FABRICATION AND CHARACTERIZATION OF LEAD FREE PEWTER ALLOYS

by

CHOU SOKLIN

Thesis submitted in fulfilment of the

requirement for the degree of

Master of Science

August 2011

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled **“FABRICATION AND CHARACTERIZATION OF LEAD FREE PEWTER ALLOYS”**. 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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ACKNOWLEDGEMENTS

First and foremost, I would like to thank to my scholarship sponsor AUN/SEED.Net for its financial support during this master program. Meanwhile, my grateful thanks also go to the lecturers, administrative and technical staffs of School of Materials and Mineral Resources Engineering (SMMRE), Universiti Sains Malaysia (USM) for their cooperation.

Second, I would like to take this opportunity to express my deepest gratitude to my respectful and helpful supervisor, Dr. Nurulakmal Mohd Sharif, Dr. Shah Rizal Bin Kasim, and Dr. Projjal Basu for the support, guidance and inspiration throughout two years to complete the master research project. The supervision, valuable comments, constructive advices and inputs given truly help the progression and smoothness of the project.

Last but not least, I would like to thank all my friends for the wise idea, invaluable supports and suggestions throughout the project.

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LIST OF SYMBOLS

Symbol	**Description**
ρ	Density
T_m	Melting temperature
σ_o	Yield stress
σ_1	Friction stress
K	Locking parameter
D	Grain diameter
%CW	Percent cold work
λ	Wave length
m	Mass of sample
v	Volume of sample
kgf	Kilogram force
s	second
P	Load
2θ	Diffraction angle

LIST OF ABBREVIATIONS

BS	British standard
HV	Micro vicker hardness number
UTS	Ultimate tensile strength
DSC	Differential scanning calorimetry
XRF	X-ray fluorescence
XRD	X-ray diffraction
OM	Optical microscope
SEM	Scanning electron microscopy
EDX	Energy dispersive x-ray
CPA	Commercial pewter alloy

FABRIKASI DAN PENCIRIAN ALOI PIUTER BEBAS PLUMBUM

ABSTRAK

Aloi piuter bebas plumbum dengan pelbagai komposisi aloi binari Sn-(1-3%wt)Cu, Sn-(1-3%wt)Al dan aloi ternari Sn-(1-3%wt)Cu-(5-7%wt)Sb disediakan melalui proses pencampuran bahan mentah,peleburan, penghomogenan dan penuangan ke dalam acuan keluli lembut. Fasa yang hadir bagi sampel aloi dicirikan melalui analisis pembelaun sinar-X (XRD) dan sifat terma pula melalui kalorimeter imbasan kebezaan (DSC). Mikrostruktur aloi dikaji menggunakan mikroskop optik (OM), mikroskop imbasan elektron pancaran medan (FESEM) dan analisis sebaran tenaga sinar-X (EDX). Sifat mekanikal dan fizikal aloi piuter bebas plumbum dicirikan melalui ujian ketumpatan, kekerasan, tegangan, kebolehtuangan dan pemerhatian terhadap permukaan aloi terhasil. Perbandingan dilakukan menggunakan aloi piuter komersial (CPA). Analisis XRD, FESEM dan EDX terhadap aloi mendapati pembentukan fasa antara logam mempengaruhi sifat kekerasan aloi berasaskan Sn. Kewujudan kompaun antara logam Cu_6Sn_5 telah meningkatkan kekerasan aloi piuter S-Cu. Selain itu, pembentukan kompaun fasa antara logam Cu_6Sb_5 dan SbSn telah meningkatkan kekerasan aloi piuter Sn-Cu-Sb. Walaubagaimanapun, kewujudan fasa antara logam ini telah merosotkan pemanjangan aloi piuter. Analisis DSC, FESEM dan EDX terhadap aloi piuter Sn-Al telah menunjukkan pembentukan fasa eutektik struktur Al+βSn membawa peningkatan kekerasan dan kekuatan aloi tetapi secara telah merendahkan sifat kemulurannya. Kandungan Sn yang tinggi di dalam aloi pewter bebas plumbum meningkatkan jarak kebendaliran sementara penambahan Cu dan Sb telah meninggikan kecerahan aloi terhasil. Aloi piuter bebas plumbum 92Sn-3Cu-5Sb memberikan nilai kekerasan dan kekuatan paling tinggi berbanding

komposisi aloi piuter bebas plumbum yang lain. Aloi ini lebih sesuai untuk penghasilan objek bersaiz besar yang memerlukan kekuatan dan kekerasan yang tinggi untuk menampung beban ketika digunakan. Secara normal, objek kecil memerlukan sifat kebolehtuangan yang tinggi bagi menghasilkan bentuk kompleks. Oleh sebab itu, aloi 99Sn-1Cu dan 99Sn-1Al didapati lebih sesuai bagi penghasilan objek kecil kerana sifat kebolehtuangannya yang tinggi berbanding aloi lain.

