SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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EFFECT OF CRYOGENIC TREATMENT PRIOR TO EQUAL CHANNEL ANGULAR PRESS (ECAP) OF SAC SOLDER

By

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(Materials Engineering)

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Effect of Cryogenic Treatment Prior To Equal Channel Angular Press (ECAP) of Lead-Free SAC Solder**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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Date : 21 JUNE 2018

Witness by

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LIST OF ABBREVATIONS

Sn	Tin
Ag	Silver
Cu	Copper
ECAP	Equal Channel Angular Pressing
CT	Cryogenic Treatment
SEM	Scanning electron microscope
XRF	X-ray Fluorescence
XRD	X-Ray Diffraction
OM	Optical Microscopy
EDX	Energy Dispersive X-Ray
RoHS	Restriction of Hazardous Substances
SPD	Severe Plastic Deformation
IMCs	Intermetallic compounds
Pb	Lead
PCB	Printed circuit board
EEE	Electrical and Electronic Equipment
SMT	Surface mount technology
UFG	Ultrafine Grain
HAGB	High-Angle Grain Boundaries
LABs	Low Angle Boundaries
HABs	High Angle Boundaries
SCT	Shallow Cryogenic Treatment
DCT	deep cryogenic treatment
FWHM	Full Width Half Maximum

LIST OF SYMBOLS

β	Beta
α	Alpha
γ	Gamma
λ	Wavelength
d	Grain diameter
σ	Yield Stress
Ɛ	Strain
Φ	Angle between the Channels
Ψ	Angle Outer Arc of Curvature
H	Hardness
Wt %	Weight percent
μm	Micrometer

KESAN RAWATAN KRIOGENIK SEBELUM MELALUI PENEKANAN BERSUDUT SAMA SALURAN (ECAP) PATERI SAC

ABSTRAK

Aloi pateri SAC telah dicadangkan sebagai pateri alternatif untuk mengatasi keprihatinan alam sekitar yang disebabkan oleh pengunaan pateri Pb-Sn. Ramai penyelidik telah mengkaji aloi pateri SAC dan mendapati bahawa isu kebolehpercayaan pateri pada sifat-sifat mekanikal seperti kekerasan dan kekuatan. Kajian ini bertujuan untuk melihat bagaimana penghalusan butir memberi kesan terhadap tingkah laku mekanikal aloi pateri SAC 305 komersial. Dalam kajian ini, aloi pateri SAC 305 telah dikenakan ubah bentuk plastik tegas yang dilaksanakan melalui penekanan bersudut sama saluran (ECAP) dengan laluan B_C. Sebelum ECAP, aloi pateri dicelup dalam nitrogen cair untuk rawatan kriogenik. Adalah dipercayai bahawa rawatan kriogenik boleh memperbaiki struktur mikro dan prestasi pateri. Kesan masa mencelupkan sampel dalam nitrogen cair dan bilangan pas melalui ECAP yang digunakan semasa menekan terhadap sifat-sifat mekanikal dikaji. Analisis elemen aloi pateri tuangan dianalisa dengan menggunakan pendarfluor sinar-X (XRF) dan ia menunjukkan komposisi yang betul aloi SAC 305. Fasa dan saiz kristalit semua solder telah diperiksa oleh difraksi sinar-X (XRD) dan sampel dengan rawatan kriogenik sebelum ECAP menunjukkan saiz kristalit yang lebih kecil. Aloi pateri dengan celupan nitrogen cecair sebelum ECAP meningkatkan kebolehan mikro-kekerasan Vickers bagi aloi pateri pukal. Ini disebabkan oleh mikrostruktur aloi pateri dengan celupan dalam nitrogen cecair sebelum ECAP menunjukkan penghalusan butir sebagaimana dilihat menggunakan mikroskop pengimbasan elektron (SEM). Selain itu, rawatan kriogenik sebelum ECAP meningkatkan sudut sebaran dan sudut pembasahan aloi pateri yang dipateri pada substrat

Cu. Bagi sifat mekanik, sampel terpateri dengan celupan nitrogen cair dalam masa yang singkat iaitu 10 minit sebelum ECAP memberikan kekuatan ricih tertinggi melalui ujian cantuman tindih tunggal dan permukaan patah menunjukkan saiz lekuk yang lebih kecil berbanding dengan yang lain. Sebagai kesimpulan, penghalusan butir dan sifat mekanik aloi pateri bertambah baik dengan rawatan kriogenik sebelum ECAP.

EFFECT OF CRYOGENIC TREATMENT PRIOR TO EQUAL CHANNEL ANGULAR PRESS (ECAP) OF SAC SOLDER

ABSTRACT

The SAC solder alloy has been proposed as the alternative solder to overcome the environmental concern of lead (Pb-Sn) solder. Many researchers have studied the SAC solder alloy and found that reliability issues of solder on mechanical properties such as hardness and strength. The present work aims to look at how grain refinement influenced the mechanical properties of a commercial SAC 305 solder alloy. In this work, SAC 305 solder were subjected to severe plastic deformation applied via Equal Channel Angular Pressing (ECAP) which was conducted through route B_C. Prior to ECAP, the solder alloy was dipped in liquid nitrogen for cryogenic treatment. It is believed that cryogenic treatment (CT) can improve the microstructure and performance of solder. The effect of the dipping time of samples in liquid nitrogen and number of passes through ECAP employed during pressing on hardness was studied. Elemental analysis of casted solder alloy was analysed using XRF and it showed correct composition of SAC 305. Phases and crystallite size of all the solders were examined by XRD and sample with cryogenic treatment prior to ECAP exhibited a smaller crystallite size. Solder alloy with dipping in liquid nitrogen prior to ECAP enhanced the Vickers microhardness of bulk solder alloy. This is due to the microstructure of solder alloys with dipping of liquid nitrogen prior to ECAP showed evidence of grain refinement as observed using Scanning electron microscope (SEM). Besides, CT prior to ECAP improved the spreading and wetting angle of reflowed solder on Cu substarate. For the mechanical properties, solder joint samples with dipping in liquid nitrogen for shortest time of 10 minutes prior to ECAP gave the highest shear strength through single lap joint test and the fracture surface showed smaller

dimples compared to others. In conclusion, grain refinement and mechanical properties of solder alloy improved through CT prior to ECAP.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Solder is a fusible metal or alloy used in a process called soldering. Soldering is a metallurgical technique which is used to join two (or more) metallic objects together by melting filler metal/ solder alloy (Schwartz, 2014). Solder alloys which melts below 450 °C and has a lower melting temperature than materials to be joint. Solder alloy is melted and applied on the joint area, then solidified to join the pieces together (Anil, 2012). This technique is an ancient joining method.

