



**DEVELOPMENT OF A ROBUST Sn-Cu BASED LEAD-FREE SOLDER PASTE**

by

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## LIST OF ABBREVIATIONS

Ag	Argentum
APR	Advanced Notice of Proposal Rule
Bi	Bismuth
BGA	Ball Grid Array
Cu	Copper
CH <sub>3</sub> OH	Methanol
DSC	Differential Scanning Calorimetry
EDS	Energy Dispersive Spectroscopy
EDX	Energy Dispersive X-ray
EPA	Environment Protection Agency
EU	Europe Union
FCC	Face Centre Cubic
HCL	Hydrochloric Acid
HNO <sub>3</sub>	Nitric Acid
IMC	Intermetallic Compound
In	Indium
NEMI	National Electronic Manufacturing Initiative
OSP	Organic Solderability Preservative
Pb	Lead
PCB	Printed Circuit Board
PWB	Printed Wiring Board
RoSH	Restriction of Hazardous Substance
SLID	Solid Liquid Interdiffusion
SMT	Surface Mount Technology
Sn	Tin
TiO <sub>2</sub>	Titanium Oxide
TLPS	Transient Liquid Phase Soldering
TSPA	Toxic Substance Control Act
UV	Ultraviolet
WEEE	Waste Electronic and Electrical Equipment
XRD	X-ray Diffraction
Zn	Zinc

## LIST OF SYMBOLS

A	Area
F	Fahrenheit
h	Hour
k	Growth rate
L	Length
$n$	Time Exponent
Q	Activation Energy
R	Universal Gas Constant
$T_m$	Melting Temperature

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## Pembangunan Teguh Pes Pateri Bebas Plumbum Sn-Cu

### ABSTRAK

Semasa perkhidmatan dan/atau penyimpanan, sambungan pateri sering terdedah kepada keadaan operasi persekitaran yang ekstrim seperti suhu, beban mekanikal, dan arus elektrik. Keadaan ini meningkatkan lagi permintaan bahan pateri yang mempunyai prestasi yang tinggi dalam kestabilan fizikal, mekanikal, elektrik, dan terma. Sehubungan itu, penyelidikan ini bermotivasi untuk membangunkan pes pateri Sn-Cu untuk meningkatkan keteguhan pateri melalui pendekatan pengalioian mikro, komposit dan pempaterian fasa cecair fana (TLPS). Kajian ini juga bertujuan untuk mengkaji sifat-sifat terma, fasa yang wujud, kebolehpaterian, evolusi mikrostruktur dan juga kekuatan ricih pes pateri baru berasaskan Sn-Cu yang teguh. Kestabilan terma setiap pes pateri dikaji dengan menentukan kinetik pertumbuhan sebatian antara logam (IMC) semasa proses penuaan sesuhu. Penuaan sesuhu dijalankan selama 24, 240 dan 480 jam pada suhu 75, 125, dan 150 °C. Pes pateri teguh disintesis dengan menggunakan Sn-0.7Cu (SC), Sn-0.7Cu-0.05Ni (SCN), Sn-0.7Cu-0.05Ni-1TiO<sub>2</sub> (SCNT) dan Sn-10Cu (SC10). Hasil kajian mendapati pengurangan sebanyak 0.81-5.91 °C dalam suhu penyejukan pes pateri dengan penambahan elemen ketiga; TiO<sub>2</sub>, Ni dan 10Cu. Selain itu, kajian juga menunjukkan terdapat penambahbaikan bagi sudut pembasahan di mana pengurangan sudut pembasahan sebanyak 1.3 °, 14.9 °, dan 9.5 ° untuk pes pateri SCN, SCNT dan SC10 masing-masing. Penambahan Ni dan TiO<sub>2</sub> membantu dalam menjadikan mikrostruktur lebih halus yang mana telah mempertingkatkan sifat mekanikal. Tambahan pula, pembentukan IMC bagi pes pateri yang diperkuat dengan TiO<sub>2</sub> telah direncatkan sebanyak 13.9 %. Kadar pertumbuhan terendah ialah SCNT (0.280, 1.390 dan 2.800 ms<sup>-1</sup> pada suhu penuaan 75, 125 dan 150 °C) dan pateri SCNT juga memaparkan tenaga pengaktifan tertinggi iaitu 37.35 kJmol<sup>-1</sup> berbanding bahan pateri yang lain. Peningkatan ketebalan IMC antara muka berlaku berkadar langsung dengan pemanjangan masa penuaan menyebabkan berlaku penurunan kekuatan ricih untuk semua sambungan pateri. Walau bagaimanapun, kekuatan ricih yang lebih tinggi diperhatikan dalam pes pateri pempaterian SC10 TLPS. Secara keseluruhannya, ketebalan IMC yang nipis, mikrostruktur yang lebih halus, dan kekuatan ricih yang tinggi menjadikan komposit SCNT pes pateri sebagai sambungan pateri yang berpotensi untuk digunakan dalam sambungan elektronik yang biasa. Tambahan pula, SC10 TLPS juga boleh dijadikan calon pengganti kepada aloi pateri untuk sambungan elektronik berkuasa tinggi.

