-158]:

$$\sigma = A \dot{\epsilon}^m \quad (6-1)$$

where σ is the tensile strength, $\dot{\epsilon}$ the strain rate, m the strain rate sensitivity, which varies between zero (in which case the material is not strain rate-sensitive) and unity (in which instance the stress increases linearly with strain rate and the material is called a viscous material). And A is a constant that signifies the material's

stress at a true strain rate of unity. The slope of each line in Fig. 6-6 gives the strain rate sensitivity, m . The m values were calculated and shown in Table 6-1. The m values range from 0.058 to 0.073 for the samples tested at 25°C, which is comparable with other's report of 0.08 at room temperature [29]. At higher temperature, solder alloys are more sensitive to strain rate. Table 6-1 shows at any temperature, Sn-3.5Ag-0.7Cu solder alloy is the most strain rate sensible among three of them.

Table 6-1 m value for different temperature

Temperature (°C)	Sb proportion (wt %)	A (MPa)	m
	0.0	64.57	0.073

Fig. 6-7 Photomicrographs revealing slip character (a) low magnification photograph of slip on planes in Sn-3.5Ag-0.7Cu solder alloy, (b) slip lines on fracture surface, and (c) enlarged slip lines of the circled region in Fig. 6-5 (b).

Based on dislocation interaction and multiplication theory [157, 159], the effect of strain rate on the tensile strength of solder alloy could be explained as follows:

When solder alloy is deformed, more and more dislocations are created. Dislocation density is related directly to the strain rate. Increasing strain rate is accompanied by an increase in the dislocation density. The interactions between dislocations result in the formation of jogs on dislocations. Not only does this increase dislocation length (and hence energy), but also jogs formed in this way are generally less mobile than the unjogged portion of the dislocation. Hence, dislocation intersections can lead to reduced dislocation mobility and attendant work hardening. Therefore, the increase in dislocation density will in turn increase the stress, so as to the UTS of the solder specimens.

6.2.3 Effect of temperature on tensile strength

Temperature greatly affects the tensile behavior of bulk solder materials as shown in Fig. 6-8. At a strain rate of 10^{-2} s^{-1} , a temperature change from 25 to 125 °C results in a loss of strength to about one third of its value at the lower temperature. The general trend of increasing strength with increase of strain rates is obeyed. Fig. 6-9 indicate that the effect of temperature on ultimate tensile strength at strain rates of 1×10^{-4} , 10^{-3} and 10^{-2} 1/s respectively. Apparently, strength deteriorates at elevated temperatures. It can be seen that the curves demonstrate a linear relationship between UTS and temperature.

Fig. 6-8 Typical stress–strain curve of eutectic Sn-3.5Ag-0.7Cu alloy strain rate at 10^{-2} s^{-1} for different temperature

Fig. 6-9 Effect of testing temperature on UTS at different strain rate: (a) 10^{-2} s^{-1} , (b) 10^{-3} s^{-1} , and (c) 10^{-4} s^{-1} .

It also reveals that, at all strain rates examined, Sn-3.5Ag-0.7Cu-2.0Sb has the highest tensile strength at temperature of 25 °C and the Sn-3.5Ag-0.7Cu-1.0Sb alloy has a least sensitivity to temperature than either the Sn-3.5Ag-0.7Cu or the Sn-3.5Ag-0.7Cu-2.0Sb alloys at lower strain rate. The strength of the Sn-3.5Ag-0.7Cu-1.0Sb alloy is least affected by temperature, and at the lowest strain rates, 10^{-2} s^{-1} , it is lowered by around 20% when the temperature is raised from 25 to 125 °C. In comparative terms, the Sn-3.5Ag-0.7Cu is generally the weakest.

From the experimental data, it is justified that the mechanical behavior of the solder specimens is greatly affected by the testing temperature. The UTS decreases with increasing temperature. The decrease in tension strength can be assessed by the Hall-Petch relation [158]:

$$\sigma_y = \sigma_i + k_y d^{-1/2} \quad (6-3)$$

where σ_y is the yield strength, σ_l is the overall resistance of lattice to dislocation movement, k_y is the hardening contribution by grain boundaries and d is the grain size of crystal. σ_l could be separated into two components: σ_{sl} , which is structure sensitive where dislocation-dislocation, dislocation-precipitate, and dislocation-solute atom interactions are important; and σ_T , which is strongly temperature sensitive and related to the Peierls stress, which is the force required to move the dislocations through the lattice. Since the Peierls stress depends on the short-range stress field of the dislocation core, it is sensitive to the thermal energy in the lattice and, hence, to the test temperature. At low temperature, where dislocation motion is limited, the Peierls stress is large. But at high temperature, thermal enhanced dislocation is easier to slip, which results the decrease of Peierls stress, so as to the strength of testing material [158].

6.2.4 Effect of Sb additives on mechanical strength - solid solution hardening

Previous results show the effect of Sb on tensile strength of Sn-3.5Ag-0.7Cu solder alloy. Tensile strength of Sn-3.5Ag-0.7Cu increases with Sb addition due to solid solution hardening since the Sb is almost in solid solution in matrix. The solid solution hardening mechanism can be also explained by the interaction between a moving dislocation and the solute Sb atoms it encounters during dislocation slip.

