STUDY THE EFFECT OF ISOTHERMAL AGING ON Sn-Ag-Cu (SAC) LEAD-FREE SOLDER ADDED WITH SILICON CARBIDE (SiC)

by

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS AND SYMBOLS

°C	Degree Celcius
µm	Micrometer
Ag	Silver
Al	Aluminium
Al_2O_3	Alumina
ASTM	American Society for Testing and Materials
At %	Atomic Percent
Au	Gold
Bi	Bismuth
Cd	Cadmium
Ce	Cerium
CH_3OH	Methanol
cm	Centimeter
Co	Cobalt
CTE	Coefficient of Thermal Expansion
Cu	Copper
d	Days
EDX	X-ray Spectrometer
EEE	Electrical and Electronic Equipment
ELFNET	European Lead-free Soldering Network
EPA	Environmental Protection Agency
Fe	Iron
HCl	Hydrochloric Acid

HNO_3	Nitric Acid
IC	Integrated Circuit
IMC	Intermetallic Compound
In	Indium
IR	Infrared
ISO	International Organization for Standardization
J	Joule
JEDEC	Joint Electronic Devive Engineering Council
K	Kelvin
kJ	Kilojoule
mm	Millimetre
Mn	Manganese
MPa	Megapascal
NEMI	National Electronics Manufacturing Initiative
Ni	Nickel
OM	Optical Microscope
Pb	Lead
PCB	Printed Circuit Board
ppm	Parts per Million
PT	Peak Temperature
RoHS	The Hazardous Substances Directive
s	Second
SAC	Tin Silver Copper
SEM	Scanning Electron Microscope
Si	Silicon

Si_3N_4	Silicon Nitride
SiC	Silicon Carbide
SMT	Surface Mount Technology
Sn	Tin
T	Absolute Temperature
TAL	Time Above Liquidus
Ti	Titanium
TiB_2	Titanium Diboride
TiO_2	Titanium Dioxide
UBM	Under Bump Metallization
wt %	Weight percent
XRD	X-ray Diffraction
Zn	Zinc
θ	Contact Angle

Mengkaji Kesan Suhu Penuaan Sn-Ag-Cu (SAC) Pateri Bebas-Plumbum Ditambah dengan Silikon Karbida (SiC)

ABSTRAK

Pateri komposit adalah sebagai penggunaan baru untuk meningkatkan kestabilan pada penyambungan pateri. Penambahan zarah tertentu untuk membentuk pateri komposit mendapat perhatian yang besar kerana ia dapat meningkatkan sifat mekanikal pateri dan dibuktikan oleh penyelidik lain. Kajian ini tumpu ke atas kesan suhu penuaan pada sudut sentuh, pertumbuhan lapisan antara bahan logam (IMC) dan sifat mekanikal pateri. Dalam kajian ini, Sn-3Ag-0.5Cu (SAC305) pateri telah digunakan sebagai matrik asas dan 0.75% berat SiC telah ditambah ke dalam pateri tembaga perak timah (SAC) sebagai zarah tetulang. Pateri komposit telah disediakan dengan menggunakan kaedah logam serbuk yang terdiri daripada pencampuran, pemadatan dan pemanasan. Pencirian pateri bebas-plumbum, terutamanya selepas suhu penuaan adalah sangat penting untuk mengetahui secara tepat kekuatan sambungan pateri. Kajian ini terbahagi kepada dua fasa. Fasa pertama adalah proses penyediaan sampel dan kajian pencirian ketahanan pateri sebelum penuaan untuk pateri SAC dan SAC-SiC komposit. Pencirian dibahagikan kepada mikrostruktur, fizikal, ciri pencairan dan sifat-sifat mekanikal. Fasa kedua adalah berkaitan dengan kajian ketahanan pateri selepas proses penuaan. Dalam fasa ini, tindak balas antara pateri dan substrat timah (Cu) selepas penuaan telah dicerap. Didapati bahawa sudut pateri SAC dan SAC-SiC komposit meningkat dengan suhu dan masa penuaan. Sudut SAC-SiC komposit adalah lebih rendah daripada pateri SAC kerana pemisahan zarah tetulang SiC di sepanjang titik pembasahan. Ketebalan lapisan IMC dalam pateri meningkat disebabkan oleh suhu penuaan yang lebih tinggi dan penambahan masa penuaan. Kehadiran SiC dalam pateri SAC kekal sebagai zarah pepejal yang stabil semasa proses pencairan dan menghalang pertumbuhan IMC bagi pateri SAC-SiC komposit. Zarah SiC cenderung untuk berada pada lapisan IMC dan bertindak sebagai penghalang yang membantu untuk mengurangkan pertumbuhan lapisan IMC dengan menyekat penyebaran atom Cu dari substrat Cu ke pateri. Tenaga pengaktifan pateri SAC-SiC komposit juga menjadi lebih tinggi dan menyebabkan pertumbuhan lapisan IMC lebih sukar berbanding SAC. Apabila suhu dan masa penuaan meningkat, nilai kekerasan mikro pateri adalah sedikit menurun. Kekerasan mikro bagi SAC-SiC komposit adalah lebih tinggi daripada pateri SAC kerana penyebaran homogen SiC dan zarah-zarah IMC halus termasuk Cu_6Sn_5 dan Ag_3Sn ketika SiC ditambah kedalam pateri SAC. Kekuatan ricih pateri SAC dan SAC-SiC komposit menurun apabila suhu dan masa penuaan meningkat. Namun begitu, nilai kekuatan ricih untuk pateri SAC-SiC komposit meningkat dengan konsisten berbanding dengan pateri SAC kerana kehadiran SiC yang bertindak sebagai halangan bagi gerakan kehelan dan menyebabkan peningkatan kekuatan ricih. Permukaan patah antara muka pada pateri SAC-SiC komposit dan substrat Cu mempamerkan patah mulur dengan permukaan lengkungan yang kasar. Secara keseluruhan, penambahan SiC sebagai tetulang ke dalam SAC pateri bebas-plumbum telah menambah baik sudut sentuh, pertumbuhan lapisan IMC dan sifat mekanikal untuk bahan pateri selepas proses penuaan.