Solder materials are divided into two main group, which are leaded and lead free solder. Both groups of solder are different from the lead content in the solder alloy. Leaded solder or Sn-Pb solder alloy have a long history in metal interconnection. The important characteristics of solder alloy provide many benefits such as ease of handling, low melting temperature, good workability, ductility and excellent wetting on base metal such as copper and its alloys (Seelig, 2014).

In the recent past, most companies used near-eutectic Sn-Ag-Cu (SAC) alloys because of the Restriction of Hazardous Substances (RoHS) regulatory requirement restricting in the use of lead in electronic assembly. Due to the toxicity of Pb in the traditional eutectic Sn–Pb solders used in electronic products, Sn-rich lead-free solders have been extensively studied and some of them have come into use in electronic packaging (Pandher & Lawlor, 2009). Among these lead-free solders, the currently used ternary eutectic (T_m = 217 °C) or near eutectic Sn–Ag–Cu system alloys such as SAC 305 have so far received much attention and emerged as possible replacements for Sn–Pb alloys. This alloy contains 3% silver, 0.5% copper and the balance tin.

As the mechanical bonding material, the solder alloy is a crucial part in governing reliability of microelectronic devices in long-term services. To achieve this strong bond with smallest amount of solder volume, the solder alloy must wet the largest possible area. The importance of wetting of the solder alloy has increased vitally in the past decade since the sizes of the microelectronic devices have decreased drastically (Anil, 2012). For example, in flip-chip connection, the solder bump had to bear a relatively large thermal stress under a high homologous temperature condition. As the diameter of the solder bump continues decreasing to less than 100μm, stress bearing requirement for each bump keeps rising. Thus, deformation behaviour of the solder alloy becomes a critical issue, especially for fine-pitch chip scale packaging.

Recently, a lot of interest has been shown in the production of materials with sub-micron or nano-sized grains, especially in bulk alloy through Severe Plastic Deformation (SPD) techniques (Sayed et al., 2013). Severe plastic deformation techniques have been extensively utilized to fabricate a bulk material that exhibit unique physical and mechanical properties which is very fascinating for various structural and functional applications (Hilšer et. al, 2017).

In the past decade, equal channel angular pressing (ECAP) technique has attracted much attention as a method of severe plastic deformation. ECAP is a method where high shear strain is imposed by pressing to materials through a specially designed die having two equally sized channels connected at a finite angle (Fang et al., 2006). The ECAP procedures lead to substantial grain refinement so that the grains are reduced to the sub-micrometer or even the nano-meter range. The method is considered as one of the very useful techniques for producing ultra-fine microstructures with significantly improved mechanical properties and higher corrosion resistance. Moreover, ECAP have been utilized not only to obtain ultrafine-grained materials but also to produce extraordinary mechanical and physical properties without remarkably changing the geometry of a bulk material. Materials processed with ECAP become superior to that of conventional coarse-grained materials (Sayed et al., 2013). In this study, equal channel angle pressing (ECAP) and the subsequent recrystallization process were used to alter the microstructure of Sn–Ag–Cu alloy by reducing the large dendrites into fine and equiaxed grains. In this study, ECAP and the subsequent recrystallization process were used to alter the microstructure of Sn–Ag–Cu alloy by reducing the large dendrites into fine and equiaxed grains. This is due to the increased strain hardening capability of the alloy. Besides, grain refinement to sub-micrometer range by ECAP reduces grain size lead to increase in strength and a reduced ductility (Zhu et al., 2009).

In a study by Fritsch et al. (2012), the concept of cryo-forming to ECAP was applied. They presented first results on the effect of cryogenic ECAP on microstructural evolution and mechanical properties of the 7075 alloy that demonstrate the potential of cryogenic forming to produce improved properties of high-strength aluminum alloys. Cryo-ECAP results in microstructural changes (grain refinement in the sub-micrometer range) that are directly related to the increased strength of the material. Also, low deformation temperatures result in an increased ductility and improved workability due to the increased strain-hardening capability of the alloy (Fritsch et al. , 2012).

Importantly, the mechanical properties of Sn-based solders have not been adequately characterized at cryogenic temperatures and the mechanisms are not well understood (Lupinacci et al., 2013). Therefore, the aim of this work is to study the grain refinement of SAC305 produced from cryogenic treatment prior to ECAP deformation.

1.2 Problem Statements

Driven by the necessity to improve the reliability of lead free electronic products, researchers are putting intense efforts into improving the properties of Sn based solders. Sn-Ag-Cu (SAC solder) alloys have been a favored replacement for Sn-Pb solders. However, the currently used ternary eutectic (Tm = 217 ℃) or near eutectic SAC solders have some drawbacks. Reliability of solder joint is influenced by the mechanical properties of the solder joint. One of the viable method to improve mechanical properties of the solder joint on its reliability is via grain refinement of the solder alloy. There are several methods to achieve grain refinement of the solder alloys. Among all the methods, much interest has been shown on addition of alloying elements or severe plastic deformation (SPD).

Grain refinement by alloying is another approach. Grain refinement via alloying has been reported by some reseachers, among others Shi et al. (2008) who studied the effects of the fourth alloying element on the microstructure and mechanical properties. Fourth minor alloying elements (0.05–0.1 wt.%) that have been added into SAC solder include Ni, Co, Fe, Mn, Zn, Ti, Ce, In and Al (Leong & Haseeb, 2016). Improvements in mechanical properties such as shear strength, tensile strength and creep resistance have been reported by Shi et al., 2008. The addition of fourth alloying elements imparts their influence on the mechanical properties in which the increase in mechanical strength may be related to the refining of IMCs of the solder due to the addition of small amount of alloying element (Shi et al., 2008). The microalloying of the base alloy was the most effective which successfully suppressed the Ag_3Sn blade formation, this also being the addition with the lowest fourth element concentration (Anil, 2012). It promoted formation of small, equiaxed particle exhibited higher hardness and modulus. Besides, elongated shapes of new darker IMC phase are seen distributed in the lighter contrast Sn phase. It can be seen that the Sn grain size decreases with Al addition in the as-received alloys (Leong & Haseeb, 2016).

On the other hand, different severe plastic deformation (SPD) techniques have been applied to refine the microstructure. Equal channel angular pressing (ECAP) is considered the most popular SPD technique used for bulk materials. Many researchers investigated the effect of ECAP on the mechanical properties of various metals (Irfan et al., 2017). Grain refinement to sub-micrometer range by ECAP reduces grain size lead to increase in strength and a reduced ductility. Owing to the advantage of grain refinement due to ECAP, there is an opportunity to use ECAP in order to impart grain refinement on solder alloy and thus, improving the mechanical properties (Zhu et at.,2009). However, there is very limited findings reported on ECAP of solder alloy. Therefore, this project aims to explore possibility of enhancing mechanical properties of SAC 305 via ECAP combined with cryogenic treatment.

