



**Development of Lead-Free Sn-0.7Cu-Si₃N₄
composite solders**

by

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LIST OF ABBREVIATIONS

PM	Powder Metallurgy
SAC	Sn-Ag-Cu
CTE	Coefficient of Thermal Expansion
IMC	Intermetallic Compound
MWCNT	Mulwi Walled Carbon Nano Tube
SWCNT	Single Walled Carbon Nano Tube
CNT	Carbon Nano Tube
XRD	X-Ray Diffraction
DSC	Differential Scanning Calorimetry
SEM	Scanning Electron Microscope
MMC	Metal Matrix Composite
RPM	Rotation per Minute

LIST OF SYMBOLS

γ_{LS}	Force between solder and substrate
γ_{LV}	Interfacial tension between substrate and the atmosphere
γ_{SV}	Wetting force
N_0	Optimal rotational speed
d	Diameter
vol. %	Volume percentage
wt. %	Weight percentage
ρ_c	Density of composite
ρ_f	Density of fibre
ρ_m	Density of matrix
V_m	Volume fraction of matrix
V_f	Volume fraction of fibre
P	Porosity
th	Theoretical density
exp	Experimental density

σ_H	Yield Stress
σ_O	Friction Stress
D	Grain size
δ_t	Mean thickness of the IMC layer at aging time of t
δ_o	Initial thickness of the IMC layer before being aged
k	Constant for the growth rate of the IMC layer
t	Aging time

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Pembangunan Pateri Komposit Bebas Plumbum Sn-0.7Cu-Si₃N₄

ABSTRAK

Pateri berplumbum digunakan dengan meluas sebelum sains membuktikan bahawa plumbum adalah salah satu dari bahan-bahan yang berbahaya yang boleh membahayakan kesihatan dan alam sekitar. Disebabkan larangan penggunaan pateri berplumbum sebagai penyambung, pelbagai pateri bebas plumbum telah diperkenalkan dan terdapat di antaranya ketika ini digunakan secara meluas. Namun tiada satu pun di antaranya yang dapat menandingi sifat-sifat pateri berplumbum menyebabkan kajian mengenai pateri bebas plumbum masih berterusan. Di dalam projek ini, satu pateri komposit bebas plumbum telah dicipta dan dibangunkan dengan menambahkan pelbagai jumlah Si₃N₄ kepada pateri Sn-0.7Cu melalui kaedah metalurgi serbuk yang terdiri dari pencampuran, pemadatan dan pensinteran. Pateri komposit digunakan bagi menambak sifat-sifat pateri konvensional. Projek ini terbahagi kepada 2 fasa, di mana Fasa 1 adalah untuk mengkaji pencampuran, pemadatan dan pensinteran yang optimum, manakala Fasa 2 pula pateri komposit akan diuji, dianalisis dan dibandingkan dengan pateri monolit. Selesaiannya kedua-dua fasa ini, jumlah penambahan Si₃N₄ yang terbaik ke atas Sn-0.7Cu akan disarankan. Umumnya, pateri komposit Sn-0.7Cu-Si₃N₄ menunjukkan peningkatan berbanding pateri monolit dan akhirnya Sn-0.7Cu-0.5Si₃N₄ dipilih sebagai pateri komposit terbaik.

Development of Lead-Free Sn-0.7Cu-Si₃N₄ Composite Solders

ABSTRACT

Lead based solder have been widely used before science have proven lead as one of the hazardous substances which can harm the environment and human health. With the banning usage of lead based solder as interconnect, various lead-free solders have been introduced and some of them are currently being widely used. However, none of them still can surpass the properties of a lead based solder, which keeps the researches on lead-free solder still going on and on. In this project, a new lead-free composite solder was developed by adding various amount of Si₃N₄ into Sn-0.7Cu solder via powder metallurgy route which consists of mixing compaction and sintering. Composite solder was used in order to enhance the properties of the conventional solder. The project was divided into two phases, where at Phase 1, the optimization of mixing, compaction and sintering were studied while at Phase 2, the composite solder were tested, analyzed and compared with the monolithic solder. Upon completion of both phases, the best amount of Si₃N₄ was added into Sn-0.7Cu will be proposed. Generally, the Sn-0.7Cu-Si₃N₄ composite solder showed improvement compared to the monolithic solder and it was finally decided that Sn-0.7Cu-0.5Si₃N₄ was the most preferable composite solder.