FABRICATION AND CHARACTERIZATION OF LEAD FREE PEWTER ALLOY

ABSTACT

Lead free pewter alloys with various composition Sn-(1-3%wt)Cu and Sn-(1-3%wt)Al binary alloys and Sn-(1-3%wt)Cu-(5-7%wt)Sb ternary alloys were prepared by mixing raw materials, melting, homogenizing, and casting in a mild steel die. The alloy samples were characterized for phase identification via X-ray diffraction (XRD) analysis, and thermal behaviour via differential scanning calorimetry (DSC). Microstructures of the alloys were studied by using optical microscope (OM), field emission scanning electron microscopy (FESEM) and energy dispersive X-ray (EDX) analysis. The mechanical and physical properties of lead free pewter alloys were characterized via density test, hardness test, tensile test, castability test and surface appearance observation. A comparison was made by using commercial pewter alloy (CPA). XRD, FESEM, and EDX analysis of the alloys indicated the formation of intermetallic phase which may be responsible for the required hardening of Sn-based alloys. The intermetallic compound of Cu_6Sn_5 found in Sn-Cu pewter alloys resulted in higher hardness. On the other hand, formation of intermetallic compound of Cu_6Sb_5 and SbSn increase the hardness of Sn-Cu-Sb pewter alloys. However, these intermetallic compounds were found to deteriorate elongation of pewter alloys. DSC, FESEM, and EDX analysis of Sn-Al pewter alloys showed the formation of eutectic structure of Al+βSn led to an increase in hardness and strength of these alloys but deteriorates the ductility. A higher amount of Sn in lead free pewter alloys tends to increase the fluidity length while the addition of Cu and Sb in alloy increases its brightness. The lead free pewter alloy of

92Sn-3Cu-5Sb has higher hardness and strength than others. Hence, this alloy is more suitable to produce large objects that require higher strength and hardness to sustain loading during handling and use. Normally, small object requires high castability to produce a complex shape. Thus, 99Sn-1Cu and 99Sn-1Al alloys are more suitable to produce small objects since they have a higher castability than that of other alloys.

CHAPTER ONE

INTRODUCTION

1.1 Introduction

Tin is the primary element in pewter. According to the yearbook of Malaysian Chamber of Mines (2006) and Habashi (1997), the largest tin mines are mostly in Asia. The most important ore-supplying countries in the Asia are Indonesia, Malaysia and followed by China and only Indonesia and China after about 1994. Currently, the Malaysian Smelting Corporation (MSC) group is one of the largest integrated producers of tin metal and tin-based products in the world. In ASEAN countries for instance, the major consumption of tin metal is for producing tin solders, tin cans and pewter.

Pewter is an alloy containing over 90 per cent tin and it is widely used for utensils, such as tankards and goblets, or decorative items like plates and candlesticks or costume jewellery. Pewter is known to have been used extensively in Roman times and it is reported that Pliny, writing in the first century AD, stated that a tin vessel improved the taste of wine. Originally, the term of ‘pewter’ was applied to any metal with a high proportion of tin, especially a tin-lead alloy.

The history of pewter can be traced, especially from ecclesiastical artefacts, till the fourteenth century when pewter began to replace pottery and wooden items for tableware and other household purpose. To protect the craft secrets and to maintain high production standards, the Worshipful Company of Pewterers was established in London in 1348. In the eighteenth, century a new version of pewter known as Britannia metal was developed. This Britannia metal had a bright finish and contained a small amount of antimony but no lead. The behaviour property of Britannia metal is harder than common pewter and since it contained no lead it did not tarnish with age (Barry and Thwaites, 1983).

A European pewter sheet would contain 92% tin, 2% copper, and 6% antimony. Asian pewter, produced mostly in Malaysia, Singapore, and Thailand, contains a higher percentage of tin, usually 97.5% tin, 1% copper, and 1.5% antimony. This makes the alloy slightly softer (Hull, 1992).