The use of cryogenic treatment is due to low Tm of the solder, which is 217℃. Therefore, it might be able to suppress the recrystallisation along the processs, and thus, preserving the grain refinement effect. In this study, the effect of cryogenic ECAP on microstructural evolution and mechanical properties of the SAC305 alloys were observed. One very promising approach to improve the mechanical behavior of solder alloy is deformation at low temperatures. It is well known that forming at low temperatures or cryogenic regime results in high dislocation densities because recrystallisation can be avoided. As ECAP introduced ultrafine grain via severe plastic deformation in the metal such as aluminium alloys, magnesium, chromium, copper, silver, steel and titanium (Rajeshwaran & Sureshkumar, 2016). By combining cryogenic treatment via ECAP should be maintained without the risk of recrystallisation and subsequently grain growth (Fritsch et al., 2016).

1.3 Objectives

The objectives of this project are:

a) To investigate suitable parameters (dipping time in liquid nitrogen and number of passes through ECAP) to attain improved hardness of SAC305.

b) To assess the grain refinement effect on SAC305 through cryogenic treatment prior to ECAP through B_C route with different cumulative strains (or number of passes) in various of nitrogen dipping time on SAC305 alloys.

c) To investigate the effect of cryogenic treatment prior to ECAP on SAC305 solder alloy in terms of hardness, wettability and single lap joint shear test.

1.4 Project Overview

In this project, the focus is to investigate the effect of cryogenic treatment which is dipping of liquid nitrogen prior to ECAP on the grain refinement in Sn-3.0Ag-0.5Cu alloys solder. SAC305 alloys rods were prepared by melting SAC305 ingot bar and then it was casted by pouring the melted alloys into steel mould. Casted bulk solder samples were then characterized in terms of elemental using XRF, phase analysis by suing X-ray Diffraction (XRD) and bulk microstructure by using SEM equipped with EDX. For the selection of parameters, time of nitrogen dipping prior to ECAP and the number of passes through ECAP by B_C route were tested. For the selection of dipping time of samples in liquid nitrogen, SAC rod samples were dipped in nitrogen with time variation 10 minutes, 20 minutes, 30 minutes, 60 minutes and 90 minutes with trial and error based before the rod passing through 2 passes ECAP by B_C route. While for the selection of number of passes, SAC rods were dipped in nitrogen for 30 minutes prior to ECAP before passing through different passes of ECAP which is 1pass, 2 passes, 3 passes and 4 passes. The Vickers microhardness for different dipping time of nitrogen through 2 passes of ECAP and variable number of passes through ECAP by B_C route were observed. Thus, after selection of parameters, the samples were then focus on ECAP with 1 pass through B_C route with variation of nitrogen dipping time of 0 minutes, 10 minutes, 20 minutes and 30 minutes while as cast sample act as the reference sample of this project. Elemental analysis, phase analysis and microstructure of the pressed solder samples were characterized using X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD) and SEM equipped with Energy Dispersive X-Ray (EDX). Solder samples were then reflowed onto Cu sheet at 270℃. Hardness of all bulk sample solders after dipping of liquid nitrogen prior to ECAP were tested using Vickers microhardness. Reflowed samples were evaluated in terms of spreading and wetting angle on Cu sheet and tested using wetting balance test for the wettability of solder samples. For the mechanical properties, solder joint samples were tested for the shear strength through single lap joint shear test by using INSTRON machine.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Solder Development

Based on environmental considerations, global economic pressures imposed on legislation in several countries have warranted the elimination of lead from solders used in electronic applications. The solders used in electronic applications were not pointed for elimination until recently because of their limited utilization and disposal although lead was eliminated a few decades ago from applications such as paints, ceramic glazes, and plumbing solders due to poisoning considerations. However, within the last decade, microelectronics had made significant strides resulting in broad utilization and disposal of components containing leaded solders (Subramanian & Lee, 2003). Thus, health and environment matter have been taken seriously. Disposal of lead may spread into the air particle and may result in air pollution. Besides, effect of lead to human can be listed as it brings harm to foetus including brain damage or death, high blood pressure, digestive issues, nerve disorders and muscle and joint pain (Ervina & Marini, 2012).

Due to the risk imposed by the disposal of lead entering the food chain and affecting human health, the European countries and Japan have executed new environmental legislation. Some of the laws issued significant penalties to the electronic manufacturers that import leaded components into the countries. Based on the short time limits set by these countries for the changeover, vigorous research efforts to search for leadfree alternatives for electronic solders are ongoing all over the world (Subramanian & Lee, 2003).

Lead-based solders have been used for many years in the electronics industry with most common being 63% tin and 37% lead by weight referred to as Sn63Pb37. Mechanically and electrically lead-based solders make an excellent choice in the electronics industry but due to the environmental reasons, regulators now require the manufacturers to find suitable alternatives. The substitutes to Sn-Pb solders must satisfy various engineering and other criteria which includes similar properties to current alloys, same temperature range as Sn-Pb, same or better reliability and equal or lower cost, compatibility with standard finishes, ease of application with wetting properties similar to current Sn-Pb including fluidity and cohesive force and stability (Ervina & Marini, 2012). Lead-free solders must be able to resist thermal cycling, must have a coefficient of thermal expansion (CTE) that matches the joining components and have sufficient creep resistance to maintain thermomechanical loading in the longer periods in the field of use. Generally, materials used in lead free alternatives must be economical, readily available, and have no negative environmental impact now or in the future.

A lead-free substitute that satisfies all the criteria is referred to as a ‘drop in' substitute for Sn-Pb solder. Unfortunately, current manufacturers or researchers have not been able to find such a substitute, although they have come up with near solutions. The issue here is that if all the potential metals for lead free substitute were screened even on basic requirements such as melting point, cost, availability, toxicology, and chemical resistance, only very few will appear as possibilities. Among the various candidates, the Sn-Ag-Cu family of solder is the strongest candidate to become the standard lead-free solder followed closely by Bi, Sb, In, Zn, and Al. However, Bi and Sb are partially produced as by-products in lead manufacturing, therefore, strictly should not be considered (Herat, 2008). Research in Japan, Europe, and the United States indicates that Sn-Ag-Cu alloy is extremely stable and, accordingly, is considered able to meet globally acknowledged standards. Nonetheless, the compositions being recommended in Japan, Europe, and the United States have slight differences. Information obtained through simulations and high-precision scientific trials seem to call for a eutectic composition of around Sn-3.5Ag-0.7Cu (Wassink, 1989).

