DEVELOPMENT OF Sn-Cu FILLED ACTIVATED CARBON COMPOSITE SOLDER VIA POWDER METALLURGY TECHNIQUE

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by

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LIST OF ABBREVIATIONS

Sn	Tin
Pb	Lead
Ag	Silver
RoHS	Restriction of Hazardous Substance
WEEE	Waste Electrical and Electronic Equipment Directive
Hg	Mercury
Cd	Cadmium
Cr6+	Hexavalent Chromium
PBB	Polybrominated Biphenyls
PBDE	Polybrominated Diphenyl Ether
Zn	Zink
Bi	Bismuth
Sb	Antimony
TiO_2	Titanium Dioxide
Si_3Ni_4	Silicon Nitride
Al_2O_3	Aluminum Oxide
AC	Activated Carbon
PM	Powder Metallurgy
DOE	Design of Experiment
DSC	Differential Scanning Calorimetry
XRD	X-ray Diffraction
OM	Optical Microscope

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SEM	Scanning Electron Microscope
EDX	Energy Dispersive X-ray
IMCs	Intermetallic Compounds
α-Sn	Gray Tin
β-Sn	White Tin
In	Indium
Cu	Copper
NEMI	National Electronics Manufacturing Initiative
PCB	Printed Circuit Board
ISO	International Standard Organization
Fe_2O_3	Iron (III) Oxide
ZrO_2	Zirconium Oxide
SiC	Silicon Carbide
CNTs	Carbon Nanotubes
NC	No Clean
M	Malaysia
OPS	Oxide Polishing Suspension
HNO_3	Nitric Acid
HCl	Hydrochloric Acid
Ni	Nitrogen
SMT	Surface Mount Technology
FR-4	Flame Resist-4
C	Carbon

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LIST OF SYMBOLS

γ	Surface Tension of wettability
θ	Contact Angle
V	Volume
r	Radius
h	Height
ρ	Density
m	Weight
t	Thickness
A	Area
L	Length
C	Solubility
T	Temperature
Γ	Surface tension of intermetallics compound
γ	Fractional porosity of sintered sample
x	Mass fraction
R	Resistance
ρ	Resistivity
s	Probe tips spacing
I	Electric current

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Penghasilan Pateri Komposit Sn-Cu terisi Karbon Teraktif Melalui Teknik Kaji Logam Serbuk

ABSTRAK

Revolusi dalam perkakasan elektronik di mana bahagian komponen digunakan semakin kecil telah membuatkan teknologi pateri menjadi sebahagian penting di dunia. Aloi bertakat lebur yang rendah harus mempunyai beberapa sifat unik untuk memastikan kebolehharapan dalam pemasangan elektronik yang membolehkan sambungan untuk berfungsi lebih baik. Pateri komposit berasaskan Sn-0.7Cu telah berjaya dihasilkan melalui teknik kaji logam serbuk (PM) yang terdiri daripada proses pencampuran, pemadatan dan pensinteran. Komposisi karbon teraktif (AC) telah dipelbagaikan kepada 0, 0.05, 0.1, 0.15 and 0.2 wt% digunakan sebagai pengisi dalam pateri bebas plumbum. Parameter teknik PM seperti masa pencampuran, beban pemadatan dan masa pensinteran telah dipelbagai dan pengoptimuman telah dilakukan sebelum proses penghasilan pateri komposit. Seterusnya, pateri bebas plumbum kemudiannya diperhadapkan kepada ujian mekanikal, fizikal dan elektrik. Dalam kajian ini, masa pencampuran, beban pemadatan dan masa pensinteran optimum yang terpilih adalah 1 jam, 390 MPa dan 141 saat, masing-masing. Mikrostruktur pateri pukal selepas pemanasan mendedahkan penambahbaikkan yang ketara melalui penambahan zarah AC dalam kuantiti sedikit terhadap Sn-0.7Cu. Zarah AC telah tersebar secara seragam sepanjang sempadan ira β-Sn. Hasil kajian telah menunjukkan bahawa suhu takat lebur telah menurun sedikit dengan penambahan zarah AC, namun begitu, ianya masih didalam julat yang boleh diterima. Penambahan zarah AC telah menaikkan keberintangan elektrik pateri Sn-0.7Cu. Kebolehbasahan pateri komposit telah dipertingkat dimana sudut sentuh terbaik merupakan 24.6⁰ bagi penambahan 0.2 wt% zarah AC. Semantara itu, sifat mekanikal khususnya mikrokekerasan dan kekuatan ricih telah mengalami penambahabaikkan dimana dengan penambahan 0.1 wt% zarah AC telah menghasilkan keputusan terbaik iaitu 12.14 Hv dan 13.19 MPa masing-masing. Tambahan lagi, kekasaran pada permukaan patah telah menaik dengan penambahan zarah AC sehingga 0.15 wt%. Ketebalan lapisan sebatian antara logam Cu_6Sn_5 pada permukaan penyambungan pateri telah menaik kepada 2.16 µm dengan penambahan 0.1 wt% zarah AC. Keseluruhannya, penambahan zarah AC sebagai pengisi menguat terhadap pateri bebas plumbum Sn-0.7Cu menghasilkan penambahbaikkan dari segi mekanikal dan fizikal pateri komposit tersebut.

