



UNIVERSITI PUTRA MALAYSIA

***MORPHOLOGICAL AND MECHANICAL CHARACTERISATION OF
BI-AG ALLOY AS HIGH TEMPERATURE LEAD FREE SOLDER***

MAHDI NAHAVANDI

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**MORPHOLOGICAL AND MECHANICAL CHARACTERISATION OF
BI-AG ALLOY AS HIGH TEMPERATURE LEAD FREE SOLDER**

By

MAHDI NAHAVANDI

**Thesis Submitted to the School of Graduate Studies, Universiti Putra
Malaysia, in Fulfilment of the Requirements for the Degree of Master of
Science**

April 2014

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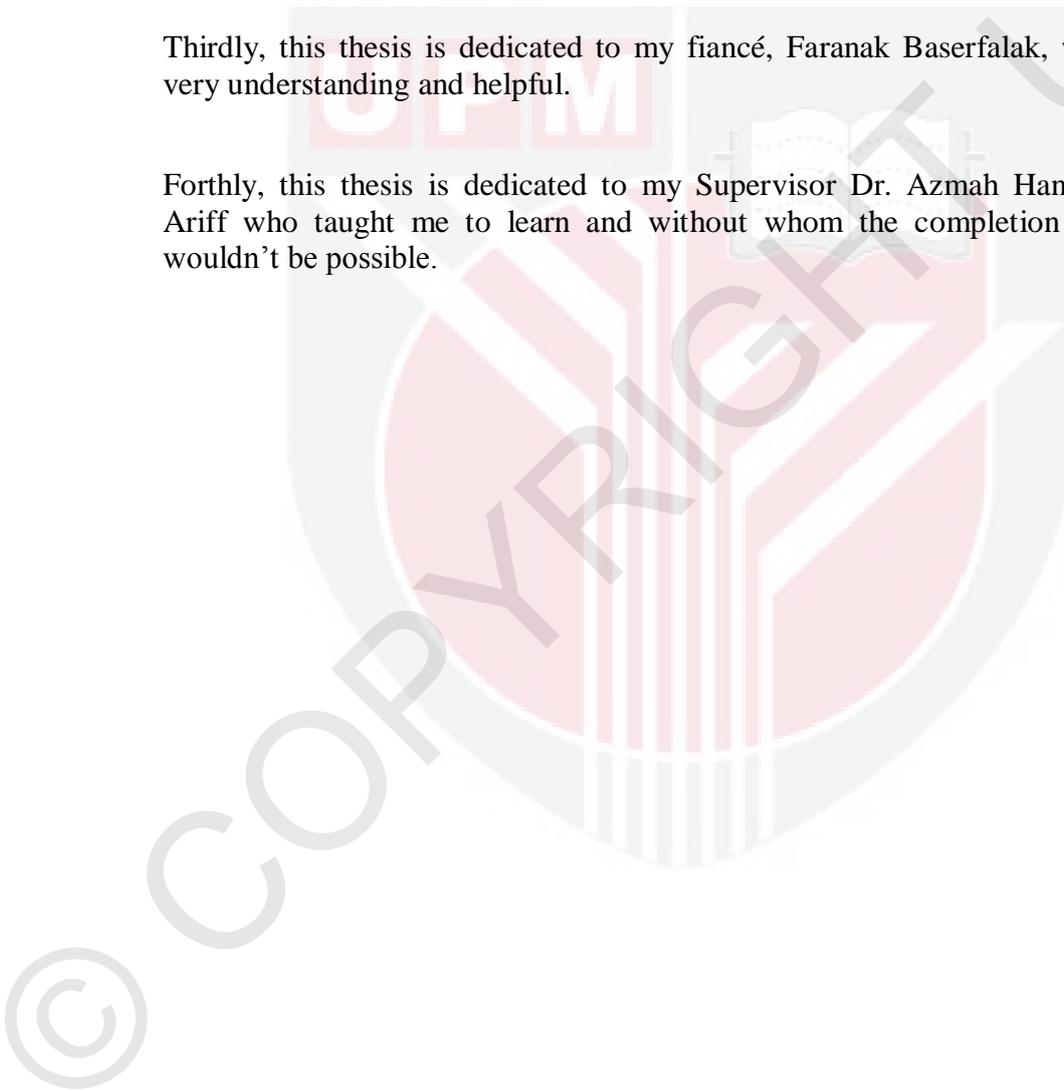
DEDICATION

Firstly, this thesis is dedicated to my beloved parents, Mohammad Ali Nahavandi & Rogayeh Sorayaie, who have always been on my side in spite of the little time I have been able to devote for them especially during these three years. They have never failed to give me moral and financial support especially during my master studies and finishing my thesis.

Secondly, I am dedicating this thesis to my beloved siblings, Mahdiyeh and Naemeh Nahavandi for their endless kindness and supports.

