Effect of Ni, Ge and Bi Alloying Additions to the Hot Air Solder Leveling (HASL) Coating Properties

by

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LIST OF ABBREVIATIONS

SMT	Surface-Mount Technology
HASL	Hot Air Solder Leveling
Cu	Copper
DSC	Differential Scanning Calorimetry
EDX	Energy Dispersive X-Ray Spectroscopy
HCl	Hydrochloric Acid
HNO_3	Nitric Acid
IMC	Intermetallic Compound
OM	Optical Microscope
PCB	Printed Circuit Board
SAC	Sn-Ag-Cu
SEM	Scanning Electron Microscope

LIST OF SYMBOLS

Tm	Melting temperature
A	Area
t	Thickness
L	Length
v	Voltage
I	Current
Ts	Solidus temperature
TL	Liquidus temperature

Kesan Tambahan Ni, Ge dan Bi Aloi Kepada Sifat Permukaan Bersadur Pateri Panas

ABSTRAK

Selama beberapa dekad, Sn-Pb aloi telah digunakan secara meluas sebagai lapisan pateri untuk aplikasi kemasan permukaan dalam industri pembungkusan elektronik. Walau bagaimanapun, disebabkan kebimbangan mengenai keracunan plumbum (Pb) dalam eutektik pateri Sn-Pb, para penyelidik telah memberi tumpuan untuk menbangunkan salutan pateri bebas Pb untuk aplikasi kemasan permukaan. Lapisan solder ini mengunakan bahan pateri untuk melingdungi papan litar bercetak (PCB) daripada pengoksidaan serta mempunyai dua fungsi penting iaitu melindungi papan daripada terdedah dan menyediakan permukaan boleh lekat apabila digunakan untuk proses pematerian pateri. Terdapat beberapa kemasan permukaan yang digunakan dalam pembuatan PCB, dan perataan pateri udara panas (HASL) menjadi kemasan pemukaan yang paling popular untuk PCB yang akan digunakan untuk litar yang megandungi komponen penting dalam aplikasi yang rumit dan persekitaran yang melampau. Kemasan pemukaan yang digunakan pada PCB peningkatan ketahanan dan ketahanan kakisan pada substrat kuprum dan menyediakan sambungan penting antara komponen. Kajian ini membuktikan hubungan antara ketebalan, ketebalan pateri bebas, dan ketebalan sebatian intermetalik (IMC) salutan pateri pada substrat kuprum. Pemahaman tentang kinetik reaksi diantara pateri dan substrat kuprum adalah penting untuk membolehkan memanjangkan hayat perkhidmatan sendi pateri dalam perhimpunan elektronik. Oleh itu, adalah penting bahawa kesan penyimpanan jangka panjang ke atas pembuatan dan kebolehpercayaan kemasan permukaan HASL dijelaskan. Dalam tesis ini, satu siri aloi pateri Sn-0.7Cu, dengan penambahan Nikel (Ni), Germanium (Ge), dan Bismuth (Bi) telah dihasilkan, dan tingkah laku mikrostruktur dan pematerian aloi ini disiasat. Hasilnya menunjukan bahawa kelebihan solder berkaitan dengan ketebalan solder percuma, dimana peningkatan masa dan suhu penuaan, ketebalan solder bebas berkurang disebabkan oleh pertumbuhan sebatian intermetalik antara muka. Siasatan ini juga melibatkan penjelasan prestasi aloi pateri dalam konteks sifat-sifat termos mekanik dan pengaruhnya terhadap struktur mikro aloi. Sampel tersebut dicirikan dengan menggunakan teknik canggih seperti synchrotron pengimejan dan synchrotron micro-XRF, di mana digunakan untuk menganalisis perkembangan mikrostruktur yang merangkumi nukleasi dan tingkah laku pertumbuhan intermetallik utama yang berlaku di dalam pateri, sedangkan teknik ini digunakan untuk menentukan perkembangan intermetallik utama. Nukleasi kristal Cu_6Sn_5 dan kristal β-Sn utama dalam aloi pateri Sn-0.7Cu-0.05Ni dan Sn-0.7Cu-0.05Ni-1.5Bi kemudian dijelaskan. Hasil kajian ini menunjukkan pemahaman yang terperinci mengenai pembuatan lapisan pateri Sn-0.7Cu dan mekanisma pembentukan mikrostruktur. Hasilnya adalah untuk kepentingan industri dan mempunyai implikasi yang saintifik berbanding mengawal struktur mikro dan meningkatkan prestasi dan kebolehpercayaan salutan pateri Sn-0.7Cu untuk aplikasi kemasan permukaan. Kesimpulannya, penambahan Ni, Ge dan Bi meningkatkan ketahanan dan meningkatkan sifat-sifat thermo mekanikal salutan pateri.