1.2 Problem Statement

Lead is a non-essential element that occurs naturally in the environment. Many of its physical and chemical properties such as softness, malleability, poor conductibility, ductility, and resistance to corrosion, have favoured that man uses lead and lead compounds since ancient times for a great variety of applications (García-Lestón et al., 2010).

In the past, pewter alloys were mixed with varying amounts of lead, but now lead content in pewter is strictly limited, principally on health grounds. Health hazards of lead have led modern pewter to contain little or no lead, which has been replaced with antimony. Old pewters with higher lead content are tarnish faster, heavier, and oxidation gives them a darker silver-grey colour which is usually undesirable (Young and Shane, 1985). According to Lewis et al., (1960), although until recent times the usual hardener for tin was lead, the alloy so produced has the disadvantage that it rather rapidly loses its brilliant luster and goes grey or black and it also suffers from being too susceptible to corrosion.

Besides the issue of toxicity, lead containing pewter alloys which are used for solder would cause reliability problems. According to Shen et al., (2006), considerations on the environment protection and health hazards of Sn-Pb solders used in electronic packaging have promoted the development for lead-free solder alternative in electronic industry. The present of lead in solder is considered world wide to be very dangerous for the environment due to the huge number of printed circuits and electronic devices needing to be recycled for dumps (Tao, 2008).

Since the use of lead has been proven a major hazard to the environment and human health, the only possible solution is the elimination of lead from the existing composition of pewter alloy. As such, not only is it important to develop a lead free pewter alloy, but also to determine the effect of absence of lead in future pewter alloy compositions.

Modern pewter is composed of about 92 per cent tin with normally about 6 to 7 per cent antimony and 1 to 2 per cent copper (Barry and Thwaites, 1983).

Table 1 shows the compositions of the chemical composition of pewter alloys covered in BS 5140. In commercial alloys, some bismuth and silver or other elements may also be present.

Table 1. 1: Chemical composition of pewter (BS 5140, 1973)

Tin	Antimony		Copper		Lead	Cadmium
	min.(%)	max.(%)	min.(%)	max.(%)	max.(%)	max.(%)
Balance but not less than 91%	5.0	7.0	1.0	2.5	0.5	0.05
Balance but not less than 93%	3.0	5.0	1.0	2.5	0.5	0.05

1.3 Objective

In this work, an attempt was made to develop and characterize properties of lead free pewter alloys with various compositions in order to meet their high performance requirements. The objectives can be briefed as the following:

- Fabrication of lead free pewter alloys with various compositions of Sn-(1-3%wt)Cu, Sn-(1-3%wt)Al, and Sn-(1-3%wt)Cu-(5-7%wt)Sb in order to get the appropriate properties that can be applicable in various applications by using stir casting route.
- Characterization of the morphology, microstructures, physical properties and mechanical properties of lead free pewter alloys with different compositions of Sn-(1-3%wt)Cu, Sn-(1-3%wt)Al, and Sn-(1-3%wt)Cu-(5-7%wt)Sb.
- To compare results against that of commercial pewter alloy.

1.4 Scope of Research

In this project, the commercial pewter alloys were characterized by using x-ray fluorescence (XRF) analysis technique to determine their compositions. Melting temperature of commercial pewter alloys was measured by using differential scanning calorimetry (DSC). Hardness of commercial pewter alloys was determined by using Vickers microhardness tester. Castability test was conducted to observe fluidity of pewter alloys. Surface appearance of commercial pewter alloys was observed as well.

Lead free pewter alloy samples were fabricated with various ratios of raw materials, Sn-(1-3%wt)Cu, Sn-(1-3%wt)Al, and Sn-(1-3%wt)Cu-(1-7%wt)Sb, in order to get the desired properties that can be applicable in various applications by using stir casting route. These compositions were chosen based on BS 5140 pewter alloys as shown in Table 1.1.

The solid lead free pewter alloy samples were characterized through X-rays diffraction (XRD) for phase identification, the melting temperature of binary and ternary lead free pewter alloys was measured by using differential scanning calorimetry (DSC), optical micrograph (OM) for morphology, and scanning electron microscope (SEM) for morphology and microstructure analysis. The mechanical and physical properties of lead free pewter alloys were evaluated. Density of each lead free pewter alloy samples was measured by using digital density meter. Hardness of lead free pewter alloys was determined by using Vickers microhardness tester, tensile test was conducted to determine strength, modulus, and ductile of lead free pewter alloys. Castability test was done to observe fluidity of lead free pewter alloys, and surface appearance was observed.