Thirdly, this thesis is dedicated to my fiancé, Faranak Baserfalak, who has been very understanding and helpful.

Forthly, this thesis is dedicated to my Supervisor Dr. Azmah Hanim Mohamed Ariff who taught me to learn and without whom the completion of this work wouldn't be possible.



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master Science.

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April 2014

Chairman: Azmah Hanim Binti Mohamed Ariff, PhD

Faculty: Engineering

In welding and metallurgical processes, solder is used to join two or more metallic surfaces. Today, the use of solder in modern microelectronic technology is ubiquitous. Lead solder has been widely used in the semiconductor industry for a long time. In soldering process, demands for elevated temperature application are increasing and they require large amount of lead in solder alloys like Pb-5Sn. Due to the lead toxicity, an impetus has been provided towards the development of lead-free solders by worldwide environmental legislation that prohibited the use of lead in solders. Despite numerous studies on lead free solders in recent years, only limited number of research are available on high-temperature lead-free alternative solders. Bismuth based alloys, zinc based alloys, and tin based alloys have been introduced as a tailored lead-free alternatives under consideration to substitute Pb-Sn solder alloys. Therefore, this research focused on several candidate alloys (Bi-1.5-2.5-3.5 wt.% Ag) as alternative solders in order to replace the high lead solders. To reach this end, candidates of Bi-Ag alloys with different mass compositions were put in oven at 160°C for 0, 100, 200, 350, and 500 hours. Morphological characterizations such as, grain growth behavior, Cu-rich particles size behavior in solder bulk and wetting angle formed between the solder alloys on copper plate during aging process, were performed by Optical Microscope (OM) and Scanning Electron Microscope (SEM). Area elemental analysis was performed using Energy Dispersive X-ray (EDX). Candidates of Bi-Ag alloy joint's behavior and resistance were investigated using single lap-shear test method by 10 kN universal testing machine. Failed areas were investigated by optical microscope and SEM-EDX. It was observed that wt% of Bi and Ag, and aging time affected the overall results of shear test and isothermal aging process. By increasing percentages of Ag in solder

matrix, the length of Cu-rich particle size and grain boundary grooving thickness increased. Also by increasing percentages of Ag in solder matrix and gaging time, wetting angle decreased. For shear test results, by adding of Ag content in solder matrix, the maximum shear stress and shear strain at maximum shear stress were also increased. The highest maximum shear stress and strain were observed at Bi-3.5 wt.% Ag with the value of 13.355 MPa and 44.136, respectively. Furthermore, the lowest maximum shear stress and strain were observed at Bi-1.5 wt.% Ag with the value of 11.032 MPa and 24.955, respectively.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai
memenuhi keperluan untuk ijazah Master Sains

**PENCIRIAN MORFOLOGI DAN MEKANIKAL ALOI BI-AG SEBAGAI
PATERI BEBAS PLUMBUM SUHU TINGGI**

Oleh

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Dalam proses kimpalan dan metalurgi, pateri digunakan untuk menggabungkan dua atau lebih permukaan logam. Kini, penggunaan pateri dalam teknologi mikroelektronik moden sentiasa ada. Pateri plumbum telah digunakan secara meluas dalam industri semikonduktor sejak dahulu lagi. Dalam proses pematerian, permintaan bagi aplikasi suhu tinggi semakin meningkat dan ianya memerlukan jumlah plumbum yang besar dalam aloi pateri seperti Pb-5Sn. Disebabkan ketoksikan plumbum, dorongan telah diperuntukkan ke arah pembangunan pateri bebas plumbum oleh undang-undang alam sekitar seluruh dunia yang melarang penggunaan plumbum di dalam pateri. Walaupun banyak kajian terhadap pateri bebas plumbum yang dijalankan sejak kebelakangan ini, kajian mengenai pateri alternatif bebas plumbum suhu tinggi adalah terhad. AloI berasaskan bismut, aloI berasaskan zink, dan aloI berasaskan timah telah diperkenalkan sebagai alternatif bebas plumbum disesuaikan dalam pertimbangan untuk menggantikan pateri aloI Pb-Sn. Oleh itu, kajian ini memfokuskan beberapa pilihan aloI (Bi-1.5-2.5-3.5Ag) sebagai pateri alternatif untuk menggantikan pateri plumbum tinggi. Untuk mencapai tujuan ini, pilihan aloI Bi-Ag dengan komposisi berbeza dimasukkan ke dalam ketuhar pada 160°C untuk tempoh 0, 100, 200, 350, and 500 jam. Ciri-ciri dan kajian morfologi seperti perilaku pertumbuhan butiran, perilaku saiz partikel kaya tembaga. Dalam pateri pukal dan sudut pembasahan terbentuk di antara aloI