Effect of Ni, Ge and Bi Alloying additions to the Hot air Solder Leveling (HASL) Coating Properties

ABSTRACT

For several decades, Sn-Pb alloys have been extensively used as a solder coating for surface finish applications in the electronic packaging industry. However, due to toxicity concerns of lead (Pb) in eutectic Sn-Pb solders, researchers focussed on developing Pb-free solder coating for surface finish applications. This solder coating utilises solder material to insulate Printed Circuit Boards (PCB) from oxidation, serving two essential functions; protect the exposed copper and provide a solderable surface when soldering components. There are several surface finishes utilised in PCB manufacturing, with Hot air Solder Leveling (HASL) being a popular surface finish for PCB used for circuitry with significant components in heavy-duty applications and harsh environments. The surface finish applied onto the PCB resulted in improved solderability and corrosion resistance of the copper pads while also connecting the individual components. This study elucidates the relationship between solderability, free solder thickness, and intermetallics compound's (IMC) thickness of the solder coating on a Cu substrate. An understanding of the interfacial reaction kinetics between the solder and the substrate is essential in order to allow for the maximisation of the service life of the solder joints in electronic assemblies. It is, therefore, important that the effect of long-term storage on manufacturability and reliability of a HASL surface finish be elucidated. In this thesis, a series of Sn-0.7Cu solder alloys, with the addition of Nickel (Ni), Germanium (Ge), and Bismuth (Bi) were fabricated, and the microstructure and soldering behaviours of these alloys were investigated. The results indicated that solderability is related to free solder thickness, where increased ageing time and temperature, the thickness of the free solder decreased due to growth of the interfacial intermetallic compound. The investigation also involved elucidating the performance of the solder alloy in the context of its thermo-mechanical properties and its influence upon the microstructure of the alloy. The samples were characterised using advanced techniques such as synchrotron in-situ imaging and synchrotron micro-XRF, where the former was used to analyse the development of microstructure encompassing the nucleation and growth behaviour of the primary intermetallics occurring in the solders, while the latter technique was used to determine the distribution of the primary intermetallics. The nucleation of primary Cu_6Sn_5 and β-Sn crystals in solder alloys Sn-0.7Cu-0.05Ni and Sn-0.7Cu-0.05Ni-1.5Bi were then explained. The results of this study demonstrate a detailed understanding of the fabricated of Sn-0.7Cu solder coating and the mechanism of microstructure formation. The results are of industrial significance and have significant implications in controlling the microstructure and improving the performance and reliability of Sn-0.7Cu solder coating for surface finish applications. In conclusion, the addition of Ni, Ge and Bi increases the solderability and improves the thermo-mechanical properties of the solder coating.

CHAPTER 1 : INTRODUCTION

1.1 Research Background

The use of surface mount technology (SMT), where components are placed directly onto the surface mount devices (SMD) on a Printed Circuit Board (PCB) is prevalent in the electronics industry (Nogita, Salleh, Tanaka, Zeng, McDonald, & Matsumura, 2016; Siewiorek, Kudyba, Sobczak, Homa, Huber, Adamek, & Budka, 2013). The main advantage of SMT is that it mounts components without requiring holes to be drilled into the PCB, which translates into lower initial costs and components placement closer to the actual board. Usually, PCB with copper tracks is covered with a solder mask to prevent oxidation and decrease the probability of bridges during wave soldering. However, the solder is prone to re-melting under the mask in the solder wave on the PCB board during wave soldering, which creates crinkles on the finished product (Bacior, Sobczak, Siewiorek, Kudyba, Homa, Nowak, Dziula, & Masłon, 2015). Also, the use of solder masks is unsuitable for double-sided circuit boards. Therefore, the surface finish for SMDs is needed to prevent the solder mask from wrinkling.