A dislocation in Sn lattice has associated with a stress field. Introduction of a substitutional solute atom into the crystal also produces a lattice dilation that typically gives rise to a spherically symmetric stress field surrounding the solute Sb atom. Consequently, the stress fields from these sources can interact and can mutually exert force. In the case of a positive edge dislocation, there is a compressive stress above the slip plane and a tensile stress under it. As a solute atom placed randomly in a crystal produces a stress field around it, this stress field will be minimized if the solute atom were to move to the dislocation. A substitutional Sb atom tends to move to the tensile side since it is bigger than the solvent Sn atom. This rearrangement of solute atoms forms atmospheres at dislocations and lead to an effective impediment to

dislocation movement [96]. Therefore, adding Sb enhance the strength of Sn-based solder alloy by solid solution strengthening.

6.3 Tension properties of Sb-containing solder joints

6.3.1 Effect of ageing time and Sb composition on tensile strength of Sn-3.5Ag-0.7Cu solder joints

The sample preparations for testing tensile strength of the solder joints are described in Chapter 3. Tensile tests were carried out on an Instron 5548 tensile tester at a strain rate of 1×10^{-3} at 298K in order to obtain data on tensile strength. Fig. 6-10 shows the variation of tensile strength over ageing time of Sn-3.5Ag-0.7Cu-xSb ($x = 0, 0.8$, and 2.0 wt%) solder joints aged at 150°C.

As shown in Fig. 6-10, the tensile strength of Sn-3.5Ag-0.7Cu and Sn-3.5Ag-0.7Cu-0.8Sb solder joints decreases with increase in ageing time. After an elapsed ageing time of 400 hours, it can be seen that the speed of reduction in strength decreases. However the tensile strength of Sn-3.5Ag-0.7Cu-2.0Sb solder joint, increases a little bit at short ageing time, after ageing 200 hours, the tensile strength drops gradually. Results show the decrease in strength of 32.9, 20.58, and 27.81% in Sn-3.5Ag-0.7Cu, Sn-3.5Ag-0.7Cu-0.8Sb and Sn-3.5Ag-0.7Cu-2.0Sb after 1000 hours ageing respectively. Fig. 6-10 also shows the UTS of Sb-containing solder joints are slightly higher than the Sb-free solder joints for most of ageing times. The highest strength is achieved by the addition of 0.8 % Sb.

Thermal ageing generally tends to decrease the tensile strength of the three solder joints until it reaches a relatively constant value [67, 160-161]. Quan et al. [160] reported a 50% decrease in tensile strength of Cu/Sn-37Pb and Cu/Sn-95Pb joints when the total IMC layer thickness increased from an initial 4 μm to final thickness of 15 and 11 μm , respectively. Prakash [161] reported a lower decrease in strength of 18.4 and 22% with increase in IMC layer thickness in Cu/Sn-37Pb and Cu/Sn-73Pb joints, respectively. Our results also show that the decrease in tensile strength is ascribed to the growth in IMC thickness of the solder joint upon ageing. The values of

UTS obtained for different solders are given in Table 6-2 for each ageing time, along with their corresponding total IMC layer thickness. The thicker the IMC, the lower the tensile strength. Results show that the tensile strength decreases 29.0% for an increase of 4.5 μm in IMC layer thickness in Sn3.5Ag-0.7Cu solder joints after aged for 600 hours. However, there is only 13.5 and 19.1% strength decrease in Sn3.5Ag-0.7Cu-0.8Sb and Sn3.5Ag-0.7Cu-2.0Sb solder joints, when the thickness of IMC only increases 1.7 and 2.51 μm respectively. The experimental results reveal that the tensile strength significantly depends on the IMC formation in solder joints. To understand the mechanism, it is necessary to investigate the failure modes of the solder joint, which are described in next section.

Fig. 6-10 UTS vs. ageing time of Sn-3.5Ag-0.7Cu-xSb solder joints. (a) $x = 0.0$, (b) $x = 0.8$, and (c) $x = 2.0$

Table 6-2 the relationship between the thickness of IMC and the tensile strength

Ageing time (hours)	Sn-3.5Ag-0.7Cu		Sn-3.5Ag-0.7Cu-0.8Sb		Sn-3.5Ag-0.7Cu- 2.0Sb	
	IMC layer thickness (μm)	UTS (MPa)	IMC layer thickness (μm)	UTS (MPa)	IMC layer thickness (μm)	UTS (MPa)
0	3.56	46.63	3.07	52.38	3.23	44.55
200	5.98	39.73	4.46	47.62	3.94	45.97
400	7.47	34.82	4.67	43.71	5.09	39.8
600	8.08	33.09	4.77	45.29	5.74	36.05

6.3.2 Failure analysis of tensile testing solder joints

From the observation of the tested specimen, the fracture pattern can be classified into three types. Fig. 6-11 shows the fracture surface of Sn-3.5Ag-0.7Cu-0.8Sb solder joints aged at 150 °C for different time. Fig. 6-11 (a) shows the fracture occurred within the solder and Fig. 6-11 (c) shows that the fracture occurs close to the IMC layer. Mixed fracture type of these two types is shown in Fig. 6-11 (b). The fracture surface images indicate that the Sn-3.5Ag-0.7Cu-0.8Sb solder joints undergo ductile fracture in the solder and the brittle fracture at the solder/IMC interface. The fracture path was observed to go through various constituents and locations depending on the ageing time and solder composition.

Fig. 6-12 shows the magnified fractography of Fig. 6-11(a). Typical microvoids coalescence mechanism of ductile failure [162] is apparent. The EDS results shown in Fig. 6-13 reveal that the fracture path of the as-soldered specimen is through the bulk solder. The underlying layer of solder is the Cu_6Sn_5 layer, which is identified by EDS results shown in Fig. 6-14.