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Development of Sn-Cu Filled Activated Carbon Composite Solder Via Powder Metallurgy Technique

ABSTRACT

The revolution of electronic applications which have been assembled in smaller parts, lighter and more functional, causes the solder to become crucial over the worlds. These classes of low melting point alloys must provide a unique set properties to ensure the reliability of the electronic assemblies also allowing the joints to become more functional. A composite Sn-0.7Cu based solder was successfully fabricated via powder metallurgy (PM) technique which consist of mixing, compacting and sintering processes. Varying amount of activated carbon (AC); 0, 0.05, 0.1, 0.15 and 0.2 wt% were used as reinforcement to obtain a new lead-free composite solder. The parameters of PM technique which are mixing time, compacting loads and sintering time were varied and these parameters were optimized prior to composite solder synthesis. Subsequently, the lead-free composite solder were then subjected to physical mechanical and electrical tests. In this study, the best mixing time, compacting load and sintering time selected were 1h, 390 MPa and 141 s, respectively. Microstructure of the bulk solder after reflow process exposed significant improvements through addition of a small amount of AC particles into Sn-0.7Cu which had refined the microstructure of Sn-0.7Cu composite solder. The various percentages of AC particles were uniformly distributed along the β-Sn grain boundaries. The results revealed that melting temperature was slightly decreased with increasing the addition of AC particles; however still in acceptable range. The addition of AC particles slightly increased the electrical resistivity of Sn-0.7Cu solder. The wettability of the composite solder was improved where the best contact angle was 24.6° for 0.2 wt% of AC particles. Meanwhile, the mechanical properties in terms of microhardness and shear strength experienced enhancements with addition of AC particles reinforcement where the 0.1 wt% of AC particles shows the best results among other percentages which was 12.14 Hv and 13.19 MPa, respectively. Furthermore, the roughness of the fracture surface increased with the increasing number of amounts of AC particles up to 0.15 wt%. The thickness of Cu_6Sn_5 IMC layer at the interface of the solder joint decreased to 2.16 µm with the addition of 0.1 wt% of AC particles. Overall, the addition of AC particles as reinforcement into Sn-0.7Cu lead-free solder based exhibit the enhancement of physical and mechanical properties compared with the solder matrix.

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CHAPTER 1

INTRODUCTION

1.1 Background of Studies

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Nowadays, solder remain among the most important joining materials in electronic assembly. A revolution in the electronic devices such as capacitors, transistors, diodes, resistors and integrated circuits was assembled in smaller parts, lighter and more functional, causes the study in solder technology becomes essential worldwide. Therefore, the solder must provide a unique set of properties to ensure cost-effective production of reliable electronic assemblies since solder serves both mechanical and electrical functionality to the connection of electronic components. Nowadays, the most widely used solders for electronic assemblies are low temperature near-eutectic SnPb alloys such as 60Sn40Pb, 63Sn37Pb and Ag-bearing 62Sn36Pb2Ag (Evans, 2007a). These alloys are used in applications ranging from consumer products to space communications systems and have been essential to the worldwide electronics industry.

However, based on legal foundation from Restriction of Hazardous Substance (RoHS) that took effect on 1 July 2006, which also closely linked with the Waste Electrical and Electronic Equipment Directive (WEEE) were approved the directive restriction of use of six hazardous materials in the manufacture of various types of electrical and electronic equipment (Restriction of Hazardous, 2010). The six hazardous materials are Lead (Pb), Mercury (Hg), Cadmium (Cd), Hexavalent Chromium ($Cr6^{+}$), Polybrominated biphenyls (PBB), and Polybrominated diphenyl ether (PBDE). Understanding the effects of these materials awaken many countries to take action in banning the usage of lead on all electrical and electronics components. Thus, the developments of lead-free solders have become an urgent affair nowadays.

Recently, lead-free solders had received considerable attention from the field of electrical and electronic applications. There are assortment of candidates in order to replace high-lead solder which are Sn-Cu, Sn-Ag-Cu, Sn-Ag, Sn-Zn, and Bi-Sn. Lead-free solders have been used in particularly step soldering technology, flip–chips connection, solder ball connections and the bonding of semiconductor devices onto substrates. Unfortunately, the deficiency among these lead-free solder in fulfill the high-functional requirement and the miniaturization of electronic components in advance solder technology can no longer guarantee the reliability of the solder joints. Thus, to enhance the reliability of the solder interconnects; new solder materials with combinations of good electrical, mechanical and thermal properties have to be produced (Lee & Lee, 2007; Wu et al., 2004; Han et al., 2012; Han et al., 2010a).