The PCB needs to be coated with a surface finish to protect it from impurities such as oil and dust while preventing the formation of oxide layers. Surface finish has two essential functions; to improve solderability and to act as a barrier to prevent copper from oxidising, which could cause assembly problems (Bin, Yudong, & Daojun, 2013). The surface finish also forms a critical interface between the component and the PCB. The application of chip scales packages (CSPs) in harsh environments requires the conformal surface finish to meet the reliability requirement (Ratzker, Pearl, Osterman, Pecht, & Milad, 2014). Thus, in the PCB industry, ideas for coating the PCB to protect the copper has been floated. Dipping or passing the boards over molten solders can be used to form thin functional coatings. As the molten solder is exposed to the solder, a system of hot air knives removes the excess molten solder from the pad, leaving a thin layer of solder over the Cu. Coating the PCB protects it from a harsh environment, moisture, and contaminants such as dust that can cause shorts in electronic components. Also, the solder coating is designed to improve the appearance and extend the life of electronic components. The required properties of coating solders include a low rate of Cu dissolution and stable interfacial intermetallics. The coating can also stabilise the intermetallic layer that forms on the surface and act as a barrier against further dissolution.

The previous paragraph described the process of coating the exposed Cu with solder via the Hot Air Solder Leveling (HASL) technique to prevent oxidation. This HASL-surface finish is a common surface finish technique used in PCB surface finishing technology. The surface finish has a long shelf life and low cost compared with other PCB finishes, such as Electroless Nickel Immersion Gold (ENIG), Electroless Nickel Electroless Palladium Immersion Gold (ENEPIG), immersion tin (ImSn), and immersion silver (ImAg) (Ratzker et al., 2014). The advantages of HASL surface finish is that it delivers solder to the surface, forming a thin coating of an intermetallic compound (IMC) on solders on a wet-on Cu/pad (Cu_6Sn_5) instantaneously. Currently, the usage of solder coating is highly developed; for example, the Sn-Cu-Ni-Ge (Sn100CL) solder alloy is standard in industrial applications (Sweatman, 2009). In solder coating, the formation of interfacial IMC between the interface of solder and substrate is realised via chemical bonding. IMCs form instantly via solder melting on the Cu pads and continue growing when exposed to high temperatures.

However, thicker IMC layers could result in decreased strength of the solder joints due to its brittle nature. The properties and reliability of a solder joint are highly correlated to the condition of solder material and the IMCs' thickness and morphology. The growth of IMC layers during isothermal ageing has been the focus of many studies (Liu, Hon, Wang, Chen, Chang, & Li, 2014; Said, Salleh, Derman, Ramli, Nasir, & Saud, 2016; Zhang, Xue, Zeng, Gao, & Ye, 2012b). Studies on IMC formation and (layers) thickness are similarly significant due to both factors' correlation to wetting behaviour and interfacial reactions (Liang, Dariavach, Callahan, & Shangguan, 2006). Wetting is crucial in the soldering process due to its role in ensuring excellent bond formation between solder material and substrate. If the solder coating fails to provide a secure layer of free solder, the unreacted solder over the intermetallic layer solderability is quickly lost. It is, therefore, useful to understand how free solder affects solderability, which is closely related to wetting force and surface tension. The wetting balance method is used to evaluate solderability by immersing Cu into molten solder, with the wetting force measured as a function of time (Sobri, Salleh, Ghazali, & Narayanan, 2016).

The effect of the addition of Nickel (Ni), Germanium (Ge) and Bismuth (Bi) on the Sn-0.7Cu solder coating for surface finish application has been investigated. Understanding the interfacial intermetallic kinetics and free solder thickness between the solder and substrate is vital as it allows for the maximisation of the service life of solder joints via mimicking the storage condition and estimating the shelf life of the surface finish (Sobri et al., 2016). The IMC thickness and growth rate of Sn-0.7Cu and Sn-0.7Cu-

0.05Ni solder coating have also been studied. Different IMC thickness solder coating was then investigated using the globule test using different Sn-0.7Cu-0.05Ni+xBi solder ball compositions to determine the solderability of the solder coating. Results of wetting time and maximum force for both solder coating was collected and analysed. There have been interests in developing an Sn-0.7Cu-0.05Ni solder coating with improved solderability via the addition of Bi and the results thus far have been promising vis-a-vis solderability properties.

This research explored the formation and growth kinetics of primary intermetallics. The synchrotron radiation imaging technology is useful for the in-situ observation of the solidification of alloys. This technique allows us to understand the development of microstructures in the event of solder alloy solidification. The morphology and distribution of the IMC formed during the soldering process will dramatically affect the solderability properties of the solder joints. Thus, understanding the influence of the IMC on the solder joints is vital in the context of predicting the reliability of the solder joints. In this work, real-time imaging technology was used to analyse the influence of Bi on the formation and growth of primary IMCs during the solidification process.