Fig. 6-11 SEM fractographs of Sn-3.5Ag-0.7Cu-0.8Sb solder joints after tensile test: (a) as-soldered specimen, (b) aged at 150 °C for 600 hours, and (c) aged at 150 °C for 1000 hours.

Fig. 6-12 (a) SEM fractographs of Sn-3.5Ag-0.7Cu-0.8Sb as-soldered solder joints and (b) enlarged SEM images in circle region in Fig. 6-12 (a).

Fig. 6-13 EDS result of fracture surface shown in Fig. 6-12 (a)

Fig. 6-14 EDS result of fracture surface shown in Fig. 6-12 (b)

After ageing for 600 hours, as shown in Fig. 6-15, both ductile and brittle fractures are found in the Sn-3.5Ag-0.7Cu-0.8Sb solder joints. When ageing time reaches 1000 hours, as shown in Fig. 6-16, fracture occurred at the interface between solder and IMC layer in most of regions. The EDS result in Fig. 6-17 shows that the ratio of Cu and Sn on the fracture surface is 62.82: 37.18, which reveals that the failure might occur at the Cu₃Sn/Cu₆Sn₅ interface.

Fig. 6-15 Different fracture fractographs of Sn-3.5Ag-0.7Cu-0.8Sb solder joints aged at 150 °C for 600 hours: (a) ductile fracture in the solder, (b) brittle fracture at the solder/IMC interface.

Fig. 6-16 Brittle fracture fractograph of Sn-3.5Ag-0.7Cu-0.8Sb solder joints aged at 150 °C for 1000 hours.

Fig. 6-17 EDS result of circle region shown in Fig. 6-16

The fracture properties of the solder joints depend on constitute of the joints. As discussed in Chapter 5, the IMC layer is formed in solder joint after reflow. The longer the ageing time, the thicker the IMC. Because IMC is more brittle than solder, it would significantly affect the fracture of the solder joint. The ductile fracture occurred in as-soldered Sn-3.5Ag-0.7Cu-0.8Sb solder joint because the IMC layer is quite thin. When the ageing time is prolonged, the growth of IMC results in brittle fracture so that the combination of ductile failure in solder and brittle failure at solder/IMC layer is observed. After further prolonging ageing, the IMC grew thicker; which leads to brittle fracture at the solder/IMC interface as shown in Fig. 6-16.

Furthermore, the effect of Sb additives on the mechanical strength of Sn-Ag-Cu solder system is evident from the fracture surface analysis. Previous study showed the IMC thickness of Sb-free solder joints is thicker than that of Sb-containing solder joints, resulting in the earlier brittle failure at the solder/IMC interface. As shown in Fig. 6-18, the fractograph of Sn-3.5Ag-0.7Cu solder joints, brittle failure occurred in some as-soldered specimens. It indicates that the IMC thickness in Sn-3.5Ag-0.7Cu solder joints influence the failure modes of the solder joints.

Fig. 6-18 SEM fractograph of Sn-3.5Ag-0.7Cu as-soldered solder joints

6.3.3 Effect of Sb addition on tensile strength – particle hardening

As discussed in the last section, thicker IMC leads to brittle failure. Since the IMC of Sb-containing solder joint is thinner than that of Sb-free solder joint, the UTS of Sb-containing solder joint is higher than that of Sb-free solder joint. On the other hand, as mentioned in Chapter 5, more $\text{Ag}_3(\text{Sn,Sb})$ particles precipitate on Cu_6Sn_5 layer after adding Sb, it might be another reason why adding Sb increases the strength of Sn-3.5Ag-0.7Cu solder joint.

Orowan [163] pointed out that if a ductile matrix has second-phase particles interpenetrating the slip plane of dislocations, an additional stress will be necessary to make a dislocation expand between the particles. Should the stress be sufficiently high to bend the dislocations in roughly semicircular form between the particles, the dislocations go around the particles, leaving dislocation loops around them [157, 164]. Dislocation loops encircle the particles after the bypass of dislocation; hence there will be an increase in the dislocation density. The higher the dislocation density, the stronger the solder joint. Therefore, the particle hardening effect is achieved.

6.4 Summary

Based on the tensile tests and analysis of solder alloys and solder joints, following conclusions can be addressed:

The tensile strength of Sn-3.5Ag-0.7Cu-xSb ($x = 0.0, 1.0$ and 2.0) solder alloys is dependent on the strain rate and testing temperature. UTS of solder alloys has a logarithmic increase relation with strain rate. The effect of strain rate on the tensile strength can be explained by dislocation multiplication and dislocation-dislocation interaction. Higher strain rate creates more dislocation. With the increase of density of dislocations, the mobility of the dislocations is reduced. At high strain rates, movement of dislocations is restricted in a very short time, so that the large number of accumulated dislocations progressively increase resistance to deformation due to dislocation-dislocation interaction. UTS of solder alloys decreases with the increase of testing temperature. This is because the thermal-enhanced dislocation is easier to slip at high testing temperature, which causes the lower resistance for mechanical deformation.

Tensile strength of solder joints drops with the ageing time. IMC growth leads to the ductile failure mode transferring to brittle failure at solder/IMC interface with increase in ageing time.

