SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
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EFFECT OF ADDING INDIUM AND ZINC ALLOYING ELEMENTS TO CREEP BEHAVIOR OF Sn-0.7Cu SOLDER ALLOY

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "Effect of Adding Indium and Zinc Alloying Elements to Creep Behavior of Sn-0.7Cu Solder Alloy". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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TABLES OF CONTENTS

Contents **Page**

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVATIONS

Ag	Silver
Bi	Bismuth
BGA	Ball Grid Array
Cu	Copper
DSC	Differential Scanning Calorimetry
EU	European Union
EDX	Energy Dispersive X-ray
In	Indium
IMCs	Intermetallic Compounds
Pb	Lead
PCD	Printed Circuit Board
RoHS	Restriction of Hazardous Substances
Sn	Tin
SEM	Scanning Electron Microscope
SMT	Surface Mount Technology
WEEE	Waste Electrical & Electronic Equipment
XRF	X-ray Fluorescence
Zn	Zinc

LIST OF SYMBOLS

α	Alpha
β	Beta
γ	Surface Tension
$\dot{\varepsilon}$	Creep Strain
$\dot{\varepsilon}ss$	Steady-state Creep Strain Rate
n	Creep Stress Exponent
Q_c	Creep Activation Energy

KESAN PENAMBAHAN ELEMENT PENGALOIAN INDIUM DAN ZINK TERHADAP KELAKUAN RAYAPAN PATERI Sn-0.7Cu

ABSTRAK

Pateri Sn-0.7Cu telah digunakan dalam industri pembungkusan elektronik untuk menggantikan pateri Sn-Pb untuk mengurangkan kesan negatif oleh Pb kepada alam sekitar dan kesihatan manusia. Namun, kebolehbasahan dan sifat mekanik pateri eutektik Sn-0.7Cu yang agak rendah telah menimbulkan kebimbangan kebolehpercayaan dalam aplikasi sebenar. Mikro-pengaloian telah dilaporkan sebagai salah satu cara yang paling berkesan untuk memperbaiki sifat-sifat pateri dengan penambahan elemen-elemen pengaloian dalam sistem aloi. Dalam projek ini, 0.5 dan 1.0 wt.% Zn telah ditambah dalam aloi pateri Sn-0.7Cu-1.0In. Kesan elemen pengaloian terhadap sifat terma, kebolehbasahan, mikrostruktur dan kompaun antara logam diperhatikan, dan sifat mekanik dan kesan penuaan isoterma pada kekuatan ricih sambungan pateri telah dikaji. Pateri terbaik yang diperhatikan adalah pateri yang ditambah dengan 0.5 wt.% Zn. Kebolehbasahan, kekerasan, kekuatan ricih untuk sampel sambungan dan penuaan isoterma bagi aloi pateri ini didapati tertinggi di kalangan sampel pateri. Suhu lebur pateri meningkat dengan jumlah Zn. Namun, jeda buburan dan ketebalan lapisan IMC menurun dengan peningkatan Zn. Keputusan SEM mendapati In dan Zn telah teresap masuk ke dalam sebatian Cu_6Sn_5 membentuk $Cu_6(Sn,Zn)_5$ and $Cu_6(Sn,In)_5$. Selain itu, pembentukan sebatian Cu-Zn telah dikesan apabila penambahan Zn adalah 1.0wt.%. Rintangan rayapan untuk Sn-0.7Cu-1.0In-1.0Zn adalah pateri yang paling tinggi. Ini adalah kerana kehadiran Cu_5Zn_8 dengan zarah fasa kedua yang berkesan menghalang pergerakan kehelan.