The properties of lead free pewter alloys were then compared against the properties of commercial pewter alloys.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

In this chapter, pewter alloy is introduced with its history and development. The review of fundamental of metals and alloys will be discussed, including their physical and mechanical properties. Then, the strengthening mechanism in metal alloys and phase diagram of pewter alloy are also explained. Lastly, the applications of pewter alloys will also be described.

2.2 Introduction to Pewter Alloys

Pewter is a malleable metal alloy, traditionally 85–99% tin, with the remainder consisting of copper, antimony, and lead. Copper and antimony act as hardeners while lead is common in the lower grades of pewter, which have a bluish tint (Campbell, 2006). Pewter contained lead will become very dark with age. While this appeals to some, many others prefer the bright appearance attainable with modern pewter, in which tin is mixed with antimony and copper (Hedges, 1960).

2.2.1 History and Previous Work of Pewter Alloys

Pewter is known to have been used extensively in Roman times. It is reported that Pliny, writing in the first century AD, stated that a tin vessel improved the taste of wine. Originally, the term of ‘pewter’ was applied to any metal with a high proportion of tin, particularly a tin-lead alloy (Barry and Thwaites, 1983).

Before fifteen century, pewter was made by mixing of tin and lead. The idea of mixing these mixtures was combining the brightness, lightness, and rigidity of tin with the greater toughness and malleability of lead in order to obtain excellent and desirable properties of pewter alloys that can be applicable in vessels of Roman, dish, bowl, candlestick, communion cup, spice box, and so on (Bell, 2008).

Most of the thirty-six pewter items were found to have been made from high quality tin-rich alloys with low lead content, hardened with a small amount (0.5–3.0%) of copper; these were thought to be from the later part of 13^{th} to 16^{th}. Three items, one with the highest copper content of all the alloys, were thought to be from the earlier part of 13^{th} to 16^{th}. Five items with up to 2% of copper hardener but with lead levels up to 26.5% were thought to be of English 13^{th}-16th century pewter flatware (Brownsword and Pitt, 1984).

From 1780 to1880, pewter objects played an important role in everyday life at virtually every level of society. Millions upon millions of items of pewter were fabricated for eating, drinking, lighting, and other uses until the second half of the nineteenth century.

Pewter was made in different grades, some of which, like Roman pewter, had an unhealthy lead content. Consumers in the eighteenth and early nineteenth century observed London pewter as the best in the world (Witkowski, 1994).

2.2.2 Lead Free Pewter Alloys

In Greece, tin-copper-lead bronze alloys were quite common during the Archaic, Classical and Hellenistic periods. The lead concentrations varied, with the Hellenistic average lead content being over 13%, although in specific up to 30% lead has been found. Tin-lead solder alloy is used for sealing and joining metals. The different uses of the alloy define the composition, which is ranges from 38 to 98% lead. Another type of tin-lead alloy is pewter. The variable composition of tin-lead pewter alloy was influenced, among other factors, by the relative prices and the availability of the two metals and also by the usual practice of remelting old pieces.

Modern pewters must contain at least 90% tin and be alloyed with copper, antimony, or bismuth to be considered a pewter. Lead is commonly no longer permitted to be an alloying element. Older pewters with higher lead content are heavier, tarnish faster, and oxidation gives them a darker silver-grey color. A typical European casting alloy contained 94% tin, 1% copper, and 5% antimony. A European pewter sheet would contain 92% tin, 2% copper, and 6% antimony. Asian pewter, produced mostly in Malaysia, Singapore, and Thailand, contains a higher percentage of tin, usually 97.5% tin, 1% copper, and 1.5% antimony. This makes the alloy slightly softer (Hull, 2008).

2.2.3 Raw Materials of Pewter and Their Properties

In this project, pewter is made from mixtures of tin with copper, tin with copper and antimony, and tin with aluminium. Thus raw materials of pewter are tin, copper, antimony and aluminium.

Tin is one of the most important constituents of low-melting nonferrous alloys. As a metal its most important characteristics are low melting point, the ability to form alloys with most other metals, non-toxicity and resistance to corrosion, allied with good appearance. In its applications as a metal, tin is almost always used in partnership with other metals, either as a coating or alloying element. This is because its intrinsic softness prevents it from being used as a structural material unless strengthened by the addition of alloying elements (Barry and Thwaites, 1983).