In order to develop the new solder interconnects, a method which is composite solder was developed, where the solder matrix was reinforced by particulate fillers. The existence of reinforcements in the solder matrix provides greater reliability since the reinforcing particles was believed not to only suppress the grain boundaries sliding, intermetallic compound formation or grain growth, but also may perhaps reorganize stress uniformly (Lee & Lee, 2006). Lead-free composite solder have shown better solderability, physical and mechanical properties, also good in electrical and thermal properties too which has been published by previous researchers (Nai et al., 2008; Han et al., 2010b; Tai et al., 2005; Tai et al., 2010).

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Lately, the most typical technique used in fabricating the solder was casting technique, which was the common technique utilized in solder industries (Arenas et al, 2006; El-Daly et al., 2013a; Yu & Wang, 2008). Besides of casting technique, powder metallurgy technique is another alternative to fabricate composite solder. The powder metallurgy technique is now recognized as a competitive technology and an alternative to casting or conventional metal forming. Powder metallurgy has been defined as the art and science of producing fine metal powder and objects finished or semi-finished from individual, mixed or alloyed metal powders with or without the presence of non-metallic constituent (Angelo & Subramanian, 2008). Powder metallurgy was applied to make the metal powder which added with reinforcement form into valuable engineering component. High quality parts with complex shapes can be fabricated using powder metallurgy technique. Powder metallurgy also low in cost because it was produced low scrap with low energy consumption and there is no needs skilled worker. These advantages show the powder metallurgy as one of the best technique used in synthesizing the composite materials (German, 1994). Production of powder metallurgy parts involves in mixing the powder materials, compaction of the mixture powder and finally sintering the compacted billet.

Sn-0.7Cu solder was one of typical lead-free solder that been suggested for replacement the Sn-Pb solder. Sn-0.7Cu solder was low temperatures solder and melts at the temperature of 227^0C. Compared with other solder alloys such as Sn-5Bi-5Ag, Sn-2Ag, Sn-3.5Ag, Sn-3.2Ag-0.5Cu and Sn-5Sb, the Sn-0.7Cu solder was found to be less in toxicity (Satyanaran & Prabhu, 2011). Besides that, Sn-0.7Cu solder is a low cost and exhibit an excellent physical and mechanical properties. Moreover, Sn-0.7Cu solder reveal significant enhancement in creep and fatigue properties compared with Sn-Pb solder (Satyanaran & Prabhu, 2011).

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There are several researchers that have been investigating on Sn-0.7Cu lead-free composite solder, but none of them was studying about Sn-0.7Cu solder matrix reinforced with Carbon particles. Literature studies have shown that addition of some reinforcement to Sn-0.7Cu solder matrix can improve the properties of the solder matrix in solderability, physical, thermal, mechanical and electrical properties. Tsao et al had proven that by the addition of TiO_2 nanoparticles into Sn-0.7Cu solder, the resulted microstructure becomes more uniform and the mechanical properties of the solder was enhanced (Tsao et al., 2012). Salleh et al. investigated and founded that when Sn-0.7Cu solder added with Si_3Ni_4 particles, the composite solder had revealed better mechanical properties compared to Sn-0.7Cu solder (Salleh et al., 2012). Gupta et al. declared that the addition of Al_2O_3 nanoparticles into the Sn-0.7Cu solder where the mechanical properties of the composite solder was better than Sn-0.7Cu Solder (Zhong & Gupta, 2008). Therefore, the improvement of composite solder properties inspired an idea to synthesize a new Sn-0.7Cu-AC lead-free composite solder to enhance the solder properties.

1.2 Problems Statement

Lead-free solder is believed to be an alternative to counter these concerns regarding lead contamination. However, to make them extra functionality, better in performance, miniaturization of electronic appliances and more reliable in electronic applications, an attractive and potentially method had been created by adding the third element into them. The third element acts as reinforcement to the lead-free solder and form as lead-free composite solder.

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Powder metallurgy technique parameters are the key factors influencing the properties of lead-free composite solder. Powder metallurgy technique consists of mixing, compacting, and sintering process. The parameters that can be control during powder metallurgy technique were mixing time, compacting loads and sintering temperature. Each parameter could have restraint that could diminish the solder properties. Consideration of solder powder particles from overmixing, reach the maximum compaction loads and the optimum sintering temperature was important in powder metallurgy technique to produce the best bulk composite solder properties.