2.1.1 Traditional Pb-Sn Solders

Tin-lead (Sn-Pb) solders have been used in the electronics industry for decades. Lead is used in electronics due to its unique properties such as malleability, low melting point, excellent conductivity, and high resistance to corrosion. Besides, it is used to attach electronic components in Electrical and Electronic Equipment (EEE) to a printed circuit board (PCB) via soldering. The process involves exposing the electronic components and the PCB to high temperatures to melt the soldering alloys which then form an acceptable solder joint. The most common processes used for such operation are wave soldering and reflow. Wave soldering the electronic components are inserted or placed on the printed circuit board and is passed across a pumped wave molten solder which is held in a tank while reflow soldering attaches a surface mounted component to a circuit board, apply the solder paste, position the devices, and reflow the solder in a conveyorized oven (Herat, 2008).

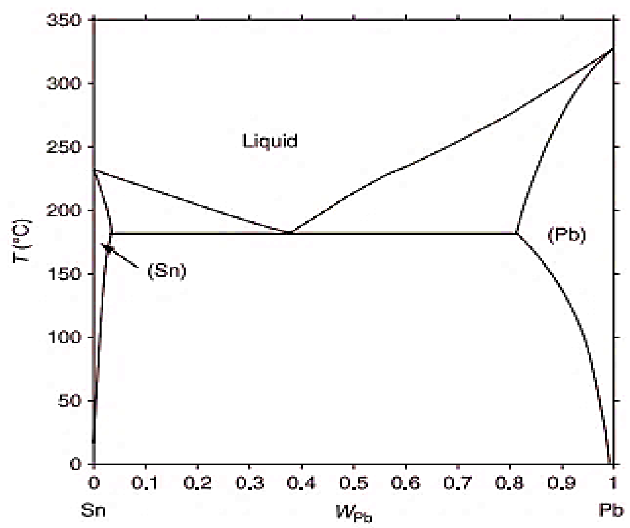


Figure 2.1: Sn-Pb phase diagram (Handwerker et.al, 2007).

As shown in Figure 2.1, Sn-Pb has low eutectic temperature of 183°C. Great strength and good ductility makes it can endure thermal cycling. Pb is an adequate solubility but it combines rapidly with Sn. In board level packaging the solder used is primarily 63Sn37Pb, a eutectic composition, or 60Sn-40Pb, a near eutectic composition. Since Sn-Pb is used as primary components of eutectic solders, Pb provides many technical advantages, in which Pb as an impurity in tin, even at levels as low as 0.1wt%, Pb prevents the transformation of white or beta (β) tin to alpha (α) tin upon cooling past 13°C. The transformation, if it occurs, results in a 26% increase in volume and causes loss of structural integrity to the tin (Ervina & Marini, 2012). Besides, Pb serves as a solvent metal, enabling the other joint constituents such as Sn and Cu to form intermetallic bonds rapidly by diffusing in the liquid state. Moreover, Sn-Pb is inexpensive. Also, for soldering, it needs simple equipment which is soldering iron and torch. Furthermore, Sn–Pb solders have a low melting temperature of 183°C for eutectic solder, which allows the use of a low reflow temperature in the electronic packaging process and ensures the reliability of the packages (Ma & Suhling, 2009).

2.1.2 Soldering Technologies

In year 1921, Ernst Sachs (founder of ERSA) was the first man who invented the first electric and mass-produces soldering iron for industry. Soldering is a metallurgical joining method using solder with a melting point of below 315°C as filler. Besides, soldering can be explained as any of various alloys fused and applied to the joint between metal objects to unite them without heating the objects to the melting point (Subramanian & Lee, 2003). Solder are used extensively in the electronics industry to physically hold assemblies together: they must allow expansion and contraction of the various components, transmit electrical signals, and dissipate any heat that is generated. The bonding action is accomplished by melting the solder material and allowing it to flow among and contact with components to be joined (which do not melt). Lastly, upon solidification solidification, it forms a physical bond with these components (Callister & Rethwisch, 2014).

2.1.3 Wave Soldering

In wave soldering method, the assembled PCB is passed over a molten solder wave with a speed of 5-10 cm/s. Solder alloy wets both the surfaces of the pins of the electronic components and the surfaces of the conductor substrates and solidifies between them forming a solder joint. A schematic representation of this method is shown in Figure 2.2. Unlike reflow soldering of Surface mount technology (SMT), the temperature profile of wave soldering cannot be controlled precisely during soldering operation and lead to undesired microstructures and possible cracks. Some surfaces on PCBs, which are not desired to come in contact with the solder such as previously soldered SMT components, are masked prior to this operation. This is called selective soldering (Anil, 2012).

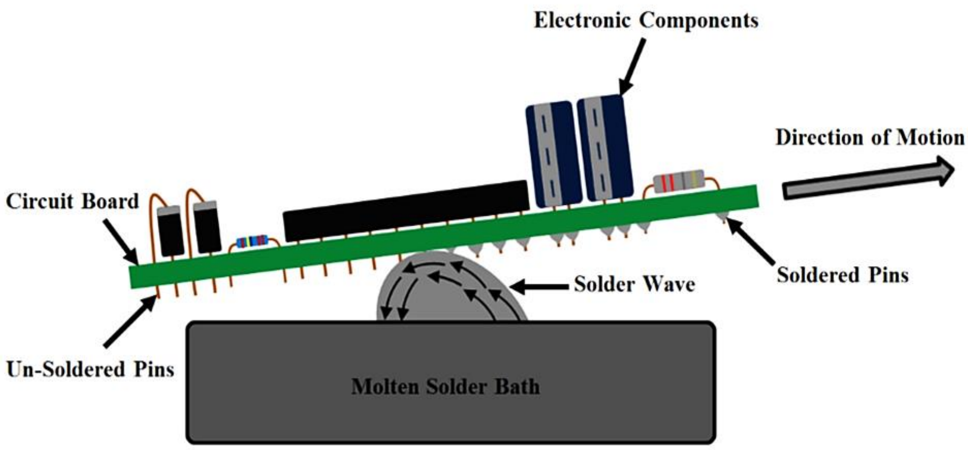


Figure 2.2: Wave soldering of a PCB (Anil, 2012).