Antimony is a silvery, lustrous gray metal. It is usually used as a coating for decorative and protective coating on steel. Excellent fusibility of antimony ensures that it combines readily with other metals to produce alloys. It is useful in alloys because it improves the alloy capacity to reproduce details and it hardens soft metals such as tin. Furthermore, it provides hardness and expansion on solidification. As reported by Suraski and Seelig (2001), antimony also has been known to improve thermal fatigue properties of an alloy. Furthermore, the addition of antimony as a dopant in the Sn-Ag-Cu alloys reduces the melting temperature and refines the grain structure marginally. In pewter tableware, commonly used in the preparation of food, Sb often is found at levels of 7% to 9%. In addition, the Sb-doped alloy will not leach Ag or Cu into ground water (Suraski and Seelig, 2001).

Copper is a ductile metal, with very high thermal and electrical conductivity. Pure copper is rather soft and malleable, and a freshly exposed surface has a reddish-orange colour (Smith and Hashemi, 2003). About 98% of all copper is used as the metal, taking advantage of distinctive physical properties being malleable and ductile, a good conductor of both heat and electricity, and being resistant to corrosion. Copper is often too soft for its applications, so it is incorporated in numerous alloys. For example, brass is a copper-zinc alloy, and bronze is a copper-tin alloy (Gupta, 2009).

Aluminum is a soft, durable, lightweight, ductile and malleable metal with appearance ranging from silvery to dull gray, depending on the surface roughness. The characteristics of its alloys relatively low density (2.7 g/cm^3 as compared to 7.9 g/cm^3 for steel), high electrical and thermal conductivities, and a resistance to corrosion in some common environments, including the ambient atmosphere and its melting temperature of 660 C^o. The mechanical strength of aluminum is enhanced by cold work and alloying, however, both process tend to diminish resistance to corrosion (Callister, 2007). The development of applications for aluminum and its alloys, as well as the sustained rise in consumption can be attributed to several of its properties which are decisive criteria in user's choice of metals, especially in the fields of transport, building, electrical engineering and packaging (Vargel, 2004).

2.2.4 Mechanical and Physical Properties of Pewter

Normally, the products of solely Sn are too soft for most practical purposes, so the metal is hardened by alloying with small amount of other metals (Lewis, 1960). Pewter is an alloy consisting of primarily Sn with small amounts of Cu, Sn, and occasionally Bi. It traditionally consists between 85 and 99 percent Sn, with the remainder consisting of copper and antimony, acting as hardeners. However, in the past, pewter alloys were adulterated with varying amounts of Pb, but now Pb content in pewter is strictly limited, principally on health grounds (Young and Shane, 1985).

According to Witkowski (1994), pewter is an alloy of tin. Since tin is a soft, brittle substance, varying proportions of lead, copper, antimony and bismuth are added to improve durability and malleability. Pewter has a lower melting point than such harder metals as brass, bronze, silver, and gold. Easily cut and soldered, it resists oxidation and the action of almost all acids.

According to Jacobs and Kildulf (1997); physically, if not identical, pewter is a bright, shiny alloy that is very similar in appearance to silver. Like silver, pewter will also tarnish to a dull gray appearance over time if left untreated. Pewter is a very malleable alloy, being soft enough to carve with hand tools, and it also takes good impressions from punches or presses. Because of this inherent softness and malleability, however, pewter cannot be used to make tools itself. Some types of pewter pieces, such as candlesticks, would be turned on a metal lathe. Pewter has a low melting point of around 225-240°C (437-464°F) depending on the exact mixture of metals. Duplication by casting will give excellent results.

Pewter alloys are used mostly because of their ease of fabrication into the required shape and little importance on the final strength properties. Since tin alloys, including pewter, work-softened during rolling or spinning, cast pewterware is mechanically stronger than items fabricated from sheet. However, if about 2 per cent bismuth or 0.1 per cent silver is present in the tin-antimony-copper alloy and the fabricated material is heat-treated at about 150 ^{o}C, it develops a hardness value somewhat similar to that of cast pewter (Table 2.1).

Table 2. 1: Hardness of pewter alloys after working and heat treatment (Barry and Thwaites, 1983)

Nominal composition (%)				Vickers Hardness Value (HV)		
Sn	Sb	Cu	Others	As cast	Rolled 90% Rolled	+ 1 h/200^{o}C
Bal.	6.0	1.5	---	23	13	19
Bal.	6.0	1.5	0.1 Ag	26	13	24
Bal.	6.0	1.5	2.0 Bi	30	15	28

2.3 Fundamental of Metal Alloys

2.3.1 Definition of alloys and the mode of alloying

When two or more metals are dissolved together in a solid solution, the new material is known as an alloy (Brandt and Warner, 2005).

