EFFECT OF KAOLIN GEOPOLYMER CERAMIC ADDITION TO THE PROPERTIES OF Sn-3.0Ag-0.5Cu (SAC305) LEAD-FREE SOLDER

by

NUR SYAHIRAH BINTI MOHAMAD ZAIMI
(1840412731)

A thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy

Faculty of Chemical Engineering Technology
UNIVERSITI MALAYSIA PERLIS

2023

ACKNOWLEDGEMENT

In the name of Allah, The Most Gracious and The Most Merciful blessed me throughout my postgraduate journey.

First, I would like to express my deepest sincerity and gratitude to my main supervisor that I have the highest and immense respect, Assoc. Prof. Ir Dr Mohd Arif Anuar Mohd Salleh. Thank you for your consistent support, guidance, motivation and understanding to complete this study. Thank you for all the invaluable opportunities you provided me throughout this study. Thank you for believing in me and always encouraging me to work hard and finish this study. Your never-ending support means so much to me. Even though there were moments I feel like to giving up and stuck in the middle of the journey. I am truly grateful to have you as my supervisor. It has been an incredible experience to work under someone so multi-talented and resourceful.

Besides that, I would like to express my sincere gratitude to my co-supervisor, Prof. Mohd Mustafa Al Bakri Abdullah for his invaluable guidance, knowledge and encouragement throughout the whole period of study. Thank you for always keeping me on track and encouraging me always to do better.

Then, I would like to thank the Faculty of Chemical Engineering Technology for all the utilities and facilities. Thank you to all the respected lecturers, staff, vocational training officers and technicians for always assisting and giving permission to run the lab and testing related to my study. I believe, without them, satisfying results couldn’t be obtained. I also would like to thank all my fellow friends especially Rosnita Mohamed for your endless support, positive advice, and kind help throughout this study.

Lastly, the most important and precious people in my life go to my parents, siblings and my best friend. I would like to express my deepest and sincere gratitude to my father, Mohamad Zaimi Bin Ahmad, and my mother, Sakinah Bt Abdullah for always believing in me and being my greatest supporter emotionally and financially. Without their support, I don’t think I couldn’t finish this study and even chose to pursue this study in the first place. Thank you also to my siblings, Nur Liyana, Mohamad Azim and Muhammad Arif Fakhrullah for all your support and understanding. Thank you also to my little nephew, Nik Lutfil Hadi who never fails to brighten me up, especially when I’m working on my thesis. Lastly, I would also like to express my utmost gratitude to my best friend, Nur Hayatun Syamila for always being there from the day one I decided to pursue this study. Thank you for your endless motivation, especially during the difficult time of this postgraduate journey.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
Al_2O_3	Aluminium oxide
Ag	Silver
Al	Aluminium
BGA	Ball-Grid Array
BFR	Brominated flame retardants
Cu	Copper
Ca	Calcium
CeO_2	Cerium (IV) oxide
CXC	Color X-ray Camera
Cd	Cadmium
EDX	Energy Dispersive X-Ray
EPMA	Electron probe micro-analyzer
Fe_2O_3	Iron (III) oxide
Fe_2NiO_4	Iron nickel oxide
Hg	Mercury
IMC	Intermetallic compound
IPC	Institute for Printed Circuits
KOH	Potassium oxide
K_2SiO_3	Potassium silicate
La_2O_3	Lanthanum (III) oxide
MMC	Metal matrix composite
NaOH	Sodium hydroxide
Na_2SiO_3	Sodium silicate
NiO	Nickel oxide
Ni	Nickel
OPC	Ordinary Portland Cement
Pb	Lead
PCB	Printed circuit board
PBDE	Polybrominated diphenyl ether
PBB	Polybrominated biphenyl
RoHS	Restriction of Hazardous Substance
Si_3N_4	Silicon nitride