Sb-containing solder alloys and solder joints have higher UTS than Sb-free solder alloy and solder joints due to solid solution hardening and particle hardening. When Sb atoms solutes in Sn lattice, an additional deformed field is created and it counteracts the stress field of dislocation, so as to inhibit the dislocation movement. When Sb precipitate in forms of $\text{Ag}_3(\text{Sn}, \text{Sb})$, dislocation density increases by particle-dislocation interaction. Therefore, the mobility of dislocation reduces and the strengthening effect is achieved. The tensile strengths of both Sn-3.5Ag-0.7Cu solder alloy and solder joint reach the highest value when 0.8-1.0 Sb is added.

Chapter 7

Rapid Temperature Cycling test methodology for reliability assessment of solder interconnection

7.1 Introduction

A key issue in the long-term reliability of solder joints is joint failure during thermal cycling. The components and substrates that are soldered together in an electronic package typically have differing coefficient of thermal expansion (CTE). Temperature variations in the package are caused by power dissipation of chips as well as power on and off switching of the equipment causing differential thermal expansions and contractions. When a soldered assembly undergoes a temperature change, interconnects are subjected to cycling shear stresses. These stresses produce elastic, inelastic strains, as well as time-dependent inelastic strains in the joint. These thermally induced strains are often cyclic in nature which results in the thermomechanical fatigue. Accelerated temperature cycling (ATC) method is widely adopted to validate the reliability of solder joints in various electronic products. It normally takes several months to complete a test and this is very time-consuming and expensive. Especially, it takes more than half year to evaluate lead-free components. The electronic packaging industry is motivated to shorten product development cycle time while maintaining desirable levels of quality and reliability. Moreover, due to the non-uniform temperature distribution in high power device and optoelectronics packaging, ATC testing is inappropriate for the accelerated testing of this kind of packaging. Hence, a highly accelerated testing method that reduces the cycle time and can mimic true operating environments is greatly sought after for the understanding of wear-out reliability characteristics of packages.

This chapter reports the development of a thermoelectric cooler (TEC) based rapid temperature cycling (RTC) testing methodology which is applied to advanced tape BGA (TBGA) package for the long-term reliability assessment. ATC tests were conducted from same lot of TBGA devices and the results were used as a basis of

comparison of the results from the RTC methodology. RTC numerical analysis was further studied for the understanding of the failure mechanism and the long-term reliability of the TBGA assembly. Finally, a new and quick reliability assessment methodology was established as a possible alternative to ATC for high power device and optoelectronic packages.

7.2 Thermal distribution of RTC

The configuration and working principle of the RTC testing method have been described in Chapter 3. Owing to the low thermal mass and ceramic construction of TECs, very high heating and cooling rates can be achieved in RTC testing system. Comparing to the conventional ATC test, the RTC cycle time can be shortened by one order of magnitude. Furthermore, unlike the ATC test where the board and component are exposed to uniform temperature, RTC test can mimic the lateral temperature distribution of real packaging. In the RTC test, only the device itself is heated and cooled, the PCB surrounding the device remains at room temperature throughout the testing sequence. This results in a very strong lateral temperature distribution in the area surrounding the device. Fig. 7-1 shows the thermo-mechanical simulation result of RTC at 100°C (the IR images were used as a temperature-input profile for the devices during the finite elemental simulations), which indicates that the device under test (DUT) is subjected to strongly non-isothermal conditions.

(a)

(b)

Fig. 7-1 (a) Simulation results of RTC temperature distribution at 100°C and (b) temperature profile for points A to D

According to the bathtub curve of failure rate [27], only wear-out failure rate increase with time, and failure mode and mechanism must not be altered in the acceleration reliability test. To reduce the quantities of reliability tests, three main acceleration parameters, *i.e.*, the ramp rate, the dwell time, and the temperature extremes were optimized so as to ensure the validity of the acceleration test. Since TECs have very high heat and cool rate, in order to prevent the devices fail because of large strain rate, the temperature cycling for the RTC test was carried out between temperature extremes of 0 and 100°C. The duration of a cycle was approximately 6 minutes. The temperature profile can be seen in Figure 3-10. Standardized ATC test with temperature profile shown in Fig. 3-8 was carried out for comparison. The ATC chamber temperature was ramped between -40 and 125°C. Each cycle lasted 60 minutes with 15 minutes rise and drop times, and 15 minutes hold times at either temperature extreme.

7.3 Failure analysis of ATC and RTC testing

The preparation of samples for failure analysis is described in Chapter 3. Scanning electron microscope (SEM) was used to investigate the failure sites and failure modes of the solder joint. It was found that in both tests most of the failures initiate at the upper corner of the solder joints. Most importantly, the crack propagated in the solder along the copper pad, as shown in Fig. 7-2 (a) and (b). In other words, the RTC test gave a similar failure site (upper corner of solder joint) and failure mode (crack propagates along Cu pad) as the ATC tests. However, Fig. 7-2 (a) shows phase coarsening in the solder, while Fig. 7-2 (b) shows more shearing activities. This indicates that creep deformation is more dominant during ATC test, while dislocation induced plasticity is more dominant during RTC test. It means that failure mechanism has partial difference between ATC and RTC tests. However, the failure site and failure path are the same, which might indicate that reliability assessment of the two methods does not have much discrepancy.

Fig. 7-2 Cross-sectional SEM view of a solder joint after failure (a) ATC and (b) RTC test

7.4 Statistical Analysis of ATC and RTC testing

As discussed in literature review, for the fatigue test of the solder joints, the failure distribution is usually modeled by Weibull distribution. To build the Weibull models, sample sizes of 36 and 14 were used for ATC and RTC tests respectively. For 3 early failure samples from ATC and one early failure sample from RTC, it is found that the crack propagated from a pre-void which produced in reflow process, as shown in Fig. 7-3. These solder joint failures appeared to be due to random failure and need to be separated from the wear out failure distribution when analyzing life test data [165]. Finally, 33 and 13 samples were used to build the Weibull model for ATC and RTC tests respectively, whose fatigue life (cycles to failure or time to failure) are listed in Table 7-1 and 7-2.