EFFECT OF ADDING INDIUM AND ZINC ALLOYING ELEMENTS TO CREEP BEHAVIOUR OF SN-0.7CU SOLDER

ABSTRACT

For several years, Sn-0.7Cu solder has been used in electronic packaging industries to replace the Sn-Pb solder in order to reduce the negative impact of lead to the environment and human health. However, the relatively poor wettability and mechanical properties of Sn-Cu solder alloys has raised reliability concern in the actual application. Micro-alloying has been reported as one of the most effective approaches to improve the properties of solders by minor additions of alloying elements to the alloy system. In this project, 0.5 and 1.0 wt.% Zn had been added to the Sn-0.7Cu-1.0In base solder, and the effect of alloying elements on thermal behaviour, solderability, microstructure and intermetallic compounds (IMCs) observation, mechanical properties, and effect of isothermal aging on shear strength have been studied. The best performing solder is one with 0.5 wt.% Zn solder. The wettability, hardness, reflowed and aged shear strength were found to be highest amongst the solder samples. The melting temperature of solder increased with the amount of Zn content. However, the pasty range and thickness of IMC layer decreased with increasing of Zn. From SEM observation, In and Zn have been observed to dope into the Cu_6Sn_5 forming $Cu_6(Sn,Zn)_5$ and $Cu_6(Sn,In)_5$. Besides, formation of Cu-Zn compound became favourable when 1.0 wt% Zn is added. For creep test, Sn-0.7Cu-1.0In-1.0Zn has the highest creep resistance among the sample due to the presence of Zn-rich second phase particles which effectively impeding the dislocation movement.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Solder is a key element in the electronics packaging industry. It is a soft metal used to join two harder metals together by melting itself to form a solder joint between them. Solder acts as the interconnecting material to provide a mechanical and electrical joint to connecting components, securing and holding them in place after a circuit has been assembled (Hwang, 2004). Solder alloys were first being used as metal joint materials thousands of years ago. In the past few decades, however, the development of modern electronic packaging technology has extend the usage of solders to provide mechanical support and electrical connection to the printed wire board (PWB) (Ma and Suhling, 2009).

Solder alloys can be categorized into two major groups, which are leaded and lead free solders. Leaded solder, which usually known as eutectic Sn-Pb solder has always been the dominant option in electronic packaging industry due to its low melting point (T_m = 183°C), good solderability and reliability (Ma and Suhling, 2009). However, the reasons that lead to the current interest of lead-free solders are due to the environmental risk that brought by lead. Lead is believed to leach from the discarded equipment that consists of lead solders in landfill sites, causing groundwater and soil contamination. On the other hand, handling of dross from soldering process and powder production for pastes could bring health hazard to the manufacturers and users, where the lead-bearing particles can be inhaled into human body and hazard to the person health.

A numbers of lead-free solders have been developed since the implementation of RoHS and WEEE. Both directives are meant to prevent the use of materials and chemicals that deemed to be harmful to the environment, and identifying products that are safe for recycling and preventing the products from being disposed entirely to the landfills (Bath, 2007). Nonetheless, most of the lead-free solders are having electronic application drawbacks due to their performance deficiencies, like high melting temperature, poor wettability or mechanical strength. One of the most critical drawbacks are most of the lead-free alloys are having melting temperatures more than 215°C (Hwang, 2004). Therefore, the objectives of many current researches are focused on developing a lead-free solder that provide low melting temperature, high strength and good wettability.

In lead-free primary alloy design criteria, eutectic Sn-Pb solder alloys have always been used as a baseline in developing the new lead-free solders in order to have similar or even better properties in replacing the Sn-Pb solders. The principal requirements in selection of lead free solder alloys are physical properties, mechanical properties, microstructural characteristic etc (Shangguan, 2005). For example, the basic requirement of a lead-free solder is having similar melting temperature to the existing eutectic Sn-Pb solders, and high enough to withstand the operating temperatures. Generally, melting temperature of solders do not exceed more than 230°C in order to prevent PCB and electronic components damaged. After taking all these considerations, the screening process of qualified solder alloys have been identified. Sn-Cu, Sn-Ag and Sn-Bi are qualified for the binary alloys. While in the right soldering temperature range, there are Sn-Bi-Ag, Sn-Ag-In, Sn-Ag-Cu, Sn-Bi-Ag-Cu and Sn-Ag-Sb-Bi are qualified as the alternative of leaded solder alloys (Zhang, 2011). Due to cost consideration, Sn-Cu alloy system have been widely chosen as replacements for Sn-Pb solders. The absence of costly metals allow it to have competitive edge than the others in term of costs, which makes it as the favourite solder alloys of the manufacturers. In order to overcome the poor performances of Sn-Cu alloy system, alloying elements were used to improve its performances deficiencies.

In most electronic packaging applications, it is not a single high stress event that breaks a solder joint component, instead it is prolonged or repeated load applications that result in creep failure of solder. Creep in electronic assembly is the physical phenomenon of a time dependent increasing irreversible deformation when a material acts upon the thermal and power cycles during practical service. In addition, electronic devices that have been used in industrial and vehicle products are more commonly loaded into the more severe environments (Hidaka et al., 2006). Since solder alloys are having low melting temperature around 180°C to 240°C, the solder joints are prone to creep deformation at both ambient environmental and high temperature conditions. In thermal cycling condition, creep is expected to be controlling deformation mode to determine the reliability of circuit board assemblies. Because of creep effects, the total strain range during given loading cycle can be a strong function of solder temperature, the loading time per cycle and the applied solder stress. Besides, the solder metallurgical state, including solder composition, aging condition, and grain size could also influence the creep rate of solder alloys. Hence, it is important to understand the creep behaviour of solder joints in the electronic packaging as it can significantly influence the reliability of the electronic devices.