Study the Effect of Isothermal Aging on Sn-Ag-Cu (SAC) Lead-free Solder Added with Silicon Carbide (SiC)

ABSTRACT

The usage of composite solder is one of the method in improving stability of the solder joints. Addition of certain particles such SiC to form a composite solder has been given greater attention since it can enhance the mechanical properties of solder and has been proven by other researchers. This study was focus on the effect of isothermal aging on the contact angle, intermetallic compound (IMC) layer growth and mechanical properties of solder. In this study, Sn-3Ag-0.5Cu (SAC305) solder was used as based matrix and 0.75 wt% of SiC was added into tin silver copper (SAC) solder as reinforcement particles. The composite solder was prepared by using powder metallurgy method which consists of mixing, compacting and sintering. The characterization of lead-free solders, especially after isothermal aging, is very important in order to accurately predict the reliability of solder joints. This study was divided into two phases. Phase one is about the process of sample preparation and characterization studies of solder reliability before isothermal aging process for both SAC and SAC-SiC composite solder. The characterization divided into microstructural, physical, solderability and mechanical properties. Phase two is related to reliability of solder after isothermal aging process. In this phase, the reaction between solder and copper (Cu) substrate after aging was observed. Found that, the contact angle of SAC and SAC-SiC composite solder were increased with aging temperature and time. The contact angle of SAC-SiC composite was lower than SAC solder due to the segregation of SiC reinforcement particles along the wetting point. IMC layer thickness of solder was increased when the aging temperature and time was higher. The presence of SiC in SAC solder remain as stable solid particles during reflow process and retard the IMC growth for SAC-SiC composite solder. The SiC particles tend to stay preferentially on IMC layer and act as a barrier which helps to reduce the IMC layer growth by blocking the diffusion of Cu atoms from Cu substrate to the solder. The activation energy of SAC-SiC composite also becomes higher and caused the growth of IMC layer more difficult than SAC solder. As the aging temperature and time increased, the microhardness of solder was slightly decreased. The microhardness for SAC-SiC composite was higher than SAC solder due to the homogenous distribution of SiC and fine IMC particles including Cu_6Sn_5 and Ag_3Sn when SiC was added into SAC solder. The shear strength of SAC and SAC-SiC composite solder were decreased when aging temperature and time increased. However, the shear strength value for SAC-SiC composite solder was consistently higher compared with SAC solder due to the presence of SiC which acts as obstacles for dislocation motion and leads to the increasing of shear strength. The fracture surface at the interface between SAC-SiC composite solder and Cu substrate exhibit the ductile fracture with rough dimple surface. Overall, the addition of SiC as reinforcement into SAC lead-free solder matrix has improved the contact angle, IMC layer growth and mechanical properties of the solder materials after isothermal aging process.