Fig. 7-3 Cross-sectional SEM view of a solder joint failed with a pre-void at the corner

Table 7-1 Fatigue life (hour) for ATC reliability test, -40~125°C at 60min./cycle

No.	Time to failure (hour)	Cycle to failure	No.	Time to failure (hour)	Cycle to failure	No.	Time to failure (hour)	Cycle to failure
1	2066	2066	12	2387	2387	23	2546	2546
2	2190	2190	13	2401	2401	24	2574	2574
3	2237	2237	14	2406	2406	25	2609	2609
4	2285	2285	15	2430	2430	26	2650	2650
5	2323	2323	16	2430	2430	27	2650	2650
6	2338	2338	17	2458	2458	28	2688	2688
7	2353	2353	18	2521	2521	29	2718	2718
8	2362	2362	19	2521	2521	30	2774	2774
9	2374	2374	20	2521	2521	31	2822	2822
10	2376	2376	21	2521	2521	32	2836	2836
11	2384	2384	22	2521	2521	33	2905	2905

Table 7-2 Fatigue life (hour) for RTC reliability test, 0~100°C at 6min./cycle

No.	Time to failure (hour)	Cycle to failure	No.	Time to failure (hour)	Cycle to failure	No.	Time to failure (hour)	Cycle to failure
1	111.8	1118	6	185.0	1850	11	243.8	2438
2	114.2	1142	7	200.7	2007	12	263.8	2638
3	140.5	1405	8	202.4	2024	13	280.0	2800
4	142.5	1425	9	209.8	2098			
5	170.0	1700	10	220.0	2200			

In this study, both of the two-parameter and three-parameter Weibull distributions were used to model the cumulative failure of the solder joints. Two-parameter Weibull plots are shown in Fig. 7-4. The parameters are listed in Table 7-3. As shown in two parameters Weibull plot, two straight lines are not parallel. Normally, if two tests have the same failure mechanism, the lines should be parallel.

Fig. 7-4 Two-parameter Weibull plots of ATC and RTC test failure data

Table 7-3 Characteristic lives under ATC and RTC tests according to 2P Weibull plot

	Shape parameter, β	Characteristic life, η (hour)	Correlation coefficient, ρ	MTTF (hour)
ATC (60 min./cycle)	16.1322	2570.05	0.968	2489.34
RTC (60 min./cycle)	3.8967	210.66	0.981	190.66

The results seem to reveal that the failure mechanisms are quite different for ATC and RTC test. However, two-parameter Weibull distribution does not consider the failure free time- the time required for crack initiate. Therefore, it is necessary to model the failure data with three-parameter Weibull distribution. Three parameter Weibull plots are shown in Fig. 7-5. The results of parameters β , η , γ and MTTF are tabulated in Table 7-4. The results show that two and three parameter Weibull plots have about the same mean time to failure but three-parameter Weibull plot gives a better fit to the test data (The R^2 values in three-parameter Weibull distribution are higher than those in two-parameter Weibull distribution).

Most importantly, introduce of the third parameter of γ in the three-parameter Weibull distribution reveals that the failure mechanisms at ATC and RTC tests might not have much difference, as two straight lines are almost in parallel. The additional parameter, γ , failure free time, represents the minimum amount of time required for cracks to initiate and propagate through the weakest solder joints of a population. The failure free time defines a warranty period during which thermo-mechanical fatigue failures of solder joints are not expected [165-166]. Shown in Fig. 7-6, the failure rate plots of the two tests, and Fig. 7-7, the probability density functions of the two testings, there is no failure before 19.17 hours for RTC and 1895.23 hours for ATC. RTC test has a much lower value of γ because of the one order faster ramp rate. When the testing times are beyond the failure free time, samples begin to failure. Because the stress level in RTC test is much higher than that in ATC, the failure rate of RTC is much higher than that of ATC.

Fig. 7-5 Three-parameter Weibull plot of ATC and RTC test failure data

Table 7-4 Characteristic lives under ATC and RTC tests according to 3P Weibull plot

	Shape parameter, β	Characteristic life, η (hour)	Failure free time, γ (hour)	Correlation coefficient, R^2	MTTF (hour)
ATC (60 min./cycle)	3.268	665.89	1895.23	0.983	2492.24
RTC(6 min./cycle)	3.329	192.31	19.17	0.982	191.75

Fig. 7-6 Failure rate plot of three-parameters weibull for ATC and RTC testing

Fig. 7-7 Probability density function of three-parameter Weibull for ATC and RTC testing

As mentioned previously, the retard time of failure is not been considered in two-parameter Weibull analyses, which shows the failure mechanism of these two methodologies do not correlate very well. The failure rates of two testing, shown in Fig. 7-8, do not have much difference in two-parameter weibull analysis. However, the parallel Weibull plots and the failure rate plots in three-parameter Weibull analyses indicate ATC and RTC have similar failure mechanism of wear-out. In other words, RTC increases the failure rate through the higher stress level but it does not change much of the failure mechanism. Hence, the acceleration factors were experimentally

obtained as $AF = \frac{N_{fATC}}{N_{fRTC}} = \frac{2489.34}{190.66} \approx 13.0$ compare to ATC test.