1.2 Problem Statements

For many years, lead-containing solder alloys have been the most eminent solders for electronic interconnection and packaging technology in semiconductor industry. The high favourable status of lead-containing solders in semiconductor industry are due to their low cost, good physical and mechanical properties (Zhang, 2011). However, the selection of materials in modern manufacturing industry no longer only driven by product performance, reliability and cost, but also the environmental and health considerations. The disposal of lead-soldered electronic components has caused a serious concern to human health and environmental. Therefore, a new generation of lead-free solder alloys are developed to replace the current one (Hidaka et al., 2006).

After years of many alloys investigation, lead-free solders are now the new favourite solder in semiconductor packaging industry due to their friendly-behaviour to the environment. Among these lead-free solder alloys, Sn-0.7Cu alloys are deemed as the strong alternative candidate for the replacement of tin-lead alloys. This is because of its good solderability, near cost to lead-free alloys and the environmental advantages (Zeng et al., 2015). Sn-Cu eutectic (Sn-0.7Cu) is one of the best solder alloys that has been extensively used in the industry today due to its good reliability and mechanical properties.

With the rapid development of technology, however, the requirements and severe service conditions of the solders are getting rigorous. A better and more reliable Sn-Cu solder alloy in terms of melting point, wettability, mechanical strength and creep resistance are needed to serve the conditions. Recent investigations have proven that one of the most effective ways for alloy development is micro-alloying additions to the alloy systems, which modified the microstructure of the alloys and hence made improvements in mechanical and/or physical properties (Nobari et al., 2016). However, there were not much studies of adding alloying elements like In and Zn in Sn-Cu eutectic solders. Most of the researches were studied only on the effect of alloying Sb, Ti, Ga, Al, Fe and rare earth to Sn-Cu solder (Nobari et al., 2016, Sun and Zhang, 2015, Chuang et al., 2012).

Sun and Zhang (2015) have stated that the addition of small amount of In in SnAgCu (SAC) solder can significantly reduce the its melting temperature. Moreover, the wettability of SAC solders can be improved by adding a small amount of Zn element (Zhang et al., 2012). In this study, therefore, the effects of alloying elements (In and Zn) on the creep properties of Sn-Cu eutectic, as well as melting temperature, wettability, microstructure, mechanical properties and intermetallic compound (IMC) formed at the as-reflowed and aged solder joints will be examined.

1.3 Objectives

The objectives of this project are:

I. To investigate the effect of Zn and In alloying elements to Sn-0.7Cu solder alloy in terms of eutectic melting point, wettability, microstructure, mechanical strength, creep resistance and intermetallic compound (IMC).

II. To study the effect of alloying elements (Zn and In) on the creep behaviour of Sn-Cu solder alloy.

1.4 Project Overview

The focus of this project is upon the addition of Zinc and Indium to Sn-Cu solder alloy. Four composition of solder alloys, Sn-0.7Cu-1.0In, Sn-0.7Cu-1.0In-0.5Zn and Sn-0.7Cu-1.0In-1.0Zn were prepared. The casted bulk solders were sent for thermal analysis by using Differential Scanning Calorimetry (DSC) to identify the melting temperature of solder alloys. Elemental analysis and bulk microstructural observation were done by X-Ray Fluorescent (XRF), Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX). Solder samples were then cut into specific dimension and reflowed it onto a Cu plate at 270°C for isothermal aging and 280°C for tensile and creep tests. The reflowed samples were then evaluated the thickness of IMC formed at the interface after reflow. The types of IMC formed at the solder/substrate interface were analysed by SEM equipped with EDX. The spreading and wetting angles tests on reflowed samples and wetting balance test were identified to determine the wettability of solder alloys. For mechanical properties, shear strength of both reflowed and aged solder joints were determined by using INSTRON machine via single lap joint shear test. Creep test was carried out to study the creep behaviours of solder joints in terms of steady state creep rate.