CHAPTER 1

INTRODUCTION

Solder material have an important role in the solder joint reliability. They offer electrical, mechanical and thermal continuity in an electronic assembly. Previously, lead based solders have been widely used in electric and electronic industry, especially in assembling electronic circuits as it is known that lead have good mechanical properties, good wettability, low cost with low melting point. Due to great and fast advancement of electric and electronic technology, most of the products of electric and electronic industry are considered disposable whenever there is an introduction of a newer product. The outdated products that contain lead will then end up in the landfills. Recycling lead contain products are not a good option as it is not cost effective with most of the circuit boards are too complex to be disassemble (Mohd Salleh et al., 2012).

Lead can leach from the landfills into water sources, contaminating it and thus being a potential hazard to human health as lead is a hazardous element due to its toxicity. Realizing this, major countries such as the European Union (EU) have started taking action by banning the usage of lead in electric and electronic products. The EU has adopted two directives which are Waste of Electrical and Electronic Equipment (WEEE) and the Restriction of Hazardous Substances (RoHS). The WEEE required that lead to be removed from any end-of-life electrical or electronic components while the RoHS banning the usage of lead on all electric and electronic components manufactured after July 1, 2006 (Ma & Suhling, 2009).

As a result, various researches on lead-free solders have been made by researcher all over the world. Several lead-free solders have been developed and introduced to the industry but none of them were better than lead based solders. One of the best replacement for Sn-Pb alloys are Sn-0.7Cu alloys as this solder wettability are good and the cost for its production is low. However, this solder has poor mechanical properties. The solder alloy is relatively weak in tensile strength compared to other commonly used lead-free solder alloys such as Sn-Ag-Cu and Sn-Ag (Zhong & Gupta, 2008). It is the idea to enhance the strength of the Sn-0.7Cu solder alloy by incorporating Silicon Nitride (Si_3N_4) as reinforcement.

Si_3N_4 is well known for having a good combination of mechanical, thermal and thermo-mechanical properties. It has high strength at high temperatures, good thermal stress resistance with low coefficient of thermal expansion. It is also relatively good resistance to oxidation comparing with other high-temperature structural materials and has low density which may offer components of light weight (Ziegler et al., 1987). Combining metal with ceramic homogenously resulted a material with high fracture toughness (Wanbao et al., 2005).

There are several methods to produce a composite of solder alloys. There are methods of mechanical alloying, casting and to date is the method of fabricating composite solder alloy by following the powder metallurgy route. Powder metallurgy (PM) is a study of processing metal powders into a useful engineering component. PM is able to fabricate high quality parts with complex shapes, close to its tolerance with near net shape. This technique is also economical as it produced low scrap with low energy consumption and it needs no skilled worker to operate the machines. All of these advantages make PM as one of the best technique in fabricating composites (German, 1994).

There are several researches (Alam & Gupta, 2009; Alam et al., 2009; Babaghorbani et al., 2009; Guo, 2007; Gupta, 2008; Kangooie et al., 2009; Kumar et al., 2008; Kumar et al. 2006; Nai et al., 2010; 2009; 2006; Shen & Chan, 2009; Zhong & Gupta, 2008) that have done composite solder but none of them have explored on Sn-0.7Cu base solder with Si_3N_4 as reinforcement (Sn-0.7Cu- Si_3N_4). Literature studies have shown that solder properties can be improved by adding ceramic particulates into Sn-0.7Cu solder using PM method. Gupta (2008) has proved that by adding nano sized Al_2O_3 into the monolithic Sn-0.7Cu solder fabricated via PM technique, the solder mechanical properties were improved.

1.1 Problem Statement

Industries are moving towards into producing green products which means that the products contain no materials that are listed in the RoHS directive. The directive restricted the use of any six hazardous substances in electric and electronic manufacturing. The six restricted substances are Lead (Pb), Mercury (Hg), Cadmium (Cd), Hexavalent Chromium (Cr^{6+}), Polybrominated Biphenyls (PBB) and Polybrominated Diphenyl Ether (PBDE). Lead has been proved as a toxic substance which can endanger the environment and the human health. Recycling all lead contain products are not practical due to vast advancements in electronic technology and recycling program involve a very high cost which is undesirable. In 1998, it has been reported that less than 2% of the computers produced were recycled. Other than the EU, countries such as Japan, China, South Korea and The United States of America (USA) are also moving towards producing lead-free products. In USA, both industry and academic institutes are encouraged to do research in developing a lead-free assembly

processes (Ma & Suhling, 2009). Countries in the world are actively moving towards banning the usage of lead-based solder in every consumer products.