SiO_2	Silicon dioxide
SEM	Scanning electron microscope
Sn	Tin
SiC	Silicon carbide
Sm_2O_3	Samarium (III) oxide
SnO_2	Tin (IV) oxide
$SrTiO_3$	Strontium titanate
Si	Silicon
TiC	Titanium carbide
TiO_2	Titanium dioxide
TiB_2	Titanium diboride
TSV	Through-silicon via
Ti	Titanium
UTS	Ultimate tensile strength
WEEE	Waste electrical and electronic equipment
XRD	X-ray diffraction
XRF	X-ray fluorescence
ZrO_2	Zirconium dioxide
ZnO	Zinc oxide
ZCT	Zero cross time
3D	Three-dimensional
2D	Two-dimensional
μ-XRF	Micro X-ray fluorescence
YS	Yield strength

LIST OF SYMBOLS

%	Percent
℃	Degree Celsius
°	Degree
wt.%	Weight percentage
µm	Micrometer
µm/s	Micrometer per second
W	Watt
Mpa	Megapascal
W/m K	Watt per meter by Kelvin
GeV	Giga-electron volt
θ	Theta
h	Hours
m^2/s	Meter squared per second
kJ/mol	Joule per mole
g	Gram
α	Alpha
β	Beta

Kesan penambahan seramik kaolin geopolimer kepada sifat-sifat pateri bebas plumbum Sn-3.0Ag-0.5Cu (SAC305)

ABSTRAK

Sn-Pb digunakan secara meluas dalam industri pembungkusan elektronik selama lebih dari 50 tahun lalu. Walau bagaimanapun, penggunaan plumbum dalam pateri telah menimbulkan kebimbangan terhadap alam sekitar. Oleh itu, peralihan dari pateri plumbum kepada pateri bebas plumbum telah berlaku. Penggunaan pateri bebas plumbum pada masa kini masih tidak dapat memenuhi keperluan dan permintaan untuk teknologi semasa. Selain itu, pembentukan berlebihan intermetalik rapuh sama ada sebagai kristal primer atau lapisan intermetalik dalam pateri Sn-3.0Ag-0.5Cu (SAC305) boleh merendahkan kebolehpercayaan sendi pateri terutamanya untuk perkhidmatan jangka panjang. Oleh itu, kajian ini bermotivasi untuk membangunkan Sn-3.0Ag-0.5Cu (SAC305) pateri bebas plumbum dengan pendekatan komposit. Dalam kajian ini, pateri komposit telah dibangunkan dengan menggunakan pateri bebas plumbum SAC305 sebagai matrik dan seramik kaolin geopolimer (KGC) sebagai tetulang. Oleh itu, matlamat kajian ini adalah untuk mengkaji kesan pelbagai peratusan berat (0, 0.5, 1.0, 1.5 dan 2.0 wt.%) seramik kaolin geopolimer kepada sifat-sifat pateri bebas plumbum SAC305. Selain itu, matlamat kajian ini juga adalah untuk mengkaji prestasi pateri komposit dalam penuaan isoterma dan pematerian aliran semula berganda. Fabrikasi pateri komposit SAC305 adalah dengan menggunakan teknik metalurgi serbuk berserta penggunaan teknik pensiteran gelombang mikro hybrid dan dianalisis berdasarkan pembentukan struktur mikro, sifat terma, kebolehtebaran dan kekuatan ricih. Mikroskop electron pengimbas dan sinar-X pendarfluor dengan sinaran synchrotron digunakan untuk menganalisis pembentukan struktur mikro. Selain itu, kalorimetri pengimbasan pembezaan digunakan untuk mengkaji sifat terma pateri komposit. Sementara itu, kekuatan ricih pateri komposit diperoleh melalui ujian kekuatan ricih. Keputusan membuktikan bahawa dengan penambahan 1.0 wt.% KGC dalam pateri SAC305, pembentukan struktur mikro, sifat terma, kebolehtebaran dan kekuatan ricih telah dipertingkatkan dengan ketara berbanding dengan SAC305 biasa. Selain itu, semasa penuaan isoterma pada suhu 85 °C, 125 °C, 150 °C dengan masa penuaan 100 jam, 500 jam dan 1000 jam, pembesaran intermetalik untuk SAC305 dengan penambahan KGC tidak ketara. Dengan peningkatan suhu dan masa penuaan isoterma, kekuatan ricih menunjukkan trend penurunan. Tetapi, nilai penyusutan kekuatan ricih dalam SAC305 dengan penambahan KGC masih lebih rendah daripada SAC305 biasa. Selain itu, semasa kitaran berganda pematerian aliran semula terbukti penindasan dalam pembentukan struktur mikro dan peningkatan kekuatan ricih adalah disebabkan oleh kewujudan KGC pada butiran Cu_6Sn_5 IMC dan kristal primer Cu_6Sn_5 IMC melalui teori penjerapan. Selain itu, dengan penggunaan teknik pengimejan synchrotron “in-situ”, pertumbuhan kristal primer Cu_6Sn_5 IMC boleh diperhatikan secara “in-situ” untuk setiap kitaran dalam pematerian aliran semula. Kadar pertumbuhan kristal primer Cu_6Sn_5 IMC untuk SAC305 dengan tambahan KGC ialah 38 μm/s dengan kepanjangan kristal primer Cu_6Sn_5 yang lebih pendek. Sebagai kesimpulan, zarah tetulang KGC berpotensi menjadi zarah tetulang dalam aloi pateri bebas plumbum melalui pendekatan teknologi komposit.