2.1.4 Reflow Soldering

The main challenge on the reflow process to lead-free solder has a huge impact with the higher melting point of the Sn-Ag-Cu alloy. Most lead-free solder pastes that were initially available had the same flux formulation that was used for Sn-Pb solder pastes, which lead to reflow issues such as excessive voids caused by the flux not being rated to the higher lead-free soldering temperatures. Since then there has been major development in the flux formulation for lead-free solder pastes. The newer generation solder pastes have fluxes with higher activation temperatures to account for the higher soak and reflow temperatures required for the lead free solder (Bath, 2007).

In reflow soldering, the solder paste must be heated sufficiently above its melting points and become completely molten to melt the balls of BGA components, causing them to collapse and form reliable joint. In the case of components with leads, the solder paste must wet the plating on component leads to form the desired heel and toe fillets. However, for lead free reflow requires relatively high temperature because of the high melting range of typical leadfree solder. Lead free reflow soldering requires a narrow temperature range to produce reliable joints without damaging components. Solder joint formation depends on time and temperature which are reflected in the reflow profile (Corporation, 2016). Figure 2.3 showed the schematic of reflow oven.

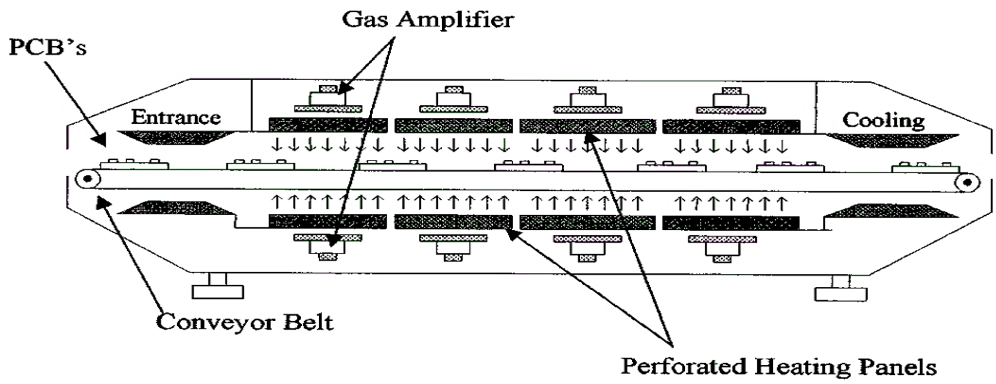


Figure 2.3:Schematic of reflow oven (Taverez & Gonzalez, 2003).

The temperature profile that should be achieved during reflow soldering is shown in Figure 2.4. The reflow profile for Sn-Ag-Cu solder paste can be categorised into 4 stages which is preheat stage, soak stage, reflow stage and cool down stage. During the preheat stage the PCB and components are heated up gradually from room temperature to about 170°C. The critical parameter in the preheat stage is the ramp rate which controlled between 1-3°C/sec. Higher ramp rates may cause thermal shock to the PCB and the components while rapid heating could also result in flux splattering leading to solder balling.

In soaking stage, also known as the dry-out or pre-reflow stage, the temperature is maintained between 170 to 220°C for an extended period, typically about 60 seconds for a Ramp-to-Peak profile and 120 seconds for a Ramp-Soak-Spike profile. During this stage, the activated flux cleans the surface oxides on the solder particles, component leads and PCB pads. Longer soak times could cause the fluxes to breakdown prior to reflow, leading to solderability issues (Bath, 2007).

During reflow stage**,** the solder particles melt and form a bond between the PCB and component terminations. Peak temperature usually in the range of 235°C- 250°C at the solder joint with time above liquidus ranging between 45-75 seconds with adequate time for wetting and lead to formation of a quality solder joint. Higher peak temperatures (typically > 250°C) may result in flux charring and potential PCB/component damage. Longer reflow times should be avoided as it can result in excessive Intermetallic Compounds (IMC) formation (Anil, 2012). Cooling rate of the joints is critical since ultimate microstructure of the solder will be determined at this step. A rapid cool down would be preferred which helps form a finer grain structure (typically 3 to 4°C/sec). Slow cooling will result in a larger grain size that may have poor fatigue resistance (Bath, 2007).

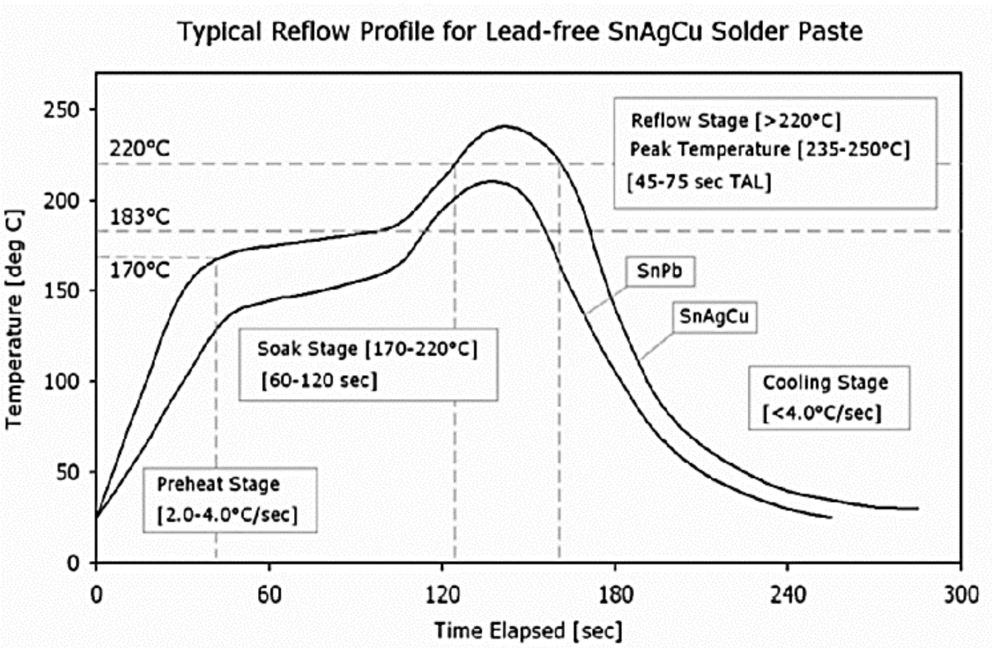


Figure 2.4: Schematic of reflow oven (Taverez & Gonzalez, 2003).

2.2 Lead-Free Solder

Lead-free solder is solder that contains less than 0.2% lead. Lead-free solder has different properties and appearance than lead based solder. Lead-free solder is dull and grainy and requires hotter soldering temperatures. Currently, the used of leadfree solder alloy of Sn-Ag-Cu (SAC) is the most popular solder composition to replace lead solder.

Solder alloy selection involves the consideration of several critical factors such as availability, cost, toxicity, process compatibility and different performance metrics, such as surface tension, plastic range, wettability, fatigue characteristics and liquidus temperature.