CHAPTER 1: INTRODUCTION

1.1 Background

Solder means a metal alloy which is used to join with smooth and clean metal surfaces (Mohd Salleh *et al*., 2012). Soldering is broadly used as joining method to connect components by the usage of metallic alloys which having low melting temperature than the materials that will be united. Electronics industry begins in the 20th century and soldering has come to be an irreplaceable technique in the production of electronic devices. As solder is a joining material, it gives mechanical, electrical and thermal stability in electronic assemblies (Kantarcıoğlu & Kalay, 2014).

The challenge of soldering industries is mainly focused on its alloy choices based on certain applications. Lead (Pb) based solders such as tin-lead (Sn-Pb) solders are mainly chose to be used in electronic packaging over the past few decades (Kim *et al*., 2014). However, the hazardous substances (RoHS) directive and Environmental Protection Agency (EPA) restricted the use of Pb in electrical and electronic equipment (EEE) as Pb is confirmed toxic (Kantarcıoğlu & Kalay, 2014; Sadiq *et al*., 2013) to both environment and health.

EPA verified Pb as one of the top 17 chemicals posing the biggest risk to human beings and environment (Sadiq *et al*., 2013). Therefore, efforts have been conducted by many researchers to develop Pb-free solder. Pb-free solder which commonly used were tin (Sn) based such as tin-silver-copper (SAC), tin-copper (Sn-Cu) and tin-silver (Sn-Ag) to replace Sn-Pb solders (Siewert *et al*., 2002). SAC and Sn-Cu are rated as the main options and expected to be the primary alternatives solder used in electronic packaging compared to others Pb-free solder availability (Mohd Salleh *et al.*, 2013).

During soldering and aging of Pb-free solder on Cu pads, interfacial transformation occurs at the interface between solder and Cu substrate, where Cu-Sn intermetallic compound (IMC) layer known as Cu_6Sn_5 forms (Satyanarayan & Prabhu, 2011). This IMC layer is good for wetting, but high ambient temperature on solder joint results in excessive growth of IMC layer that weakens the strength of solder joints due to brittleness and weakness (Rizvi & Bailey, 2007).

Besides that, it is important to understand and control the growth factors of the IMC layer of Pb-free solder (Yoon & Jung, 2006). In order to improve the wettability and mechanical properties of solder, addition either metal or ceramic as reinforcement in the Pb-free solder functions as diffusion barrier which able to retard the rapid interfacial reaction between solder and Cu substrate (Rizvi & Bailey, 2007; Mohd Salleh & Mustafa Al Bakri, 2011).

Generally, composite solder have good creep and thermo-mechanical fatigue resistance in solder joints (Shen & Chan, 2009). Studies on composite solder have been done by many researchers as an effort to develop viable Pb-free solders which can replace the conventional Pb-based solders as Pb is considered as toxic. The termed of composite solder means the solder materials composed two or more different atoms which include metals and ceramic atoms. In this research, the usage of silicon carbide (SiC) with 0.75 wt% composition as reinforcement into SAC is a new development in composite solder.

As believed, the SiC particles will retard the excessive growth of IMC layer during isothermal aging process.

In fabricating these SAC and SAC-SiC composite solder, powder metallurgy method has been selected due to the mechanical properties and wettability results of the solder prepared by powder metallurgy method are well presented compared with casting method. Microstructure produced by powder metallurgy method shows finer grain structure compared to casting process. For the mechanical properties, solder prepared by powder metallurgy method shows great performance compared to casting method where it has higher value of microhardness, yield strength and ultimate tensile strength (Mohd Salleh et al., 2013). Owing to this reasons, powder metallurgy becomes the main method to fabricate solder compared to other processing methods since powder metallurgy method can improve the mechanical and solderability properties of Pb-free solder.

1.2 Problem Statement

The formation and the subsequent growth of the IMC layer between solder and Cu substrate becomes major issue in soldering. The excessive growth of IMC layer will increase the brittleness of solder joints and detrimentally affects the reliability of solder joints (Song & Lee, 2006). The study of IMC layer growth in isothermal aging is very important since aging process portrayed the operating environment of solder materials and shows its reliability during operating temperature in electronic packaging.