Fig. 7-8 Failure rate plot of Two-parameter Weibull for ATC and RTC testing

7.5 ATC and RTC numerical analysis

7.5.1 FEM analysis

Finite Element Method (FEM) analysis is a numerical technique used to simulate the behavior of a system under various conditions. In the context of solder interconnection, FEM analysis is used to predict the thermal stresses and strains that develop during rapid temperature cycling. The analysis involves discretizing the system into a mesh of elements, each with its own material properties. The temperature history of the system is then applied as a boundary condition, and the resulting stresses and strains are calculated for each element. This allows for the identification of potential failure locations and the optimization of the design to improve reliability.

Figure 7.5.1: FEM analysis of solder interconnection

Figure 7-10 Zoomed-in view of the FE model (a) Overview and (b) solder joint portion.

In the study, MSC.Marc 2001 software was used to conduct the numerical simulation for the TBGA package. A three-dimensional finite element model of the TBGA package, consisting of a polyimide substrate, copper stiffener, eutectic solder, epoxy encapsulant, copper pad, silicon die and printed circuit board (PCB), was generated (shown in Fig. 7-9 and Fig. 7-10). Due to geometric symmetry, only one-eighth of the model needs to be created in order to fully simulate the stress in the device. The outer solder joints are modeled fully diagonally as this solder joints are anticipated to have the highest amount of stress, and therefore be the point of failure in the device. The rest of the joints are modeled as cubes in order to reduce the number of element size and hence the computational time. Symmetrical boundary conditions are defined on two sides of the package. A node is constrained ($dz = 0$) to prevent free-body rotation.

The material properties used are shown in Table 7-5 [131, 168]. All materials are assumed elastic except solder which was modeled as viscoplastic materials. Solder

joint creep processes are expected to influence the deformation kinetics. Steady-state creep [104] is generally expressed by

$$\frac{d\gamma_s}{dt} = C_4 \frac{G}{T} [\sinh(\alpha \frac{\tau}{G})]^n \exp(\frac{-Q}{RT}) \tag{7-1}$$

where G is the shear modulus, R is universal gas constant, T is the absolute temperature, σ is the applied stress, Q is the activation energy, n is the stress exponent, α prescribes the stress level at which the power law dependence breaks down, and C_4 is a constant characteristic of the underlying micromechanism.

Table 7-5 Material properties

Materials	Young's modulus (GPa)	Yield stress (MPa)	Poisson ratio	CTE/ppm
Solder	28.2	38.5	0.34	24.5
Cu	110	-	0.31	16.5
Polyimide	5.44	-	0.3	16
FR4	21.23	-	0.28	x, y =15, z =60
Epoxy	5.19 at 25°C	-	0.4	below Tg=50, above Tg=160
Solder mask	6	-	0.4	30
Si	162.7	-	0.28	2.8

For ATC simulation, the temperature loading was simulated for three cycles based on the temperature loading profile shown in Fig. 3-8. For RTC simulation, the thermal profile of the device during the heating and cooling cycle was calculated from the steady-state temperature profile of an actual DUT determined from IR thermographs.

7.5.2 Simulation results and analysis

As the stress-state in solder joint was in multi-axial, a relationship between shear and tensile deformation is needed to account for the multi-axial stress-state in solder joints. In this study, the von Mises yield criteria [96] was employed to work out the equivalent strain. The equivalent stress and equivalent strain is given by

$$\sigma_{eq} = \frac{1}{\sqrt{2}} [(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2]^{1/2} \quad (7-2)$$

$$\varepsilon_{eq} = \frac{3}{\sqrt{2}} [(\varepsilon_1 - \varepsilon_2)^2 + (\varepsilon_2 - \varepsilon_3)^2 + (\varepsilon_3 - \varepsilon_1)^2]^{1/2} \quad (7-3)$$

where σ_1 , σ_2 , and σ_3 are the principal stresses and ε_1 , ε_2 , and ε_3 are the principal strain. The relationship between the equivalent strain and equivalent shear strain is

$$\varepsilon_{eq} = \frac{\gamma_{eq}}{\sqrt{3}} \quad (7-4)$$

In both series of simulations, failure was predicted to occur at the outermost solder joint. Figs. 7-11 and 7-12 show the simulation results of the inelastic strain contour plots of the critical solder joint under ATC and RTC loadings respectively. It can be seen from these plots that in both ATC and RTC tests, the solder joint corner on the package side is the stress/strain concentration point and hence crack will initiate from it. This was indeed the location at which failure was observed experimentally, as seen in Fig. 7-2.

Fig. 7-11 ATC inelastic contour plot

Fig. 7-12 RTC inelastic contour plot

The inelastic strain range for both RTC and ATC are shown in Table 7-6. In RTC, the inelastic strain range is 0.47% as compared to ATC which is 0.32%. It indicates that RTC has a higher stress level. This can be rationalized by considering the comparatively large thermal shock that the package experienced as it is heated and cooled very rapidly.