Sn-Ag-Cu family of alloys are obtaining wide acceptance within the electronics industry, as a viable replacement for eutectic Sn-Pb solder. Lately, the Sn-Ag-Cu alloys used for surface mount assembly process have compositions containing 3.0-4.0wt % Ag and 0.5-0.9wt % Cu with remainder tin. The assembly process is virtually identical for all the compositions within that range. They all have a small pasty range of about < 3°C with the liquidus ranging between 217°C and 220°C. Currently Sn3.0Ag0.5Cu (SAC305) and Sn3.8Ag0.7Cu (SAC387) are the main solder paste alloys used for lead-free surface mount assembly. The Sn4.0Ag0.5Cu (SAC405) and Sn3.0Ag0.5Cu (SAC305) alloys are mainly used for lead-free ball grid array (BGA) spheres. Studies conducted by IPC Solder Products Value Council showed no significant difference in reliability between the three different Sn-Ag-Cu solders paste alloys (SAC305, SAC387 and SAC405) with the recommendation to use SAC305 as a general lead-free solder paste alloy replacement. (Bath, 2007)

Over the years, great number of Pb-free solder alloys have been introduced and summarized. The solder alloys are binary, ternary and some are even quaternary alloys. A very large number of these solder alloys are based on Sn being the primary or major element. Followed by In and Bi are also the major constituents. Some of the Pb-free solder alloys compositions to replace Sn-Pb are Sn-Zn, Sn-Zn-Bi, Sn-Ag, Sn-Ag-Cu and many more (Subramanian and Lee,2014). The eutectic temperature of the stated solder alloys compositions was tabulated as in Table 2.1.

Table 2.1: Some Tin-based Lead-free solder alloys and their melting temperatures (Subramanian and Lee,2014).

Alloy Melting Composition Range (wt.%)	Melting Range (°C)
Sn-58Bi	138
Sn-52In	118
Sn-9Zn	198.5
Sn-8Zn-3Bi	189–199
Sn-20Bi-10In	143–193
Sn-3.5Ag	221
Sn-0.7Cu	227
Sn-3.8Ag-0.7Cu	217
Sn-5Sb	232–240
Sn-80Au	280

2.2.1 Sn-Ag-Cu (SAC) Alloy

Leaded solders are used in electronic assembly industry for joining purpose, because of their advantages like low melting temperature, good wettability, strength, ductility, reliability, product performance and cost. But due to its hazardous effect towards human health and environment, material science community such as researchers and manufactures had developed new alternatives to replace the Sn-Pb solders.

Of the many lead-free solder series proposed in the last decade or so, SAC series alloys have emerged as the most widely accepted. The most popular SAC are the near eutectic SAC alloys, which consist of 3.0–4.0% of Ag and 0.51.0% of copper. The melting point of these near eutectic SAC alloys is 217 °C, which is lower than the 96.5Sn–3.5Ag binary eutectic alloy at 221 °C. In the SAC system, the addition of Cu both lowers the melting temperature and improves the wettability. Figure 2.5 is the top view (2-D) of the ternary phase diagram of Sn–Ag–Cu. The area indicated in the red box is the near eutectic region. Most of the SAC alloy compositions currently in the market are within this region. In SAC alloys, the formation of intermetallic compounds between the primary elements Sn and Ag, and Cu affect all the properties of the alloys (Ma & Suhling, 2009).

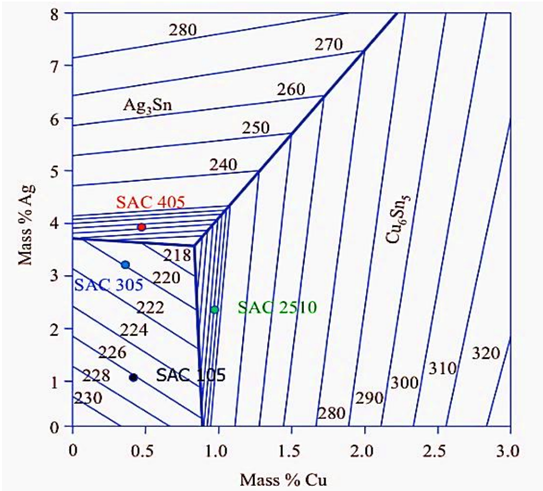


Figure 2.5: Ternary Diagram of Tin-Silver-Copper (Ma & Suhling, 2009).

According to the binary phase diagram shown in Figure 2.6, there are three possible intermetallic compounds that may be formed. Ag_3Sn forms due to the reaction between Sn and Ag as shown in Figure 2.6(a). With the help of microstructural observation, the presence of fine Ag_3Sn needles and beta Sn matrix and the interfacial bonding between these two phases results in excellent mechanical properties. Ag_3Sn needles are brittle in nature due to which liability of the solder degrades. Besides, Cu_6Sn_5 forms due to the Sn and Cu reaction as shown in Figure 2.6(b), but Cu_3Sn will not form at the eutectic point unless the Cu content is high enough for the formation of Cu_3Sn at higher temperatures, so in bulk specimens Cu_3Sn is not present (Mishra, 2014).

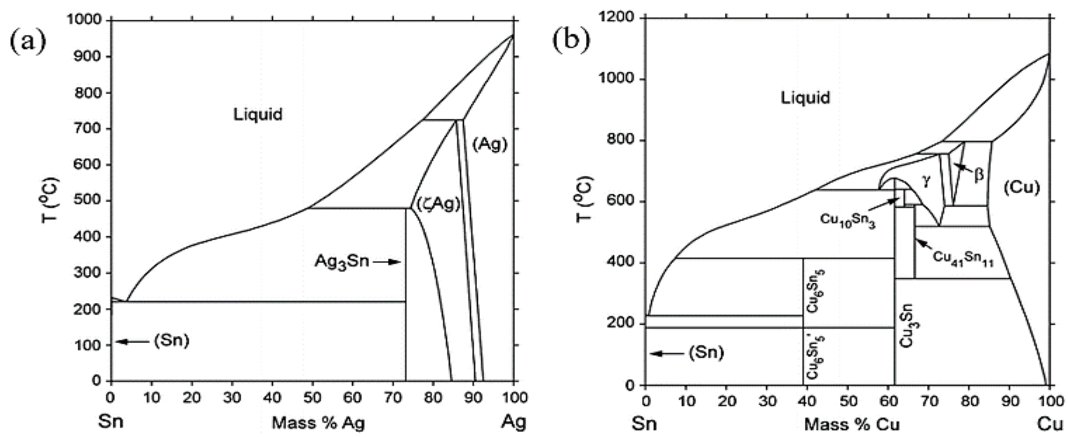


Figure 2.6: Binary phase diagram of (a) Sn–Ag and (b) Sn–Cu (Ma & Suhling, 2009).