CHAPTER 2

LITERATURE REVIEW

2.1 2.1 Solder

Solder is a fusible materials, or more specifically, fusible metal alloy used to join two or more metal workpieces together by forming a solder joint or permanent bond between them. For decades, solder has been used as the principal joining medium in electronic assemblies to create connections between components and the printed circuit board (PCB). It acts as the interconnecting material to provide mechanical joint and connect the components, securing and holding them in place, as well as electrical conduction, after a circuit has been assembled (Hwang, 2004). There are few fundamental requirements that all solder interconnection alloys must possess, i.e. solder must be able to wet and bond between the components and circuit/substrate, possess sufficiently low melting, allow the expansion and contraction of the components, and dissipate the heat generated.

For many years, tin-lead alloys have been used as the most dominant solders due to their low melting temperature (183°C). This melting point allows the Sn/37Pb solders to be used in many soldering technology, i.e. working temperature of 200-240°C for reflow soldering and 250°C in wave soldering. Lead plays an important role in the tin-lead solder alloy. Pb reduces the melting point of the Sn matrix solder significantly and enhances the mechanical properties of the solder as well. Moreover, it does not involved in the formation of intermetallic compounds with circuit metallization, neither at the ends of solder joints nor within the bulk solder (Puttlitz and Stalter, 2004).

Recent researches have focused in determining the suitable alternative solder to replace the eutectic Sn-Pb. Many metals like Silver (Ag), Copper (Cu), Nickel (Ni), Indium (In) etc have been investigated. Among the metals, Sn has been chosen as the most suitable element in being the base metal material due to its rational price and melting temperature (Manko, 2001). The melting point of its solder alloys are usually ranged in between 120°C and 280°C, which make Sn solder alloys desirable and flexible in the replacement of eutectic Sn-Pb.

2.2 Soldering Technologies

Soldering is a metallurgical joining process that used solder as a filler material to join components. Besides, soldering also involved chemical reactions between the solder and bonding surface to be joined which gives significantly influence to the properties and reliability of solder joint later (Ho et al., 2007). Soldering process has some favoured position compared to welding process in term of weldability, type of metals to be joint, amount of heat energy required etc. A lower melting point of filler metal is required to do the joining process without melting down the metal workpieces. There are mainly two types of soldering technologies being used in the industry today to manufacture of printed circuit boards, which are wave soldering and reflow soldering. They are widely been used for through-hole and surface mount circuit assemblies. Through-hole soldering refer to the electronic components being soldered via inserts through the holes drilled in the PCB. While surface mount technology is mounted or placed the components directly onto the surface of PBC.

2.2.1 Wave Soldering

Wave soldering is a large scale soldering process that allows multiple lead wires to be soldered to a PCB by passing through a molten solder wave, forming solder fillet between the circuit board and the lead wire (Updike et al., 2001). In this process, a through-hole load PCB is passes through the waterfall of molten solder for soldering. When PCB passes through the waterfall, the exposure areas of the underside board (the areas do not protected by the solder mask), creating a strong mechanical and electrical connection. While for the surface mount assembly, the electrical components are first being glued by the placement machine arm onto the PCB surface before running through the wave of molten solder (Pecht, 1993).

2.2.2 Reflow Soldering

Reflow soldering is a process where using the mixture of powdered solder and flux, known as solder paste to temporarily attach the electrical components to the contact pads on the circuit board. In this process, the solder paste was applied on the board followed by the placed the surface mount components on it. The function of solder paste is to act as a temporary glue to hold the components in place before the soldering process. The loaded PCB is then subjected to a controlled heat temperature that is above the melting point of the solder. In the meanwhile, the solder paste melted and formed a permanent solder joint between the components and circuit.

2.3 Driving Forces for Lead-Free Solders

2.3.1 Legislation

Previously, Sn-Pb eutectic alloy systems are the principal solder alloys in soldering applications in semiconductor industry. But the high toxicity of lead to health and the environment has raised the attention of relevant organisations and public. In 2002, the European Parliament and EU Council have implemented the Waste Electrical and Electronic Equipment (WEEE) Directive to reduce the amount of hazardous substances from the E&E equipment in landfill disposal (Ramli et al., 2016). Meanwhile, the Restriction of the use of certain Hazardous Substances (RoHS) Directive was also implemented in 2003 with the aim of restricting certain hazardous substances that commonly used in E&E equipment (Shina, 2008). Both of the directives were issued at the same time and are linked in purpose.

2.3.2 Health-Related Aspects

There are nearly 5 million tons of Pb are being used annually on a global basis. However, majority of the usage were not been recycled after used. This arises the awareness of people towards the potential health hazards and toxicity of lead in human and leads to the elimination or reduction the use of Pb in the products. For examples, the presence of lead in body can caused neurological effects like coma and convulsions, renal effects, haematological effects, endocrine effects etc (Goyer, 1996).