Table 7-6 Comparison of strain range and lifetimes for the devices as determined by both experiment and simulation

	Inelastic strain range	N_f (predicted) (hour)	N_f (experimental) (hour)
ATC	0.32%	2337.22	2492.24
RTC	0.47%	188.73	191.75
AF	-	12.384	12.997

The modified Coffin-Manson type of relationship was used to predict the failure of the devices from the FEM simulations [115], given by

$$[N_f \nu^{(k-1)}]^m \Delta \epsilon = C \tag{7-5}$$

$$\text{where } k = 0.919 - 1.765 \times 10^{-4} T - 8.634 \times 10^{-7} T^2 \tag{7-6a}$$

$$m = 0.731 - 1.63 \times 10^{-4} T + 1.392 \times 10^{-6} T^2 - 1.151 \times 10^{-8} T^3 \tag{7-6b}$$

$$C = 2.122 - 3.57 \times 10^{-3} T + 1.329 \times 10^{-5} T^2 - 2.502 \times 10^{-7} T^3 \tag{7-6c}$$

where N_f is the fatigue life, $\Delta \epsilon$ is inelastic strain range, ν is frequency, k is frequency exponent, m is fatigue exponent, and C is the material ductility coefficient.

For the life prediction of the solder joints, the inelastic strain range during a thermal cycle was used. The strain range was obtained from one whole temperature cycle excluding the first half-cycle. It was then used to predict the total number of cycles required to result in mechanical failure of the device. The simulated lifetimes, along with the experimentally determined lifetimes are shown in Table 7-6. It is noted from Table 7-6 that the lifetimes predicted from the FEM simulations are in good agreement with the experimental. In both simulation and experiment, the determined lifetime of the devices was one order lower for the case of the RTC test when compared to the ATC test.

7.6 Summary

This work is to set up a rapid temperature cycling testing system to evaluate the long-term reliability of TBGA eutectic solder package. Thirteen devices were tested with the RTC setup, and was analyzed by SEM to determine the failure site. Similarly, thirty-three similar devices were tested in a standard ATC test for comparison. The three-parameter Weibull analyses were used to evaluate the failure mechanism and both of ATC and RTC tests show the typical wear-out failure mechanism. A crack was initiated and propagated through the solder joint near the device side of the joint. The simulations provide insight in understanding the differences and similarities between the RTC and ATC tests. For both the RTC and ATC test, it was shown that the highest stress occurred at the corner of the outer solder joint. This is in excellent concurrence with the experimentally observed failure location.

The correlation of two different reliability assessment methodologies is also studied in this work. RTC is much faster than the ATC methodology. The mean lifetime to failure of the devices was determined from a Weibull plot analysis to be 191.75 hours for the RTC test and 2492.24 cycles for the ATC test. RTC test gives a fast reliability evaluation with an acceleration factor of 13 related to ATC test. Another advantage of RTC is that the test more closely mimics the field conditions than the ATC test, due to the highly non-isothermal temperature distribution during the test. Based on the mathematical statistical theory and the failure mechanism, the RTC methodology has been established as a possible alternative to the ATC test for quick assessment of the long-term reliability of the TBGA assembly. It would be interesting to further study whether the new RTC methodology could be applied to other advanced microelectronic packages, such as chip scale package (CSP), flip chip, etc, and if it could replace other fatigue testing such as thermal shock, *etc.*

Chapter 8 Conclusions and Recommendations

8.1 Conclusions

The objectives of this thesis lie in studying the overall properties of Sn-Ag-Cu-xSb solder alloys. It includes the formation of IMCs in the solder joints during reflow and ageing processes, the growth kinetics and microstructural evolution of the solder joint, and the tensile strength of the solder joints. The effects of Sb additives during reflow, ageing and mechanical testing have been analyzed in detail. Effect of testing conditions, such as strain rate, temperature, and thermal aging on the strength and fracture behavior of solder alloy and solder joints formed by Sn-Ag-Cu-xSb solders with Cu substrate have also been investigated.

From this work, the following conclusions can be summarized:

When Sb is added in the Sn-Ag-Cu solder alloy, additional Sn-rich phase (with Sb) and $\text{Ag}_3(\text{Sn}, \text{Sb})$ form during reflow. Adding Sb inhibits the excessive IMC growth and refines grains in Sn-Ag-Cu solder joints efficiently during both reflow and ageing processes. The effect of Sb addition on the IMC growth during reflow might be explained by heterogeneous nucleation theory. SnSb particles precipitate from the molten solder and become heterogeneous nucleation sites of Cu_6Sn_5 IMC during reflow. The rate of Cu_6Sn_5 nucleation increases with the increase in Sb proportion. During ageing, small Ag_3Sn and $\text{Ag}_3(\text{Sn}, \text{Sb})$ particles precipitating and pinning along the grain boundary block the coalescence of the grains, which may be the reason why adding of Sb elements can refine the grain of the IMC during ageing.

Comparing with different solder systems, the solder alloy with about 0.8 - 1.0 wt% Sb has the lowest growth rate for the formation of the IMC and inhibits the grain ripening most effectively. The mechanical testing also shows the highest strength. When Sb proportion is higher than 1.0 wt%, the grain refining inoculants coarsen and distribute unevenly, resulting in the degradation of the grain refinement effect and reduce of

solder strength. Therefore, 0.8 – 1.0 wt% Sb is the best-fit additive to the Sn-Ag-Cu solder system.

There are two types of Cu-Sn intermetallics formed in solder joints: Cu_3Sn and Cu_6Sn_5 . For the as-soldered joints, Cu_3Sn layer is only to be observed under high magnification SEM. The growth exponents for IMC layer and grains in solder joints suggest that the kinetics of the IMC formation for the soldering reaction during reflow is mainly controlled by grain ripening, combined with diffusion and interface reaction. For aged solder joints, Cu_3Sn and Cu_6Sn_5 can be clearly observed. The Cu_3Sn layer grows faster than Cu_6Sn_5 layer at higher ageing temperatures, while Cu_6Sn_5 layer grows faster at low ageing temperatures. When Cu_6Sn_5 and Cu_3Sn are regarded as a single entity during ageing, its growth is controlled by the diffusion law. When Cu_6Sn_5 and Cu_3Sn are regarded as separated layers, their growth is diffusion-controlled at high temperature, but is controlled by the combination of reaction and diffusion at low temperature.