1.2 Problem Statement

For years, Tin-Lead (Sn-Pb) solder has been widely used as interconnect materials. However, the application of Pb in electronic products is banned due to environmental and health concerns (Hu, Li, Liu, & Min, 2015). The European Union (EU) directive on Waste of Electrical and Electronic Equipment Restriction of Hazardous

Substances Directive (RoHS) affirmed the disallowance of the utilisation of Pb in customer hardware (2006) (Kanlayasiri & Sukpimai, 2016).

Hot Air Solder Leveling (HASL) is a predominant surface finish extensively used in the industry. However, conventional Sn-Cu surface finish is prone to solderability problems such as de-wetting, which is related to the poor solderability of the surface finish on the PCB-based solder coatings . The solderability and shelf life of the coated PCB are ultimately dictated by the growth of IMC area between the solder and the substrate. A thicker interfacial IMC is believed to decrease the solderability performance of solder coatings. However, the optimum free solder thickness that needed for good solderability is still unknown. The formation of large and excessive intermetallic phases in an electronic joint is usually disadvantageous due to its brittleness and susceptibility to crack growth (Hu & Ke, 2014).

Additionally, the limited size and amount of intermetallic solder joint could increase the strength and reliability of the solder joint. Thus, understanding the intermetallic growth of micro-alloyed Sn-Cu coating is vital for the development of a new surface finish. Surface finish technologies should be simple, reliable, and inexpensive to meet industrial demands. It should also be flat and solderable, has a long shelf life, is cheap and cost-effective, and non-toxic.

The selection of solder used as solder coating is necessary because it influences the properties of the coating. An unsuitable solder will alter the surface finish performance and prolong the soldering process. The solder coating is also expected to provide corrosion protection throughout the lifetime of the equipment.

1.3 Objective

This research proposed the study of the effect of the addition of Ni, Ge and Bi to solder alloy for use as solder coating. The objectives of this study are:

a) To investigate the relationship between free solder thickness and the solderability of the solder alloy properties.
b) To investigate the effect of the addition of Ni and Bi on the solderability of Sn-0.7Cu solder coating.
c) To examine the effect of the addition of Ni and Bi to the nucleation rate, nucleation site, and growth rates of primary intermetallics in Sn-0.7Cu solder alloy.

1.4 Scope of Research

This work is divided into three phases, summarised below:

Phase 1: Investigate the relationship between free solder thickness and solderability of solder coating.

The relationships between solderability, free solder thickness, and the intermetallic thickness of Sn-0.7Cu-0.05Ni solder coatings on the Cu substrate has been investigated. The annealing method was proposed to control the free solder's thickness by controlling the ratio of free solder and interfacial IMCs. The solderability of the solder coating was investigated using a purpose-designed microwetting balance. The interfacial intermetallic microstructure was analysed, and the thickness measured in the as-coated condition with the ageing process. These results can be used as a basis to obtain optimum wettability of the solder coating during soldering.

Phase 2: Explore the effect of Ni and Bi addition to the solderability of Sn-0.7Cu solder coating.

This investigation explores the influence of the addition of Ni and Bi on the solderability of Sn-0.7Cu solder coatings. The minor addition of 0.05wt.% Ni into the Sn-0.7Cu solder alloy results in an improvement to the wettability, based on the dipping tests. The solderability investigation using a globule mode shows the influence of the addition of Ni and Bi on the interfacial IMC. The addition of Ni to an Sn-0.7Cu solder coating resulted in the formation of $(Cu, Ni)_6Sn_5$ interfacial IMC, which enhanced the solderability performance of the coating, as per the globule test. Increasing the ratio of Bi in the Sn-0.7Cu-0.05Ni-xBi solder ball decreases the surface energy of the solder alloy, which improves its solderability. The synchrotron micro-XRF results indicated that Ni is found in a relatively high concentration within the interfacial layer.

Phase 3: Examine the nucleation rate, nucleation site and growth rates of interfacial and primary intermetallic in Sn-0.7Cu-0.05Ni-xBi.