Effect of kaolin geopolymer ceramic addition to the properties of Sn-3.0Ag-0.5Cu (SAC305) lead-free solder

ABSTRACT

Sn-Pb solders was widely used in the electronic packaging industry for more than 50 years ago. However, as the environmental concerns on the usage of lead arise, the transition of lead solder to lead-free solder took placed. The introduction of lead-free solder nowadays still cannot meet the requirements and demands for current technologies. Moreover, the excessive formation of brittle intermetallic either as primary crystals or interfacial layer in Sn-3.0Ag-0.5Cu (SAC305) could degrade the reliability of the solder joints especially during the long-term service. Thus, this research was motivated to develop SAC305 lead-free solder with composite approaches. In this research, the composite solder was developed by using SAC305 lead-free solder as the matrix and kaolin geopolymer ceramic (KGC) as the reinforcement particles. The aims of this study were to investigate the effects of various weight percentage (0, 0.5, 1.0, 1.5 and 2.0 wt.%) of KGC to the properties of SAC305 lead-free solder and the performance of SAC305 with additions of KGC under isothermal ageing and multiple cycle of reflow soldering. The synthesized of the new SAC305 composite solder was through powder metallurgy route with hybrid microwave assisted sintering technique and was analyzed based on the microstructure formations, thermal properties, spreadability and shear strength. Scanning electron microscope (SEM) and synchrotron micro X-ray fluorescence was used to analyzed the microstructure formations. Besides that, differential scanning calorimetry (DSC) was used to investigate the thermal properties of composite solder. Meanwhile, the shear strength was obtained through a lap shear test. The results proved that with 1.0 wt.% KGC addition in SAC305 solder, the microstructure formations, thermal properties, spreadability and shear strength was greatly enhanced as compared to plain SAC305. Moreover, during isothermal ageing at ageing temperature of 85 °C, 125 °C and 150 °C with ageing time of 100 hours, 500 hours and 1000 hours, the coarsening of the intermetallic particles in SAC305 with KGC additions was not obvious. Although the shear strength showing a decreasing trend with increasing temperature and time, but still the decrement value in SAC305 with KGC additions lower than plain SAC305. Besides that, during multiple cycle of reflow soldering, it was proved that the suppression in the microstructure formations and the improvements in the shear strength was contributed by the existence of KGC at the grains of Cu_6Sn_5 IMC and primary crystals of Cu_6Sn_5 IMC through adsorption theory. Moreover, by using advance technique of in situ synchrotron imaging, the growth of primary crystals of Cu_6Sn_5 IMC could be in-situ observed during each cycle of reflow soldering. The primary crystals of Cu_6Sn_5 IMC in SAC305 with KGC additions growth at rate of 38 μm/s with shorter solidified length. As a conclusion, KGC reinforcement particles can be as a potential reinforcement in the lead-free solder alloy through composite technology approach.