## Development of a Robust Sn-Cu Based Lead-free Solder Paste

### ABSTRACT

During services and/or storage, solder joint is frequently exposed to operational conditions such as temperature, mechanical load, and electrical current. These conditions increase the demand for solder material which has high performance value in physical, mechanical, electrical and thermal stability. Thus, this research was motivated to develop Sn-Cu solder paste for robust solder joint through micro-alloying, composite and transient liquid phase soldering (TLPS) approaches. The aims of this study are to investigate the thermal properties, the phases that exist, the solderability, the microstructure evolution and also the shear strength of the new robust Sn-Cu based solder paste. The thermal stability of each solder paste has been investigated by determining the intermetallic compound (IMC) growth kinetic during isothermal aging. Isothermal aging was conducted for 24, 240 and 480 hours at a temperature of 75, 125, and 150 °C respectively. The robust solder paste was synthesized by using Sn-0.7Cu (SC), Sn-0.7Cu-0.05Ni (SCN), Sn-0.7Cu-0.05Ni-1TiO<sub>2</sub> (SCNT) and Sn-10Cu (SC10) TLPS bonding system. Findings reveal the reduction of about 1.5 °C - 33.5 °C in undercooling of solder paste with third element addition; Ni, TiO<sub>2</sub>, and 10Cu. Result also reveals the improvement in contact angle for about 1.3 °, 14.9 °, and 9.5 ° for SCN, SCNT and SC10 solder respectively. The addition of Ni and TiO<sub>2</sub> helps in refining the microstructure which had improved the mechanical properties. Furthermore, the IMC formation for TiO<sub>2</sub> reinforced solder paste has been suppressed for 13.9 %. The lowest growth rate was presented by SCNT (0.280, 1.390 and 2.800 ms<sup>-1</sup> at aging temperature 75, 125 and 150 °C respectively) and the SCNT solder also displays the highest activation energy which was 37.35 kJmol<sup>-1</sup> compared to the other solders. The thickening of interfacial IMCs thickness occurred with prolong aging time has caused a decreasing in shear strength for all solder joints. Nevertheless, the highest strength was observed in SC10 TLPS. Overall, owing to excellent in solderability, thin IMC thickness, finer microstructure, and high shear strength have proven the SCNT solder paste composite a potential solder interconnect to be applied in typical electronic assemblies. In addition, SC10 TLPS could be established as a promising candidate for TLPS solder alloy for high power electronic assemblies.

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# CHAPTER 1 : INTRODUCTION

## 1.1 Research Background

Restriction on the use of lead (Pb) containing solder paste in surface mount assemblies has promoted the development of lead-free solder paste. The Sn-based lead-free solder pastes such as tin silver (Sn-Ag), tin copper (Sn-Cu), and tin silver copper (Sn-Ag-Cu) have been identified to replace Pb containing solder in electronic assemblies (Tsao, 2011). In the electronic packaging industries, solder paste was used as primarily an interconnect material for surface mount assemblies. As the joining materials, solders paste to be used in electronic industries should provide necessary electrical, mechanical, and thermal continuity (Amin et al., 2014). Therefore, the reliability and quality of solder paste are crucial to ensure proper functioning of the solder joint during surface mount assemblies.

Tin-0.7 Copper (Sn-0.7Cu) solder paste is used as a soldering material to replace lead (Pb) containing solder due to its good physical properties and it is also less expensive compared to the other lead-free solder (Freitas et al., 2014). However, challenges were encountered when Sn-0.7Cu is used as an interconnect material. Researchers have identified the mechanical strength of Sn-0.7Cu which is relatively low compared to tin-lead (Sn-Pb) and Sn-Ag-Cu, and may lead to reliability problem (Fathian et al., 2017). Apart from that, the solderability of Sn-0.7Cu solder was poor (El-Daly & Hammad, 2011). There is a suggested way to further improve the performance of Sn-0.7Cu solder. Several approaches was identified for the development of a robust lead-free solder as depicted in Figure 1.1. The micro-alloying elements such as nickel (Ni), rare earths, zinc (Zn), cobalt (Co), gallium (Ga), indium (In), bismuth (Bi) and secondary particles were