Tensile testing shows adding Sb can improve the strength of solder alloy and solder joint. Sb dissolved in Sn dendrites or precipitated along Cu_6Sn_5 grain boundary in the form of $\text{Ag}_3(\text{Sn}, \text{Sb})$ would block the movement of the dislocation, so as to strengthen solder alloy or solder joint. The tensile strength of Sn-Ag-Cu-Sb solder alloys is dependent on the strain rate and testing temperature. UTS of solder alloys has a logarithmically linear increase relation with strain rate. Higher strain rate creates more dislocation. With the increase of density of dislocations, the mobility of the dislocations is reduced. So this large number of accumulated dislocations progressively increases resistance to deformation due to dislocation-dislocation interaction. UTS of solder alloys decreases with the increase of testing temperature. This is because the thermal-enhanced dislocation is easier to slip at high testing temperature, which causes the lower resistance for mechanical deformation.

A rapid temperature cycling testing system to evaluate the long-term reliability of advanced package is set up. Both of ATC and RTC testings show the similar wear-out failure mechanism. The simulations provide insight into understanding the differences and similarities between the RTC and ATC tests. For both the RTC and ATC tests, it

was shown that the highest stress occurred at the corner of the outer solder joint. This is in excellent concurrence with the experimentally observed failure location.

The three-parameter Weibull analyses were used to evaluate the failure life of the two testing methodologies. RTC is much faster than the ATC methodology. From the calculation of the mean lifetime to failure of the devices, RTC test gives a fast reliability evaluation with an acceleration factor of 13 comparing with ATC test. Based on the mathematical statistical theory and the physical failure mechanism, the RTC methodology has been established as a possible alternative to the ATC test for quick assessment of the long-term reliability of the TBGA assembly.

8.2 Recommendations for future work

Based on the aims as well as problems and limitation encountered in the work, following work might be recommended for further studies:

To study the additive effect systemically, other elements such as Bi and In can be taken as additive respectively as well. Bismuth and Indium are common elements added in solder alloy. The different properties of the Sb, In, and Bi phases, intrinsic strengths, atomic size, as well as the behavior of the grain and interphase boundaries will be integrated to determine the optimum overall performance of the Sn-3.5Ag-0.7Cu alloy. The addition elements are supposed to refine the grain size of IMC since the heterogeneous nucleation decreases the nucleation energy barrier. According to the theory of heterogeneous nucleation, the effectiveness of a nucleation site should depend on the contact angle and the surface roughness. Low values of θ are favored by a low-energy interface between the additive and Cu_6Sn_5 nucleus, which should in turn be favored by good lattice matching between the heterogeneous nucleation nucleus and IMC.

Only UTS testing has been carried out in the present work. This seems to be too limited for an effective study of the mechanical properties of solder alloy and solder joint. Testing the Young's modulus, yield stress will help to understand the mechanical properties of solder joint. In addition, the effect of Sb on the reliability of solder joints has not been well studied because of the time limitation and short of

testing equipment. Therefore, reliability study of Sn-3.5Ag-0.7Cu-xSb solder joints is worthy to study in the future.

A thermoelectric cooler-based rapid temperature cycling (RTC) testing method has been established and applied to assess the long time reliability of solder joints in tape ball grid array (TBGA) assembly. This RTC testing methodology can significantly reduce the time required to determine the reliability of electronic packaging components. It would be interesting to further study whether the new RTC methodology could be applied to other advanced microelectronic packages, such as chip scale package (CSP), flip chip, etc, and if it could replace other fatigue testing such as thermal shock, *etc.*

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1. G. Y. Li, B. L. Chen and Y. C. Ee, "Effects of Reflow Process Parameters on the Growth of Intermetallic Compounds between Cu Substrate and Pb-free Solder", 3rd International Conference on Materials Processing for Properties and Performance (MP3), 1-3 August 2002, Singapore.
2. B. L. Chen and G. Y. Li, "Effects of Sb Additives on the Growth of Intermetallic Compounds between Cu Substrate and Sn-Ag-Cu Pb-free Solder", 2003 Electronic Components and Technology Conference, May 27 - May 30, New Orleans, Louisiana, USA, pp.1235-1242.
3. G. Y. Li and B. L. Chen, "Formation and Growth Kinetics of Interfacial Intermetallics in Pb-Free Solder Joint", IEEE Transactions on components and packaging technologies, vol. 26, no. 3, 2003, pp. 651-658.
4. B. L. Chen and G. Y. Li, "An Investigation of Effects of Sb on the Intermetallic Formation in Sn-3.5Ag-0.7Cu Solder Joints", accepted for publication in the IEEE Transactions on Components and Packaging Technologies.
5. G. Y. Li, B. L. Chen and J. N. Tey, "Reaction of Sn-3.5Ag-0.7Cu-xSb solder with Cu metallization during reflow soldering", IEEE Transactions on electronics packaging manufacturing, vol. 17, no. 1, 2004, pp.77-85.
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9. G. Y. Li and B. L. Chen, "Influence of Sb on IMC Growth and Mechanical Properties of Sn-3.5Ag-0.7Cu Solder Joints", Globalelectronics Technology Conference, Singapore, 8-9, September 2004, pp85-91.