pateri pada plat tembaga semasa proses penuaan, telah dijalankan menggunakan Mikroskop Optik (OM) dan Mikroskop Elektron Pengimbas (SEM). Analisis unsur kawasan dilakukan menggunakan Penyebaran Tenaga Sinar-X (EDX). Selain itu, perilaku sendi dan rintangan aloi Bi-Ag telah dikaji menggunakan kaedah ujian pusingan ricih tunggal dengan 10 kN mesin uji universal. Tambahan pula, kawasan yang gagal telan dikaji dengan mikroskop optic dan MEP- PTS. Adalah diperhatikan bahawa wt% Bi dan Ag, dan masa penuaan mempengaruhi hasil keseluruhan ujian ricih dan proses penuaan isothermal. Dengan kenaikan peratus Ag di dalam logam pateri, panjang saiz partikel kaya tembaga dan ketebalan belahan sempudan butiran meningkat. Kenaikan pertus Ag dalam matriks pateri dan masa penuaan turut mengurangkan sudut basahan. Untuk keputusan ujikaji ricih, nilai maksimum tekanan ricih dan tegangan ricih turut meningkat dengan pertambahan dungan. Nilai tertinggi yang dicapai oleh maksimum tekanan ricih dan tegangan ricih apabila Bi-3.5wt.%Ag adalah 13.355 Mpa dan 44.136. Manakala, nilai terendah yang dicapai oleh maksimum tekanan ricih dan tegangan ricih apabila Bi-1.5 wt.%a Ag adalah 11.032 MPa dan 24.955.

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I certify that a Thesis Examination Committee has met on 15/4/2014 to conduct the final examination of Mahdi Nahavandi on his thesis entitled "morphological and mechanical characterisation of Bi-Ag alloy as high temperature lead free solder" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science (Materials Engineering).

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LIST OF ABBREVIATIONS

BGA	Ball Grid Array
CNS	Central Nervous System
DBS.P	Pin Plastic Power DIL-Bent-SIL
EDX	Energy Dispersive X-ray spectroscopy
ENIG	Electroless nickel immersion gold
FESEM	Field-emission scanning electron microscopy
FEEPMA	Field-emission electron probe microanalyser
ICs	Internal Circuits
IMC	Intermetallic Compound
ITMA	Institute of Advanced Technology
JEDEC	Joint Electronic Devices Engineering Council
NCMS	National Centre of Manufacturing Science
OM	Optical Microscope
OSP	Organic Solderability preservative
PLCC	Plastic Leaded Chip Carrier
RE	Rare Earth
RMA	Rosin mildly activated
RoHS	Restriction of Hazardous Substances
RPM	Revolution per minute
SEM	Scanning Electron Microscopy
SLI.P	Pin Plastic Power Single-in-Line
T _m	Melting point

UBM	Under Bump Metallization
UTS	Ultimate Tensile Strength
XRD	X-ray diffractometer



CHAPTER 1

INTRODUCTION

1.1 Background of the Research

Solders are generally described as fusible alloys with liquids temperature below 400°C (750°F). Solder is a filler metal with a low melting point. In welding and metallurgical processes, solder is used to join two or more metallic surfaces. In other words, it is using low melting temperature metals to stick to the surfaces to be soldered together. Solder materials are used for many applications, including electronic assemblies, in which solder covers mechanical and physical properties like thermal and electrical. In general, elements which are frequently used in solder alloys are Plumbum ($T_m=328^\circ\text{C}$), Silver ($T_m=961^\circ\text{C}$), Bismuth ($T_m =271.5^\circ\text{C}$), Indium ($T_m =160^\circ\text{C}$), Antimony ($T_m = 630.5^\circ\text{C}$), and Cadmium ($T_m =321.2^\circ\text{C}$) (Palenzona 1971; Yatsenko et al. 1983; Karakaya and Thompson 1987; Karakaya and Thompson 1993; Okamoto 2012). Pb-Sn alloys are widely used as a solder in the electronics industry (Hwang 2004). Recently, there is a great need within the avionics, military, oil exploration, telecommunications, and automotive industries for solders. For these applications, solders perform reliably at higher temperatures and come close to or exceed the melting point of tin-lead eutectic (Dash 2006).

High percentages of Pb in conventional solder alloys (95Pb-5Sn or 90Pb-10Sn) are used for high temperature application such as die attach solders in power semiconductor packaging. However, low percentages of Pb are used for normal consumer electronics such as laptops, cell phones, and electronic toys. Majority of these products, are releasing in landfill within a few months or years because of having short service life. The lead can penetrate into the drinking water and poison humans' health. In July 2006, The European Parliament and Council agreed to the Restriction on the Use of Hazardous Substances in Electrical and Electronic Equipment Directive, which bans the use of lead, or plumbum (Pb). Also, Japan as one of the paramount electronic products producers, required all new electronic products to be lead free solder from January 2005. These directives encourage the development of high-temperature lead-free solders (Hwang 2004).