CHAPTER 1 : INTRODUCTION

1.1 Research background

Nowadays, the electronic industry is constantly evolving. The current trend in electronic devices is towards miniaturization, ever-increasing functionality, and high package density. With the emergence of current advanced technology, the reliability of electronic devices, especially for long-term services become crucial, and it is of the utmost importance (S. J. Zhong et al., 2022). The reliability of the electronic devices was greatly affected by the reliability of the solder joint. The solder joint plays a significant role in providing electrical and mechanical continuity and is responsible for the overall functionality of the circuits (El-Daly, Desoky, et al., 2015). Indeed, the solder joint was the weakest part of the electronic devices, and approximately 70% of failures occurred in the devices primarily due to the failure in the solder joints (N. Jiang et al., 2019). Therefore, the advancement of technology in electronic devices posed greater challenges to the reliability of the solder joints.

For a long time, tin-lead (Sn-Pb) was extensively used in the electronic industry as the main interconnect material in solder joints (N. Jiang et al., 2019; X. Yin et al., 2022). Nevertheless, Pb is highly toxic, and its long-term applications can cause detrimental effects on human health and ecosystems. Besides that, Environmental Protection Agency (EPA) has listed Pb as one of the top 17 harmful chemicals which could negatively affect humans and the environment. Owing to the toxicity of Pb, starting 1st July 2006, the Restriction of Hazardous Substances (RoHS) and Waste Electrical and Electronic Equipment (WEEE) has restricted the usage of Pb and other harmful substances, including mercury (Hg), cadmium (Cd), hexavalent chromium [Cr(VI)], polybrominated biphenyl (PBB), polybrominated diphenyl ether (PBDE) and certain brominated flame retardants (BFR) in the electric and electronic devices. This issue creates an inevitable driving force in the development of Pb-free solder alloys to replace traditional Pb-based ones. Since then, a large number of Pb-free solder alloys have been developed (Ali et al., 2021; N. Kumar & Maurya, 2022; P. Zhang, S. Xue, 2019; Sivakumar et al., 2021; Sonawane et al., 2020). The leading and widely used Pb-free solder alloys in the electronic industry is Sn-3.0Ag-0.5Cu, commonly known as SAC305 Pb-free solder (S. Liu et al., 2022; Pietruszka & Skwarek, 2022; Talas & Özkan, 2022; Xu et al., 2023; X. Yin et al., 2022). However, developing new Pb-free solder alloys is still necessary to keep pace with the current advanced electronic devices, which demand high reliability of the solder joints (Faizan, 2021; X. Wang et al., 2009).

In recent years, there were numerous research activities have been made to improve the properties of existing Pb-free solder alloys (Gain & Zhang, 2016; Y. Kang et al., 2022; Pietruszka & Skwarek, 2022; Tang et al., 2019a; Xu et al., 2023). Amongst all, the most viable and attractive method is the addition of reinforcing particles to the matrix of solder alloys, forming a composite Pb-free solder. Guo (2007) emphasize that the composite approach was likely to improve the service temperature capability and the joint strength in the existing Pb-free solder alloys. There were two distinct methods to incorporate reinforcement particles into the matrix of solder alloys, which are either using the in-situ method or the mechanical mixing method (Subramanian, 2007). The in-situ method involved introducing the reinforcement particles intrinsically, and the reinforcement particles using this method are generally termed intrinsic reinforcements. Meanwhile, the mechanical mixing method was carried out by adding the reinforcement particles extrinsically, and the reinforcement particles involved in this method are generally termed extrinsic reinforcements.

Ceramic particles are one example of extrinsic reinforcements. A lot of research has been executed with the utilization of different ceramic particles such as titanium dioxide (TiO_2) (Song et al., 2022; Yahaya et al., 2020), aluminium (III) oxide (Al_2O_3) (J. Wu et al., 2019, 2022), zinc oxide (ZnO) (Skwarek, Agata ; Ptak, Przemysław Piotr; Górecki, Krzysztof ; Witek, Krzysztof ; Illés, 2021), cerium oxide (CeO_2) (Z. H. Li et al., 2019), silicon carbide (SiC) (Pal et al., 2021) and so forth. The use of ceramic reinforcement particles was advantageous since it is non-reactive material and has minimal or no solubility in the matrix of solder alloy to maintain high dimensional stability (J. Wu et al., 2022). Furthermore, several literatures have reported that the improvement in the microstructure of composite solder was generally affected by the distribution of ceramic reinforcement particles along the grain boundaries (M. Qu, Cao, Cui, Liu, et al., 2019; Skwarek et al., 2021). Therefore, the existence of those ceramic reinforcement particles along the grain boundaries could inhibit grain growth as well as effectively improve the mechanical properties of solder alloy (Skwarek et al., 2021).