Currently, there are several types of lead-free solders used in industry and one of them is Sn-0.7Cu. The solder melts at 227°C with relatively good wettability properties. The only downside of this solder is that its mechanical properties is lower than other commonly used lead-free solder such as Sn-Ag-Cu (SAC) or Sn-Ag types of solder. Due to this, many researchers were not interested in studying the Sn-0.7Cu solders. However, there are several researches that have been done in order to improve the mechanical properties of the Sn-0.7Cu solder. Current literature study related to Sn-0.7Cu solder fabricated via PM route using ceramic as reinforcement were quite limited. Gupta (2008), Zhong & Gupta (2008) and Nai et al. (2010) decided to add Al₂O₃ and ZrO₂ as reinforcement into the Sn-0.7Cu solder which significantly have improved the mechanical properties of the solder when compared with the monolithic solder, but result of microhardness test from a study conducted by Nai et al. (2010) has shown that the value of the microhardness test for composite solder of Sn-0.7Cu reinforced with 1.5% Al₂O₃ is lower than the unreinforced Sn-3.5Ag solder. This showed that even though the hardness of composite solder of Sn-0.7Cu-1.5%Al₂O₃ is better than the monolithic Sn-0.7Cu solder but it still cannot surpass the monolithic Sn-3.5Ag. It is hoped that with this study, the properties of the Sn-0.7Cu solder can further be improved by adding Si₃N₄ as reinforcement.

There were several other type of ceramic such as Y₂O₃, TiB₂, SnO₂ and CNTs added purposely as reinforcement in solder fabrication by other researchers but none of them were interested in reinforcing the Sn-0.7Cu solder type. They were more focused on reinforcing the SAC types of solder, which currently are the most commonly used solder in industry. All of them managed to improve the mechanical properties of the

SAC solder greatly by introducing ceramic as reinforcement, but SAC composite solder contains Silver, Ag which is relatively expensive and the price of it is increasing from time to time as Silver were also used in making jewelry, kept for investment and making coins.

There a so little focus on enhancing Sn-0.7Cu solder due to its undesirable behavior of mechanical properties, it is hoped that by adding Si_3N_4 as reinforcement, the mechanical properties of the solder can be improved vastly. There is currently no researcher were interested on exploring the possibilities of enhancing the properties of Sn-0.7Cu solder with Si_3N_4 as reinforcement. The reinforcement was chosen due to Si_3N_4 is well known for having a good combination of mechanical and thermal properties (Ziegler et al., 1987). Combining metal with ceramic homogenously will also result a material with high fracture toughness (Wanbao et al., 2005). PM method was chosen to fabricate the composite solder as it is already proven that composite solder can be fabricated by following PM route. Studies have also revealed that it is easier to control the grain growth of the composite in PM method which resulting a composite with improved mechanical properties and solderability (Mohd Salleh et al., 2013).

1.2 Objectives

- i. To fabricate Sn-0.7Cu-Si₃N₄ composite solder via Powder Metallurgy (PM) route.
- ii. To determine the optimum parameter of mixing time, compaction pressure and sintering temperature for synthesizing Sn-0.7Cu-Si₃N₄ composite solder.
- iii. To characterize the properties of Sn-0.7Cu-Si₃N₄ composite solder.

1.3 Scope of Study

For this study, it was separated into two phases. Phase 1 which was sample fabrication and process optimization while in Phase 2 was for testing and analyzing. In Phase 1, the composite solder of Sn-0.7Cu-Si₃N₄ was fabricated via PM route which consists of mixing, compaction and sintering. For optimization purposes, the mixing speed was kept constant at 200 rotations per minute (RPM) while the sintering time was kept at 2 hour. All other parameter such as mixing time, compaction pressure and sintering temperature was varied during the optimization work. With the completion of Phase 1, samples of composite solder were prepared according to the parameter acquired from optimization process for test and analyze purposes. Si₃N₄ was used as reinforcement, added to the Sn-0.7Cu base solder with the weight percentage of reinforcement added are focused only at 0.25%, 0.5%, 1.0% and 1.5%. In Phase 2, all the reinforced composite solder was tested, analyzed and compared with the monolithic Sn-0.7Cu solder fabricated via PM route. Figure 1.1 shows the completed project flow chart for better understanding and was discussed later in chapter three.