This phase elucidated the effects of the addition of Bi element (0wt.%, 0.5wt.% and 1.5wt.%) to the microstructure and the thermo-mechanical and electrical properties of the Sn-0.7Cu-0.05Ni in the context of a high strength solder. On top of using the conventional cross-sectioned microstructure image, the real-time synchrotron radiation imaging and synchrotron micro-X-ray fluorescence (XRF) technique was also utilised to elucidate the microstructure, focussing on the *in-situ* growth behaviour of the primary $(Cu, Ni)_6Sn_5$ intermetallic and elemental distribution in the Sn-0.7Cu-0.05Ni-1.5Bi. Other essential properties of the solder material, such as wettability, electrical resistance, and shear strength, were also determined. The results confirmed that the developed material is suitable as a potential high strength solder material in the context of advanced interconnecting applications. The microstructure evolution in the lead-free solder joint has a significant effect on the mechanical behaviour of the solder joints.

1.5 Organization of Thesis

This thesis is divided into four chapters. The first chapter detail the research background, problem statement, objective, and the scope of the overall work. The significance of the study, problems associated with the current methods, approaches to solving current limitations, and the significance of the proposed method was also elucidated. Chapter 2 outlines the literature on the subject matter. The used of SMT for mounting devices, the development of solder coating, the formation and growth kinetics of primary intermetallics during solidification and the effect of isothermal ageing on solder coatings will be discussed in this chapter.

Chapter 3 compiles the published works resulted from this study. The chapter begins by summarising the theme of the articles, followed by detailing the results from 3 articles published in journals indexed in Web of Science.

Chapter 4 summarises this work and provide direction for future research endeavours made possible via the findings from this work.

CHAPTER 2 : LITERATURE REVIEW

2.1 Introduction

The chapter reviews the literature on surface finish development, reaction during solidification, interfacial reaction, the reliability of surface finish, and improvement in solder coating in the context of solder coating acting as surface finish.

2.2 Surface Finish

Selecting a suitable surface finish for the PCB is essential due to its potential influence on the cost, manufacturability, quality, and the reliability of the final product in an electronic assembly. A suitable coating for a PCB will result in an excellent solder joint due to it facilitating the soldering process during PCB assembly (Siewiorek et al., 2013). The surface finish protects the exposed Cu while also providing a solderable surface for the assembly of components onto the PCB. The surface finish also acts to limit the (further) growth of the IMC layer. The surface finish is also expected to improve solderability and provide corrosion resistance while also being cost-effective (Kim, Jeong, Yoo, Lee, & Park, 2012). Studies on surface finishes focussed on the effect of PCB surface finish on other types of solder joints. Literature review on the effect of PCB surface finishes on Pb-free solder could help us elucidate the reaction between the surface finish material and lead-free solder.

There have been extensive studies on the characterisation of the intermetallic growth at the interface between the solder and surface finishes. During assembly, tin (Sn) from the solder will react with the material from the pad or component finishes to form intermetallics. The formation and growth of intermetallic in the solder joint depends on the substrate's surface finish metallisation and the solder alloy used. The purpose of the surface finish is to protect the substrate base metal from oxidisation while also limiting the diffusion of the solder into the underlying metal (Wu, Huang, Lee, & Tzan, 2004). Different surface finishes on the PCB strongly influence the formation of IMCs and solder joint reliability. Possible surface finish alloys include organic solderability preservative (OSP), Ni/Au (ENIG), pure Ag, and pure Sn for board finishes (Collins & Punch, 2012). There is no superior finish among the examples above, as each has its respective advantages/disadvantages.

2.3 Type of Surface Finish

It needs to be pointed out that the surface finish delivers the highest possible level of solderability to the assembly line. Yoon and Jung (2008) posited that the selection of the surface finish is made based on factors such as solderability, solder joint quality, cost, ease of application, and material compatibility. There are many surface finish that has been developed for electronic packaging, such as Hot Air Solder Leveling (HASL), Electroless Nickel Immersion Gold (ENIG), Copper Organic Solderability Preservative (Cu-OSP), Immersion Silver (ImAg), Immersion Tin (ImSn), Electroless Nickel Electroless Palladium Immersion Gold (ENEPIG), and Electroless Nickel Immersion Silver (ENImAg). pointed out that HASL is the most widely used surface finish, and

Sweatman (2009) posited that HASL had been a popular surface finish for PCB used for circuitry in large components used in heavy-duty applications in harsh environments.