Therefore, as the incorporation of ceramic reinforcement particles showing improvements in Pb-free solder alloys, it is very interesting to investigate and elucidate the effect of other ceramics reinforcement particles in Pb-free solder alloys.

1.2 Problem statements

Pb-based solder alloys have been applied enormously in electronic devices as the main interconnect materials for a relatively long time (Liang et al., 2022; S. J. Zhong et al., 2022). One example of Pb-based solder alloys is eutectic Sn-37Pb solder alloys. Sn-37Pb solder alloy has good wettability, enhanced mechanical properties and a low melting temperature of 183°C (Y. Li et al., 2022). However, Pb is a harmful substance, and using Sn-37Pb solder alloy for a long period in electronic devices could adversely affect human health and the environment. Due to the toxicity issue in Pb, the usage of Pb in electronic devices was banned by RoHS and WEEE effectively on 1st July 2006. Thus, the transition from Pb-based solder alloys to Pb-free solder alloys has actively taken place by worldwide researchers. In these two decades, great efforts and activities have been carried out in finding suitable solder alloys to replace Pb-based ones. The most promising and considered suitable to replace Pb-based solder alloys was Sn-3.0Ag-0.5Cu or known as SAC305 Pb-free solder, owing to its relatively low melting temperature and good solderability (Pal et al., 2021). Although SAC305 Pb-free solder alloys have been commercialized, it is still necessary to develop new solder materials or improve the existing SAC305 Pb-free solder alloys to meet the demand of current electronic devices.

In recent years, electronic devices have been towards miniaturization with an increase in packaging density. It is known that the crucial part of electronic devices is the solder joint. As the trends toward miniaturization, the solder joints need to reduce in size as well. Further reduction in the size of solder joints brings about reliability issues, especially for the long-term performance of electronic devices (Qiu et al., 2020). One of the critical parts recognized to influence the solder joints reliability’s is the interfacial intermetallic compound (IMC) that forms between the solder and substrate. The existence of this interfacial IMC indicates the bonding between solder and substrate. However, using existing SAC305 Pb-free solder alloys can no longer guarantee the reliability of the solder joints since SAC305 Pb-free solder alloys tend to result in coarsened and thick intermetallic compounds either at the interfacial layer or as the primary IMCs crystals (Long et al., 2022; Mookam & Kanlayasiri, 2012; Rajendran, Jung, et al., 2022). The coarsened and thicker IMC layer was detrimental to the solder joints due to the inherent brittle nature of IMC. In addition, the thick IMC layer could be a crack initiation site (Long et al., 2022). As a consequence, the mechanical strength of the solder joints will eventually reduce. Therefore, one of the feasible and viable ways to improve the existing Pb-free solder alloys is by the incorporation of ceramic reinforcement particles through composite technology approach. The amount of ceramic reinforcement particle additions in solder alloys plays a role which dictates the performance of composite solder. Thus, investigation of the effects of different weight percentages (wt.%) (0, 0.5, 1.0, 1.5 and 2.0 wt.%) of ceramic particle additions on the properties of solder alloys is necessarily important.

In actual working conditions, electronic devices operated at wide ranges of operating temperatures for such a long period of time. Exposing electronic devices to wide ranges of operating temperatures over time greatly jeopardizes the reliability of the solder joints. It was generally known that the solder joints are linked with the IMC formation. The IMC formation was governed by the dissolution and diffusion of copper from the substrate and solder alloys. The dissolution and diffusion were thermally activated processes; hence the growth rate of IMC is sensitive to the changes in the temperature. During the actual working conditions under wide ranges of operating temperatures, the rapid dissolution and diffusion process of copper from the substrates took place. As a result, the IMC layer will continue to grow and get thicker, and the IMC at the bulk solder will be coarsened (Q. Jiang et al., 2019). Moreover, the stress concentration results from the thicker IMC layer and coarsening promotes the initiation of solder joint cracks. Consequently, the mechanical performance of solder joints significantly degrades. Therefore, controlling the diffusion and dissolution process during these conditions is greatly important. One attractive way to control the diffusion and dissolution process is using composite solder with the addition of ceramic particles. It is worth to mention that the optimum amount of ceramic reinforcement particles was beneficial to improve the properties of SAC305 Pb-free solder alloy in this condition. It was reported that the presence of ceramic particles at the channels between the IMC grains will able to block the diffusion and dissolution of Cu atoms and hence, retard the growth of IMC layer (Hsiao et al., 2011).