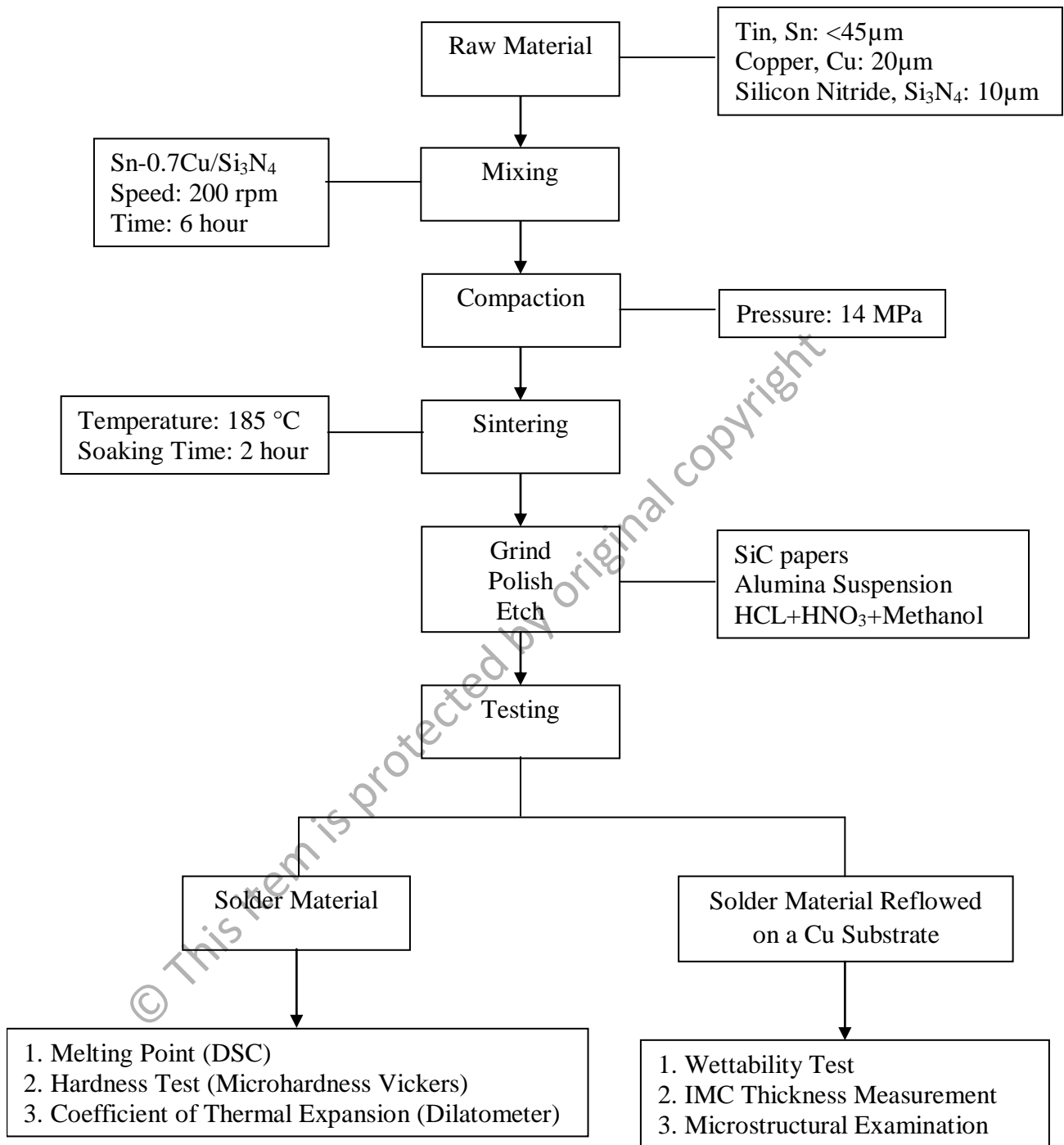


Figure 1.1: The complete flow chart of the project.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Soldering is a metallurgical joining method that uses filler metal, which is the solder itself that will melt at any point of below 425 °C (Abteew & Selvaduray, 2000). Solder have an important role in ensuring the reliability of the solder joint since they provide electrical, mechanical and thermal continuity in an electronic assembly. Lead based solder have been widely used in electronic industry, especially in assembling electronic circuits as these type of solder have a superb solderability and reliability. Due to great and fast advancement of electronic technology, most of their products are considered disposable when there is introduction of a newer product. Recycling the lead contain product is not a good option as it is not cost effective with most circuit boards are too complex to dissemble. These outdated products that contain lead will be thrown away and ended up in landfills. Lead can leach from the landfills into water sources, which were used to supply water for our daily needs. Lead is toxic and is a potential hazard to human health. Workers working in an electronic factory which especially involved wave soldering process are more prone to possible danger of lead compared to hand soldering or tinning operations. Studies have shown that at normal soldering temperatures, lead is pretty stable and posed lower threat (Abteew & Selvaduray, 2000). Wave soldering, which is fully automated, is the most common method of soldering printed wiring boards that have holes through the plate (Manko, 2001). A pump located at the bottom of the tank containing molten solder will create a wave of solder that