2.3.1 Hot Air Solder Leveling (HASL)

The Hot Air Solder Leveling (HASL) is the most robust solderable finish for PCBs. This HASL is widely utilised in North America, Europe, and most of Asia outside of Japan during the tin-lead (Sn-Pb) era (Sweatman, 2009). The early trial of lead-free HASL involved the tin-silver-copper (Sn-Ag-Cu) as the coating alloy. The trial results were adequate, and the alloy was then promoted as a universal lead-free replacement for Sn-Pb over time. This protective coating must be solderable while also able to act as a barrier to prevent the Cu on the PCB board from oxidation, which would cause problems for the eventual end-users (Sobri, Salleh, Ghazali, & Narayanan, 2015). The HASL finish is preferred due to its excellent solderability, long shelf life (12 months), universal acceptance, multiple heat cycle capability, and simplified visual inspection (Bin et al., 2013). Figure 2.1 shows a PCB with a HASL surface finish. The PCB is immersed in a pot of molten solder, withdrawn, then the excess solder is removed using a strong blast of hot air.

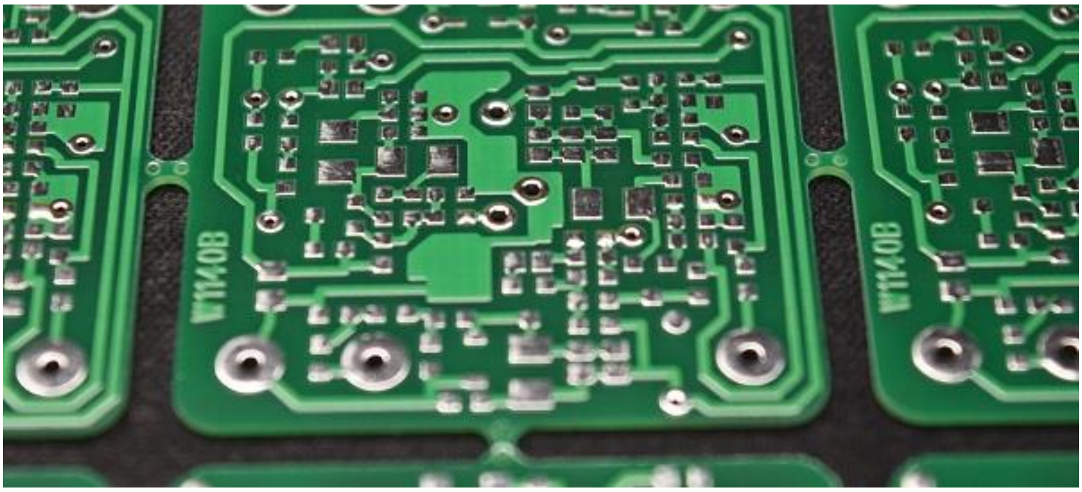

Figure 2.1: Printed circuit board with hot air solder leveling.

The flow process of HASL consist of a pre-clean, preheat, flux coating, solder coating, levelling with hot air knives, cooling, and a post-clean section, as summarised in Figure 2.2.

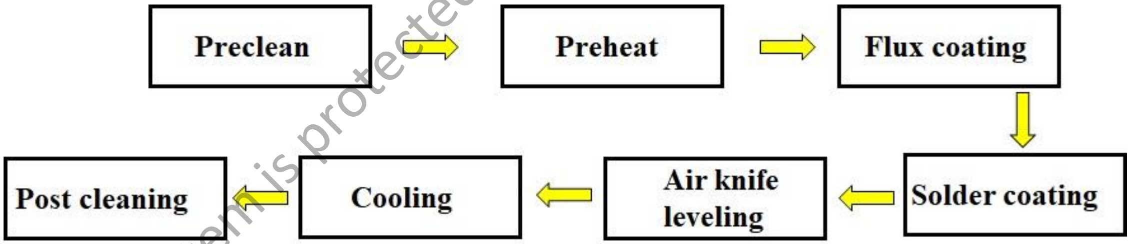

Figure 2.2: The flow process of hot air solder leveling (HASL).

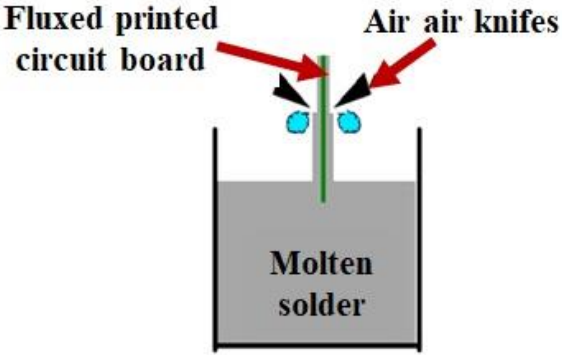

Figure 2.3: Schematic diagram of hot air solder leveling (HASL) technique (Sweatman, 2009).