2.3 Requirements of Pb-free Solders

When trying to identify an alternative to the Sn-Pb solders, it is important to ensure that the properties of the replacement solder are comparable to or superior than Sn-Pb solders. There are strict performance requirements for solder alloys used in microelectronics. In general, the solder alloy must meet the expected levels of electrical and mechanical performances and must also have the desired melting temperature. It must adequately wet common printed circuit board (PCB), form inspectable solder joints, allow high volume soldering and rework of defective joints, provide reliable solder joints under service conditions and must not significantly increase assembly cost. Some performance characteristics of the solder should be met. Firstly, it is non-toxic. Besides, it has a narrow paste range in which the temperature range between solidus and liquidus, where alloy is part solid and part liquid. When the pasty range is narrow, the solder requires a shorter time to solidify. Narrow paste range is to prevent rupture during wave soldering. Thus, the criteria set by NIST (National Institute of Standards and Technology), the acceptance level is <30℃. (Ervina & Marini, 2012).

In addition, acceptable melting and processing temperature (soldering temperature) are one of the most sensitive parameters for the quality of soldered joints. The melting temperature of Sn-Pb eutectic alloy is 183℃, and the typical soldering temperatures are 230℃ and 250℃ for reflow and wave soldering, respectively. The temperature margin beyond the melting temperature of solder is 50℃ for reflow. The melting point of a solder should be low enough to avoid thermal damage to the assembly being soldered and high enough for the solder joint to bear the operating temperatures (Ervina & Marini, 2012). Furthermore, it should be easily available and affordable where there is adequate supplies or reserves of candidate metals. Moreover, the solder must perform good wetting. The bond between the solder and the base metal is formed only when the solder wets the base metal properly. A high Sn content ensures this and thus forms a strong bond (Puttlitz & Stalter, 2004). Lastly, it should form reliable joint. Reliability of a solder alloy is mainly dependent on the coefficient of thermal expansion, elastic modulus, yield strength, shear strength, fatigue and creep behaviour of the alloy.

2.4 Severe Plastic Deformation (SPD)

There are several factors which determine the physical and mechanical properties of metals, but basically average grain size plays a very significant role. Hall and Petch found a relationship between yield strength and the grain size in the early 1950s (Hegedűs & Gubicza, 2013). In terms of yield stress, Hall-Petch strengthening is a phenomenon occurring due to the present of grain boundaries and dislocations that act as obstacles for dislocation movement which leads to strengthening effect (Ramesh et.al. 2017). Therefore, the formula describing the correlation between the grain size of a polycrystalline material and its yield strength is called Hall–Petch-equation:

$$\sigma_y = \sigma_0 + (K / d^{1/2}) \quad (2.1)$$

where, σ_y is the yield stress, σ_0 is the frictional stress opposing the dislocation motion, K is the Hall–Petch slope and d is the grain diameter.

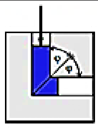
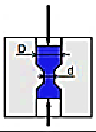
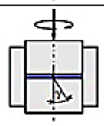
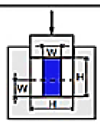
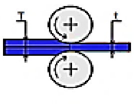
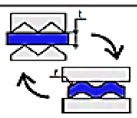
From this equation, strength of material is inversely proportional to grain diameter square root with σ_o and K being materials constants. Thus, yield strength increases with the reduction of the grain size. However, previous studies have shown that there is a critical grain size under which no additional strengthening occurs (Ramesh et.al. 2017).

High strength materials can be processed by refining the grain size into ultrafine grain (UFG) or nanocrystalline regimes. UFG material refer to polycrystals having very small grains with average grain sizes less than ~1µm with reference to the characteristics of polycrystalline materials. For bulk UFG materials, there are the additional requirements of reasonably equiaxed microstructures, fairly homogeneous and with a majority of grain boundaries having high angles of misorientation. The presence of a high fraction of high-angle grain boundaries (HAGB) is vital for achieving advanced and unique properties (Valiev & Langdon,2006). At the same, time polycrystalline materials having grain size smaller than ~ 100 nm are termed as nanocrystalline materials (Hegedűs & Gubicza, 2013).

2.4.1 Process in Severe Plastic Deformation (SPD)

SPD processing refers to various experimental procedures of metal forming that may be used to impose very high strains on materials which lead to the exceptional grain refinement (Rosochowski & Olejnik, 2009). SPD methods are used to change coarse grain metals and alloys into ultrafine grained (UFG) materials. By possessing improved mechanical and physical properties after obtaining UFG materials, it was then destined for a vast commercial use. The major SPD processes employed for grain refinement of bulk materials are summarized in Table 2.2 with schematic configurations and the attainable plastic strain.

Table 2.2: Schematic representation of major SPD processes (Rosochowski, 2005).

Process name	Schematic representation	Equivalent plastic strain
Equal channel angular extrusion (ECAE), Segal, 1977		$\varepsilon = n\frac{2}{\sqrt{3}}\cot\varphi$
Cyclic extrusion-compression (CEC), J. and M Richert, Zasadzinski, Korbel, 1979		$\varepsilon = n4\ln\left(\frac{D}{d}\right)$
High-pressure torsion (HPT), Valiev et al., 1989		$\varepsilon = \frac{tg\gamma}{\sqrt{3}}$
Cyclic closed-die forging (CCDF), Ghosh, 1988		$\varepsilon = n\frac{2}{\sqrt{3}}\ln\left(\frac{H}{W}\right)$
Accumulative roll-bonding (ARB), Saito, Tsuji, Utsunomiya, Sakai, 1998		$\varepsilon = n\frac{2}{\sqrt{3}}\ln\left(\frac{T}{t}\right)$
Repetitive corrugation and straightening (RCS), Zhu, Lowe, Jiang, Huang, 2001		$\varepsilon = n\frac{4}{\sqrt{3}}\ln\left(\frac{r+t}{r+0.5t}\right)$

2.4.2 Grain refinement in Severe Plastic Deformation (SPD)

Severe plastic deformation (SPD) is one of the methods to acquire very fine crystalline structure in different bulk metals and alloys in which they have different crystallographic structure. SPD lead to the formation of micro meter and sub-micro meter sized sub-grains in the originally coarse grain materials. Therefore, the enhanced mechanical performance is observed. The mechanism responsible for this effect is still under investigation, however, it is believed that short and long-range intersecting shear bands produced by plastic deformation play a major role at grain subdivision and local dynamic recovery and recrystallization processes contribute to grain refinement. Sufficiently large deformation leads to a distinct structure of dislocation-free and highly misoriented fine grains (Rosochowski, 2005).