Currently, Sn-0.7Cu based solder is considered as the most potential base matrix alloy because it is a low cost material and have good potential of metals. However, the properties of Sn-0.7Cu solder is still lacks in terms of wettability and mechanical properties. Therefore, the Sn-0.7Cu solder need to be synthesized into the lead-free composite solder which is an alternative to improve the solder properties. Activated carbon has good mechanical and electrical properties which is suitable to be reinforcement in solder alloy in order to improve physical, electrical and mechanical properties. The Sn-0.7Cu solder is the lowest in cost among the other lead-free solder. It will be a great improvisation if the limitation in the wettability and mechanical properties could be overcome to improve the limitation of Sn-0.7Cu solder and make it into lead-free composite solder.

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1.3 Objectives of Study

i. To investigate the best parameters for composite solder development via powder metallurgy technique through optimization.

ii. To study the optimum physical, electrical and mechanical properties for the new bulk Sn-0.7Cu-AC composite solder.

iii. To investigate the microstructure, wettability and mechanical properties of the Sn-0.7Cu-AC composite solder joint.

1.4 Scope of Study

In this research, Sn-0.7Cu solder will be added with AC particles and fabricated via powder metallurgy techniques which comprise of mixing, compacting and sintering process. The synthesis of lead-free composite solder was prepared via optimization of process parameter for powder metallurgy technique (Phase 1). In the mixing process, the mixing speed will be constant at 200 rpm but the mixing time was varied from 1 to 5 hours. The compaction loads parameter were 217, 260, 303, 347 and 390 MPa, meanwhile the optimization of sintering time is 107, 116, 124, 132 and 141 s. According to the preeminent parameter acquired from the optimization process, the selected parameter for mixing, compacting and sintering was 1 h, 390 MPa and 180 ^{o}C. Following the optimization from the Phase 1, the samples were then prepared for the characterization testing but with different percentages composition of AC particles addition into solder matrix (Phase 2). The percentages of AC particles added into Sn-0.7Cu composite solder were approximately about 0, 0.05, 0.10, 0.15 and 0.20 wt. %. The investigation involved for the Phase 2 was including with the bulk composite solder and composite solder joint. The bulk Sn-0.7Cu-AC composite solders was carried out with the melting temperature, phase analysis, resistivity and hardness test. The composite solder were then reflowed to make a joint and the composite solder joint have investigated for the wettability, shear strength and microstructural analysis.

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CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Soldering is a significant process which determines the reliability of electronic assemblies and the interconnection technology in the electronics applications. An endurance and consistency of the solder joints was depending on the functionality and lifetime of an electronic product. The key in upgrading the solder properties are optimized the physical and mechanical properties to generate a strong interconnection. Soldering is a metallurgical joining technique using a filler metal known as solder. Solder joining provides electrical, thermal and mechanical connection in electronics assemblies. Solder heating up on a substrate which applied with the flux to remove the oxides at both substrate and the solder meanwhile, allowed the solder melt during the soldering process. The important things in soldering were wettability and the intermetallic compound formation to create a bonding between the solder and the substrate by applying with the melting temperature less than 315 ^{0}C (Manko, 2001). The solder will be melted and wet at the substrate surface after reaching the temperature higher than their melting temperatures, and the dissolution of the substrate and interfacial reaction between the solder and substrate were occurs (Abtew & Selvaduray, 2000; Laurila et al., 2005).

These classes of low melting point alloys must provide a unique set of properties to insure cost-effective production of reliable electronic assemblies also allowing joints

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to serve both mechanical and electrical functions. Previously, the most widely used solders for electronic assemblies are low temperature near-eutectic SnPb alloys such as 60Sn40Pb, 63Sn37Pb and Ag-bearing 62Sn36Pb2Ag (Evans, 2007a). These alloys are used in applications ranging from consumer products to space communications systems and have been essential to the worldwide electronics industry. However, recent recognition of toxicity of Pb to the environment and human health has encouraged great efforts to develop lead-free solders (Tong, 2000; Riva, 2012).

Wave soldering operation is a soldering process which has potential source of occupational exposure in electronic method. The inhalation of Pb vapors or Pb bearing dust that produced by dross during the wave soldering process has the potential risk to workers. The surface oxidation at the surface of the molten solder will generate the dross during the wave soldering process. The dross formation can be refined to pure metal for reuse was about 90 %, but the remaining will be as a waste product (Abtew & Selvaduray, 2000). Due to the modern rapid expansions in electronic technology, more assessment needed to create a new robust solder that is convenient with the solderability and reliability of solder joints needed in electronic applications.

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2.2 Lead-Free Solders

Since the toxicity of lead, which can cause the negative impacts to both the human health and the environment, new ‘green solder’ also called as lead-free solder has to be created in consequence of current rapid desired about electronic technology in the worldwide (Ma & Suhling, 2009; Manko, 2001). Sn-Pb solder have been widely used in electronic applications because of their desirable properties which is low cost, good wettability, high ductility, low shear modulus, high corrosion resistance and