In many applicationss, pure metals with a single component are unable to fulfill certain requirements. Thus, this statement is particularly valid considering the dynamic development of recent years and the consequent changes. In many cases special alloys are needed to match the increasing requirements special materials. The purpose of alloying is to establish such definite physical, mechanical, chemical or special properties that cannot be achieved with pure metals. By melting the components in liquid state, the production of alloys is most frequently achieved. Since most metals dissolve each other without limitations in the liquid state, melting method is the most obvious and simplest way of alloying. Thus, in the simplest way by melting, the homogeneous structure and important from the point of view of alloys can be ensured (Tisza, 2001).

2.3.2 Phase Diagram of Metal Alloys

A region that differs in composition and/or structure from another region is called a phase in a material. Graphical representations of what phases are present in materials system at various temperatures, pressures, and compositions are phase diagrams. Mostly, phase diagrams are constructed by using equilibrium conditions and are used by engineers and scientists to understand and predict many aspects of the behaviour of materials.

The important information obtained from phase diagram is (Smith, 1986):

1. Showing phases at different compositions and temperatures under slow cooling (equilibrium) conditions
2. Indication of the equilibrium solid solubility of one element or compound in another
3. Indication of the temperature at which an alloy cooled under equilibrium conditions starts to solidify and the temperature range over which solidification occurs
4. Indication of the temperature at which different phases start to melt

2.3.3. Phase Diagram of Pewter Alloys

a. Binary Sn-Cu Alloy System

Binary alloy is a mixture of two metals. Figure 2.1 shows the binary phase diagram of the Sn-Cu system. According to this phase diagram, the temperature increases with increasing the percentage of Cu and decreasing the percentage of Sn. The melting temperature of pure Sn is 232 ^oC and the melting temperature of Sn-(1-3%Cu) is about 290 ^oC. Thus, to produce binary pewter alloys of Sn-(1-3%Cu), the temperature of 300 ^oC is sufficient to melt this pewter alloy. According to Barry and Thwaites, (1983), the intermetallic compound of Cu_6Sn_5 inevitably forms when liquid Sn is brought to contact with Cu. Thus, the intermetallic compound of Cu_6Sn_5 is expected to be present in this research project.