Selecting an alternative high temperature lead-free solution involves two main properties, mechanical and electrical behavior. A typical lead-free high temperature solder replacement is eutectic Au-20Sn. This alloy is a hard solder with a melting temperature of 280°C which will be within range of applications for high temperature lead free solders (George et al. 2011). Hard solders have higher melting temperature and higher yield stress than Pb-5Sn. However, the cost of gold (Au) and lack of suitable mechanical properties limits its implementation. Other lead-free solutions such as Bi-5Sb have the proper thermodynamic properties, but they lack sufficient mechanical and electrical properties to be considered as a suitable high temperature replacement (Song et al. 2009). The addition of antimony to bismuth increases the strength of the material while increasing its brittleness and resistivity. A number of promising lead-free materials such as Sn-Ag-Cu alloys i.e., have been developed as replacements for the (near-) eutectic Sn-Pb solders in mainstream applications, despite the fact that there is still no 'drop-in' alternative for the traditional Pb-Sn alloy (Živković et al. 2008). Despite extensive studies on lead-free solder alternatives in recent years, direct replacement for the Pb-Sn near-eutectics have not been introduced yet (Evans et al. 2007; Zeng et al. 2012).

1.2 Problem Statement

Current high temperature solders (Pb-5Sn) are used for lots of applications, such as attachment of power semiconductors, flip chip packages, heat resistant vehicles, packages, aerospace, and variety of intrusive procedures are being used in the medicine. Environmental concerns after usage and throwing away are also driving research in this area. The concern about toxicity and health hazards means that leaded solders should be replaced with lead-free solders as soon as possible.

Prohibiting the use of lead containing solders in many industries was applied from 1st of July 2006. Recently, a new alloy system, Bi-Ag, has been considered as the replacement for high Pb solders for high-temperature applications (e.g., 95Pb-5Sn, with a melting range from 308 °C to 312 °C)(Song et al. 2007). Therefore, this research focused on several candidate alloys (Bi-1.5-2.5-3.5 wt.%Ag) as alternative solders in order to replace the high lead solders. To achieve this end, the morphology and mechanical properties of candidate alloys should be investigated under real conditions and these solders must be cautiously applied for high temperature applications step by step.

1.3 Research Objectives

The main objectives of this research are:

1. To investigate the morphology of Bi-Ag (three different weight percentages of Ag 1.5, 2.5, and 3.5) solders on Cu substrates subjected to isothermal aging at 160°C.
2. To evaluate the mechanical and morphological solder joints strength using single lap-shear test method by 10 kN universal testing machine.

1.4 Scope of Study

In this research, candidates of Bi-Ag alloys with different wt.% compositions were put in oven at 160°C at various duration of times. Characteristics and morphological investigations such as grain growth behavior, Cu-rich particles size behavior in solder bulk and wetting angle formed between the solder alloys on copper plate, during aging process, were done by Optical Microscope (OM) and Scanning Electron Microscope (SEM). Area elemental analysis was performed using Energy Dispersive X-ray (EDX). Moreover, candidates of Bi-Ag alloy joint's behavior and resistance were investigated using single lap-shear test method by 10 kN universal testing machine. Furthermore, failed areas were investigated by optical microscope and SEM-EDX.

1.5 Layout of the Thesis

This thesis is primarily divided into five chapters:

Chapter 1 introduces the explanation of background of research, problem statements, research objectives and scope of this research.

Chapter 2 provides a literature review of solder infrastructure and soldering, definition of electronic packaging, lead and leaded solders, health and environmental concerns with lead, high temperature solder, lead free solder materials and their essential properties, brief introduction of Bi-Ag alloys as a tailored candidate for high temperature lead-free solder, bismuth and effects of bismuth in solders, silver and effects of silver in solders, shear test study in solders, and thermal aging study in solders.

Chapter 3 explains in detail the methodology which were done in this study. Three stages of material development and making solder rod, samples for isothermal aging process and analysis, single-lap shear joint sample preparation, performing shear test and microstructural analysis, are explained in this chapter.

Chapter 4 explains the results, discussions and analyses on the experimental data of the effect of isothermal aging process on microstructural changes of Bi-Ag solder alloys. Furthermore, the effect of Ag on the mechanical properties and failed mode of Bi-Ag solder compositions which were investigated by single-lap shear test method, visual, optical microscope and SEM-EDX observations, are described in detail in this chapter.

Chapter 5 concludes the main findings in relations to the objectives of the research. Also this chapter gives some suggestions and recommendations for future research on the development of Bi-Ag solder as a high temperature lead-free solder alloys.

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