However, the result of a literature search revealed that only a few studies have been reported so far on isothermal aging process of SAC solder containing SiC particles. Major concern on the IMC layer has been made in this work in order to ensure for a long-term solder joint reliability performance in electronic assemblies. IMC layer must be keep at sufficient thickness because excessive amount of IMC layer can generate defect and affect the solder joint reliability (Shangguan, 2005).

Sn-Cu solder has been discovered to suffer from poor fluidity at soldering temperatures and addition of Ag into Sn-Cu solder found able to improve their fluidity and wetting characteristic (Pandher & Lawlor, 2009). However, this SAC still lack of mechanical properties cause by brittle IMC layer form during the solidification process. Due to brittle nature of IMC layer between solder and Cu substrate, numerous studies have revealed that the additions of certain particles into SAC to form a composite solder, could improve the properties of solder (Tan et al., 2015).

SiC has been selected to be added into SAC due to its good mechanical properties. The high thermal conductivity coupled with low thermal expansion and high strength gives this material exceptional thermal shock resistant qualities. SiC particles also found has no solubility in the β-Sn matrix (El-Daly et al., 2015). Addition of SiC into SAC solder was believed able to retard the IMC layer growth in different isothermal aging temperature and time.

Powder metallurgy method was used in this project to produce SAC and SAC-SiC composite solder with higher microhardness value of mechanical result and good wettability compared with casting method (Mohd Salleh et al., 2013). Powder metallurgy method also economical as it can produce near-net-shape and not required any expert employees to run the machine. According to the findings obtain from previous study of powder metallurgy method done by researchers, microstructural observation showed that SiC particles were distributed homogeneously at the grain boundaries of SAC solder which also lead to a better microhardness and shear strength of solder.

1.3 Objectives

The objectives of this research in detail consist of :

i) To investigate the formation of IMC layer of SAC and SAC-SiC composite solder on Cu substrate after isothermal aging.

ii) To study the mechanical properties of SAC and SAC-SiC composite solder on Cu substrate after isothermal aging.

iii) To understand the fracture mode occur in solder joints due to isothermal aging process of SAC and SAC-SiC composite solder on Cu substrate.

1.4 Project Scopes

The scope of this research was focused on two types of solders namely as SAC and SAC-SiC composite solder. The composition for SAC solder was 100 wt % SAC while composition used for SAC-SiC composite solder was 0.75 wt. % SiC with 99.25 wt. % SAC.

Powder metallurgy method used to fabricate SAC and SAC-SiC composite solder consists of three stages included mixing, compacting and sintering. Solder green produced after mixing and compacting process were heated under the melting point temperature. Next, solder joints were prepared by reflow soldering process of solder on Cu substrate. After reflow process, the solder joint samples were subjected to isothermal aging at 75 °C, 100 °C, 125 °C, 150 °C and 175 °C for 2, 4, 11, 20 and 41 days.

After isothermal aging process, growth kinetics and activation energy of IMC layer formed between solder and Cu substrate were analyzed. The inspection on wetting properties, microstructures evolution and mechanical properties with several testing was observed.

The contact angle image, post-reflow microstructure and IMC layer formation were obtained using Scanning Electron Microscope (SEM). To identify the phases exist between solder and Cu substrate, X-ray diffraction (XRD) characterization was done and supported by Energy Dispersive X-ray (EDX) result obtained from the SEM. The microstructure changes of the samples according to its aging temperature and time were observed through SEM. The microhardness of sample was measured by using Vickers microhardness. The shear test was done to examine the strength of solder bond to Cu substrate.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction to Solder and Soldering

Electronic packaging is a fabrication of electronic products that comprised of integrated circuit (IC) chips and electronic devices (Hsiao & Duh, 2005). The connection between electronic components and printed circuit boards use solders as their interconnect materials. Solder means a fusible metal alloy which is join with smooth and clean metal surfaces. As the joining material, solders provide the electrical and mechanical connections in electronic assemblies (Mohd Amin et al., 2014). Solder alloys are classified as either soft or hard. Soft solders melt below 350 °C and hard solders melt above 350 °C. Tin (Sn), lead (Pb), bismuth (Bi), indium (In) and cadmium (Cd) are typically found in soft solder, while hard solder often contain metals for example gold (Au), silicon (Si), aluminium (Al) and zinc (Zn) (Zhang, 2010). The historical development of solders is portrayed by the timeline as shown in Figure 2.1.