Besides that, the latest technology in electronic packaging involves the integration of three-dimensional (3D) packages. 3D integration technology can form a highly integrated system by vertically stacking and connecting various materials, technologies, and components together. In 3D integration technology, microbumps solder joints have been used for interconnections in the stacking chips. The solder interconnections at each stacked layer sometimes undergo multiple cycles of reflow soldering. Increasing the number of reflow cycles will significantly increase the thickness of the IMC layer, resulting from the rapid diffusion of Sn and Cu atoms at the IMC layer (Q. Jiang et al., 2019). In addition, the repeated melting and solidification process during multiple cycles of reflow soldering affects the reliability of the solder joints as well (Tu & Liu, 2019). In developing a new solder material, the effect of multiple reflows is important to understand the microstructure growth primarily on the intermetallics and how it affects the solder joint strength.

Kaolin geopolymer is an inorganic polymer that formed through a geopolymerization process involving the dissolution of kaolin materials which consist of SiO_2 and Al_2O_3 in highly alkaline activated solution producing amorphous to semi-crystalline structures with Si-O-Al and Si-O-Si bonds (Dimas et al., 2009). Interestingly, kaolin geopolymer can be used to produce kaolin geopolymer ceramics through a sintering process yielding crystalline phases, which require slightly lower sintering temperature but with excellent mechanical properties (Liew et al., 2017). The angular morphology with the porous surface of kaolin geopolymer ceramic (KGC) is beneficial to the lead-free solder alloy which may facilitates the adsorption process of KGC with the intermetallic compounds. In addition, KGC consists of multiple elements which may acts as additional nucleation sites to improve the properties of solder alloys.

1.3 Research objectives

This research aimed to elucidate the effects of kaolin geopolymer ceramic additions in SAC305 Pb-free solder. The following are the objectives of this research:

a) To investigate the effects of various weight percentages (wt.%) (0, 0.5, 1.0, 1.5 and 2.0 wt.%) of kaolin geopolymer ceramic addition in SAC305 Pb-free solder on the microstructure and phase formations, solderability, thermal properties and shear strength of as-reflowed solder joints.

b) To investigate the effects of kaolin geopolymer ceramic addition in SAC305 under isothermal ageing conditions on the microstructure formations, interfacial growth kinetics and shear strength.

c) To investigate the effects of kaolin geopolymer ceramic addition in SAC305 during multiple reflow soldering to the microstructure formations, interfacial growth kinetics and shear strength.

1.4 Research scope

This research focuses on developing and investigating the effects of kaolin geopolymer ceramic (KGC) addition in SAC305 Pb-free solder during as-reflowed, isothermal ageing and multiple reflow soldering process. In this study, the composite solder will be fabricated by using Sn-3.0Ag-0.5Cu (SAC305) Pb-free solder powder supplied by Nihon Superior Co. Ltd. (Osaka, Japan) with the average particle size of ~25-45 µm. Meanwhile, KGC powder with the average particle size of ~18 µm was used as the reinforcements. The average particle size of KGC was measured using J-Image software on the scanning electron microscope (SEM) image.

The fabrication of KGC will be preceded with the formation of kaolin geopolymer through geopolymerization process as depicts in Figure 1.1. The geopolymerization process involving the dissolution of kaolin material in highly alkaline activated solution and cured at 80 °C in an oven. For the highly alkaline activated solution, a combination of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) solution was used. The molarity of NaOH, alkali activator ratio and solid-to-liquid ratio (S/L ratio) used were 12