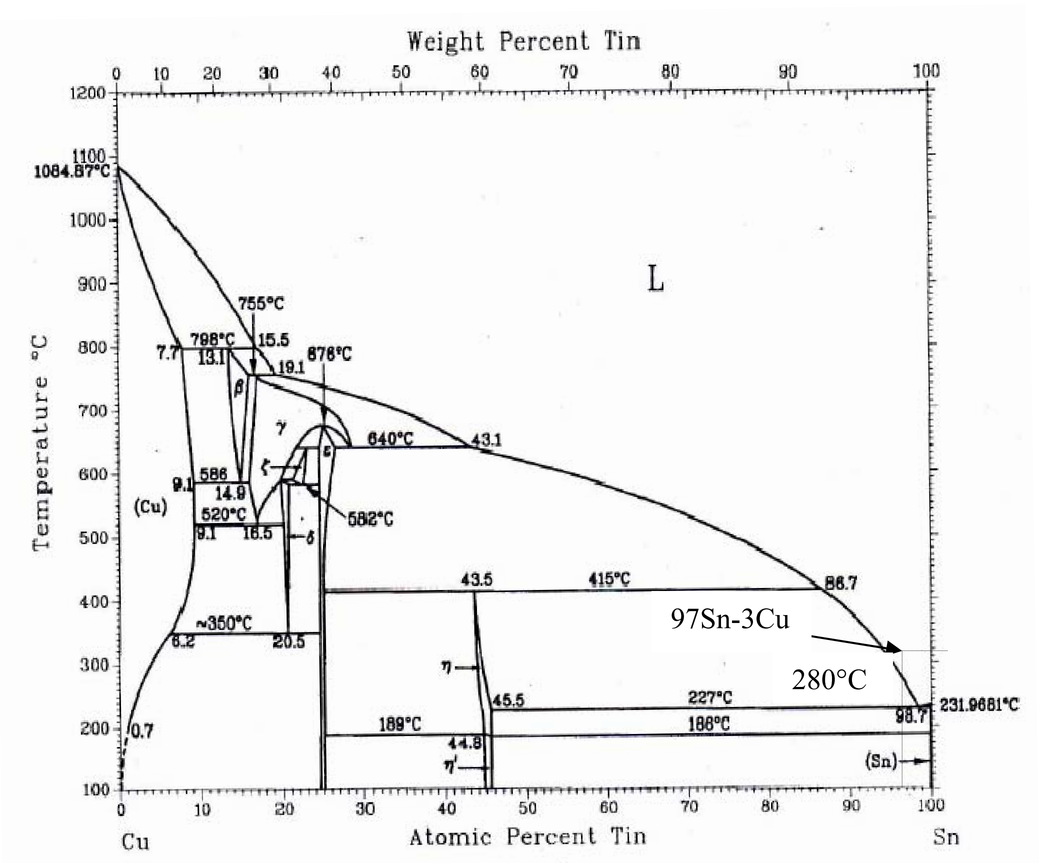

Figure 2. 1: Sn-Cu binary alloy phase diagram (Saunders and Miodownik, 1990)

b. Binary Sn-Al Alloy System

Figure 2.2 shows the Sn-Al phase diagram. In this system, binary eutectic forms at the end of this system and the liquid line increases steeply with increasing temperature and aluminium concentration. According to this phase diagram, the melting point is about 300 °C. Thus the temperature of 380 °C is sufficient to melt Sn-(1-3%Al). According to Elliott and Shunk (1980), the eutectic composition of Sn-Al alloys was placed at 99.5 wt%Sn, 99.42 wt% Sn, 98.7 wt% Sn, and 97.63 wt% Sn. Thus, the eutectic structure of Al+(βSn) should be observed easily in these alloys.

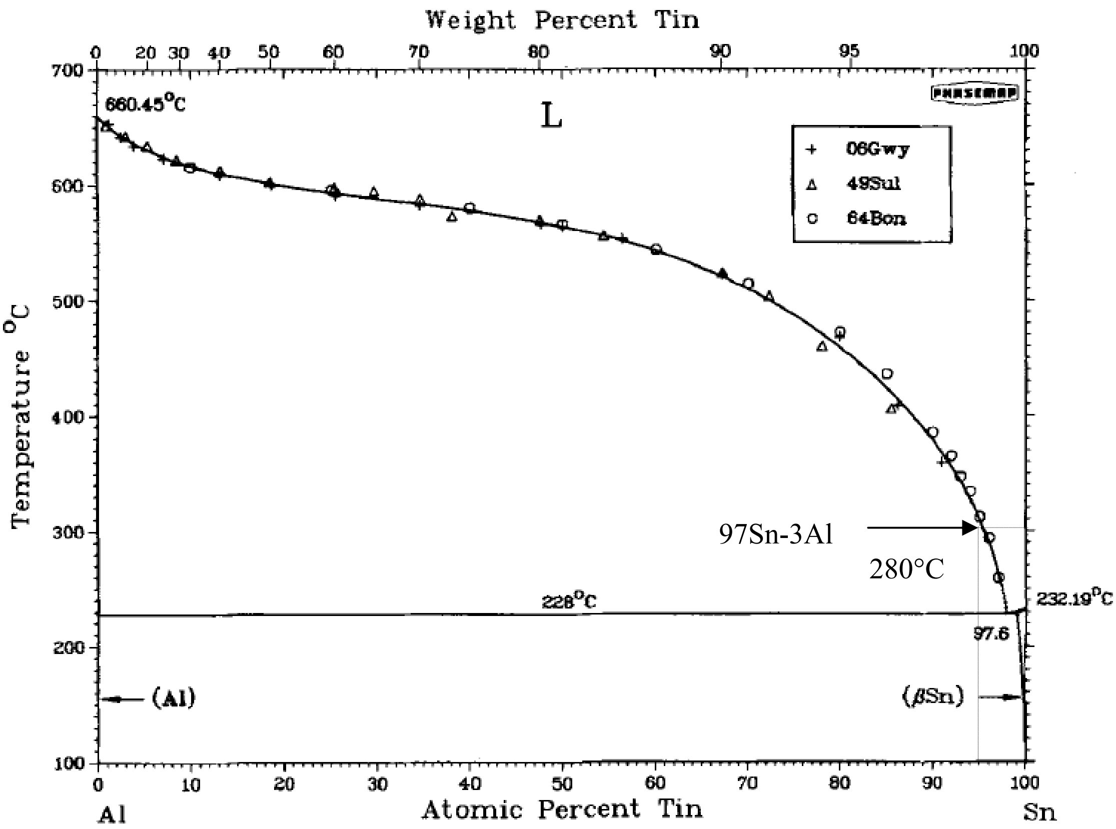

Figure 2. 2: Sn-Al binary alloy phase diagram (McAlister and Kahan, 1983)