The vital parameters which are concerned when defining a submicron grain structure are the average spacing of high angle grain boundaries (HAGB) and proportion of HAGB area. The structural changes produced by SPD indicated that the improvement of the mechanical properties in metals or alloys. The effects reported include increased in hardness and yield stress, both presenting tendency to saturation. However, the backside of ultrafine grained structure materials is their limited ductility. Some other research revealed increased ductility and toughness as well as improved dumping and physical properties. The fine grain structure of UFG materials obtained by SPD leads to superplastic behaviour of these materials at lower temperatures and yet with higher deformation rates.

Various aspects of structural changes caused by SPD have been the research goals in laboratories worldwide. Hundreds of papers are published each year in distinguished journals on UFG structure development and properties evaluation. Today the most effort is paid to the study of the mechanics of material flow and grain subdivision when low strains ($\mathcal{E}_v < 3$) and high strains ($\mathcal{E}_v > 3$) are considering at the SPD (Zrnik, & Mamuzic, 2008).

At low strain the orientation splitting and micro-shear banding are mechanisms which contributes to grain subdivision and cell bands structure dominates within deformed bands. When medium and higher strain are effective the lamellar HAGB structure, ribbon grains and formation of submicron grains structure dominates in deformed materials (Veena et.al. 2017).

The mechanism of grain refinement by SPD is still under researched. Nonetheless, the ordinary view is that refinement results from the non-uniform distribution of dislocations. Thus, cell structures within the original coarse grains tend to form. Another point of view emphasises that the role of shear bands (which is thin bands of localised shear deformation) where different bands cross each other to create a pattern resembling a chessboard. The distance between shear bands is very small and cause the creation of dislocation cells having sub-micrometre dimensions. Initially, the dislocation cells do not have very different crystallographic orientation from their neighbours are referred to as sub-grains. After that, they treated as distinct grains only while their misorientation angle exceeds 15°. To achieve this, severe plastic deformation is required. The average grain size of the UFG metals produced depends on the SPD parameters (strain, temperature, pressure) and on the material used; for pure metals, grains tend to be larger, e.g. 0.6 μm for aluminium 1070, whereas alloys respond better, e.g. 0.2 μm for Al 5083 under similar processing conditions. Sometimes, the average grain size achieved by SPD can reach the nanometre level (Rosochowski & Olejnik, 2009).

The repetition of the straining process is required to obtain a large strain and desired structural changes. When studying microstructure in SPD materials, the evolution and the character of the new interfaces appears as very important property with respect to evaluation their influence on the mechanical properties. Considering the deformation processing condition through the heterogeneity in microstructure formation was often observed across the bulk specimen in dependence of the strain introduced. Anticipating commercialisation attempts, this work addresses the processing issues. First, a choice of major SPD processes will be presented, but not analysed in detail. Later in the paper, the contribution to ductility improvement of severely deformed aluminium will be presented shortly.

2.5 Equal Channel Angular Pressing (ECAP)

ECAP is based on simple shear taking place in a thin layer at the crossing plane of the equal channels. The process has attracted considerable interest as a method to refine microstructure by deformation processing. ECAP process involves simple shear deformation that is achieved by pressing the work piece through a die containing two channels of equal cross-section that meet at a predetermined angle. Deformation occurs in the immediate vicinity of the plane lying at the intersection of two channels. The effective strain imposed on the work piece increases with decreasing channel angle.

2.5.1 Theory of Equal Channel Angular Pressing (ECAP)

The process of equal-channel angular pressing (ECAP), also known as equal-channel angular extrusion. Equal channel angular pressing (ECAP) were developed by Segal (Srinivas et al., 2013). Equal-channel angular pressing (ECAP) is a processing method in which a metal is subjected to an intense plastic straining through simple shear without any corresponding change in the cross-sectional dimensions of the sample. This procedure may be used to introduce an ultrafine grain size into polycrystalline materials. The principles of the ECAP process are examined with reference to the distortions introduced into a sample as it passes through an ECAP die and especially the effect of rotating the sample between consecutive presses. Examples are presented showing the microstructure introduced by ECAP and the consequent superplastic ductilities that may be attained at very rapid strain rates (Iwahashi et.al, 1996). Figure 2.7 showed the schematic representation of ECAP processes.

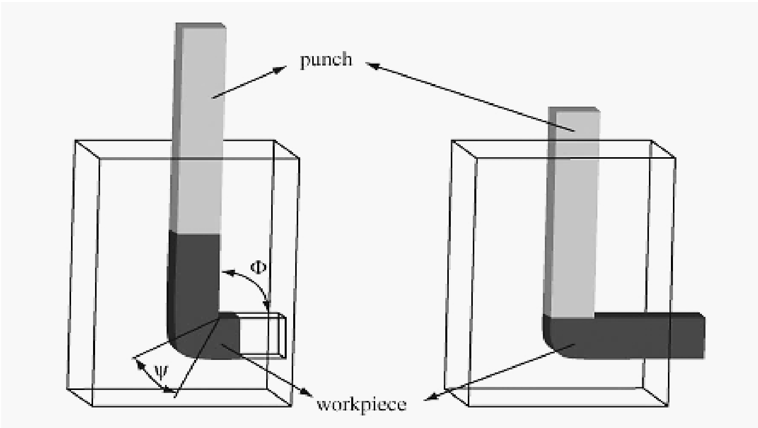


Figure 2.7: Schematic representation of ECAP processes (Rosochowski, 2005).

Equal-Channel Angular Pressing (ECAP) is the most prominent SPD technique, due to its capability of producing bulk workpieces free of porosity and inclusions. There has been also attempts to adapt this technique to continuous processing, enabling the production of materials in a large scale, efficient and cost effectively manner. When ECAP workpiece is extruded through two intersecting channels with the same cross sections. The angle between the channels is defined as Φ as shown in Figure 2.7. One important advantage of ECAP process is that it can be repeated several times without changing the workpiece dimensions and the applied strain can be increased to any level. ECAP allies severe strains and a simple shear deformation mode that contribute to strong, sometimes unusual effects on properties and structure.

An important advantage of ECAP process is that a large amount of simple shear deformation can be imposed in single or multiple processing steps without changing the cross-section of the work piece. In spite of its invention in the early 1980s, the process is yet confined to the laboratory due to problems associated with die design. Very few have extruded difficult-to-work materials like titanium alloys, magnesium alloys and have succeeded to a certain extent. Even in laboratory scale processing, problems arise when