The solder starts from 4000 years ago through the bronze and iron ages, until the present of "Silicon Age". The earliest archeological verify of soldering dates back to 4000 years ago, when gold-based solder or known as hard solders were introduced by artisans in Mesopotamia. Then, solder developed in Egypt (3600 BC), Ur (3400 BC), Greece (2600 BC) and other Mediterranean regions. The Etruscans distinctly refined hard soldering method during the Bronze Age (2500 years ago). A gold pendant clarified their skill of the "step-joining" method which is three dissimilar melting point is formed through a distance of 5 mm. There is also proving of high quality gold-based solder joints being used by the La Tolita Indians of South America (Puttlitz & Stalter, 2004; Zhang, 2010).

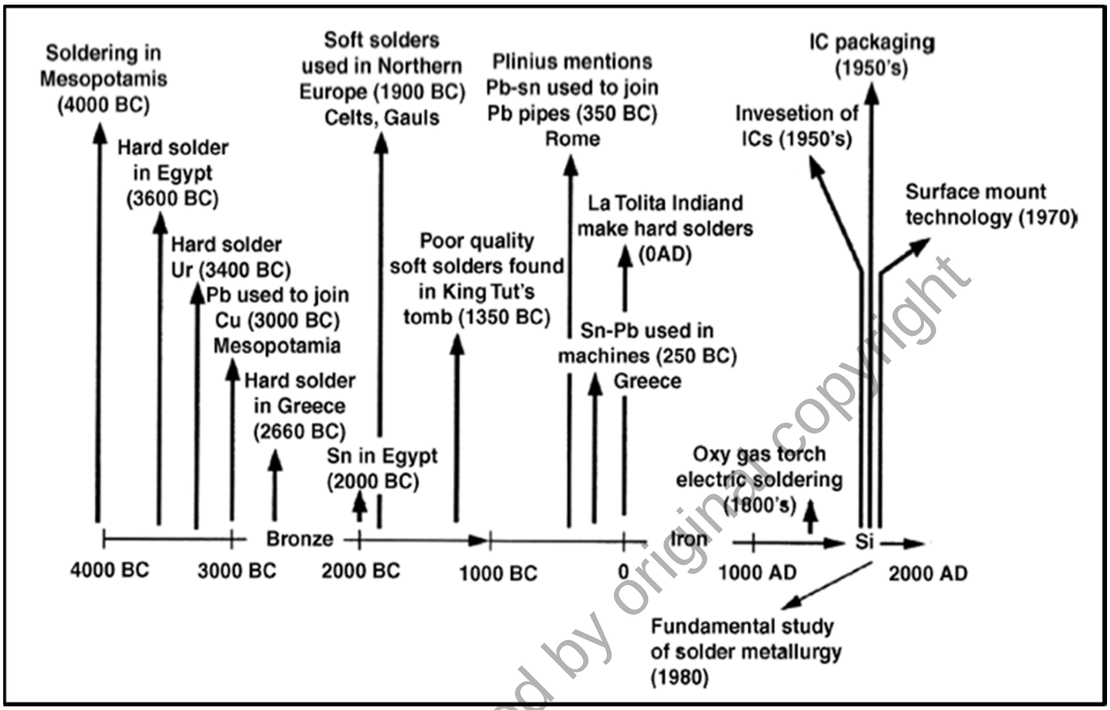

Figure 2.1: The historical development of solders (Zhang, 2010)

Soldering is a metallurgical joining process by using solder as a filler which having a melting point below 315 °C (Boardwalk, 1997). Besides, soldering also can be defined as any of alloys applied at the metal objects to join them without reaching the melting point of the objects. There are two standard types of soldering used in electronic industries including hard and soft soldering. Hard soldering uses a solder with a melting point above 450 °C, while the melting point of solder for soft soldering is below 450 °C (Vianco, 1993). Soldering techniques are divided into two categories, flow and reflow soldering. Flow soldering requires the implementation of molten solder to the component attachment site. Wave soldering, dip soldering and drag soldering among the processes that are under this category. Reflow soldering involves the melting of solder that has