c. Ternary Sn-Sb-Cu Alloy

Ternary phase diagrams are three component systems. The ternary phase diagram of Sn-Cu-Sb is shown in Figure 2.3 and 2.4. Figure 2.3 shows the composition base of a ternary phase diagram of a ternary metal alloy (pewter) consisting of pure Sn, pure Sb, and pure Cu at each corner end of the triangle. The binary alloy compositions in Sn-Sb, Sb-Cu, and Sn-Cu are represented on the three edges of the triangle. Figure 2.4 shows the liquidus surface of Sn corner for Sn-Sb-Cu ternary phase diagram. As shown in the figures mentioned, the marginal temperature used is estimated to be less than 320°C in order to produce pewter alloys with composition of Sn-Cu(1-3%)-Sb(5-7%). Thus, using temperature of 400 ^{o}C is sufficient to melt these ternary pewter alloys.

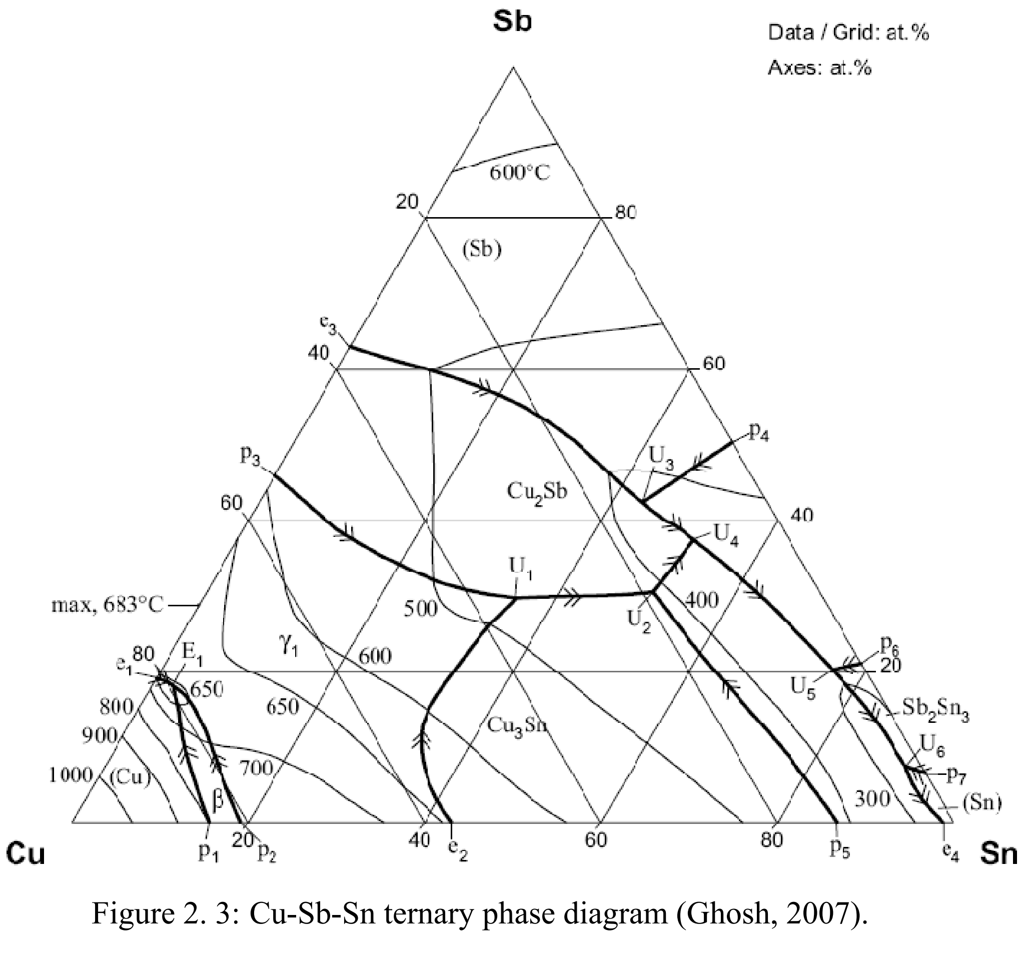

Figure 2. 3: Cu-Sb-Sn ternary phase diagram (Ghosh, 2007).

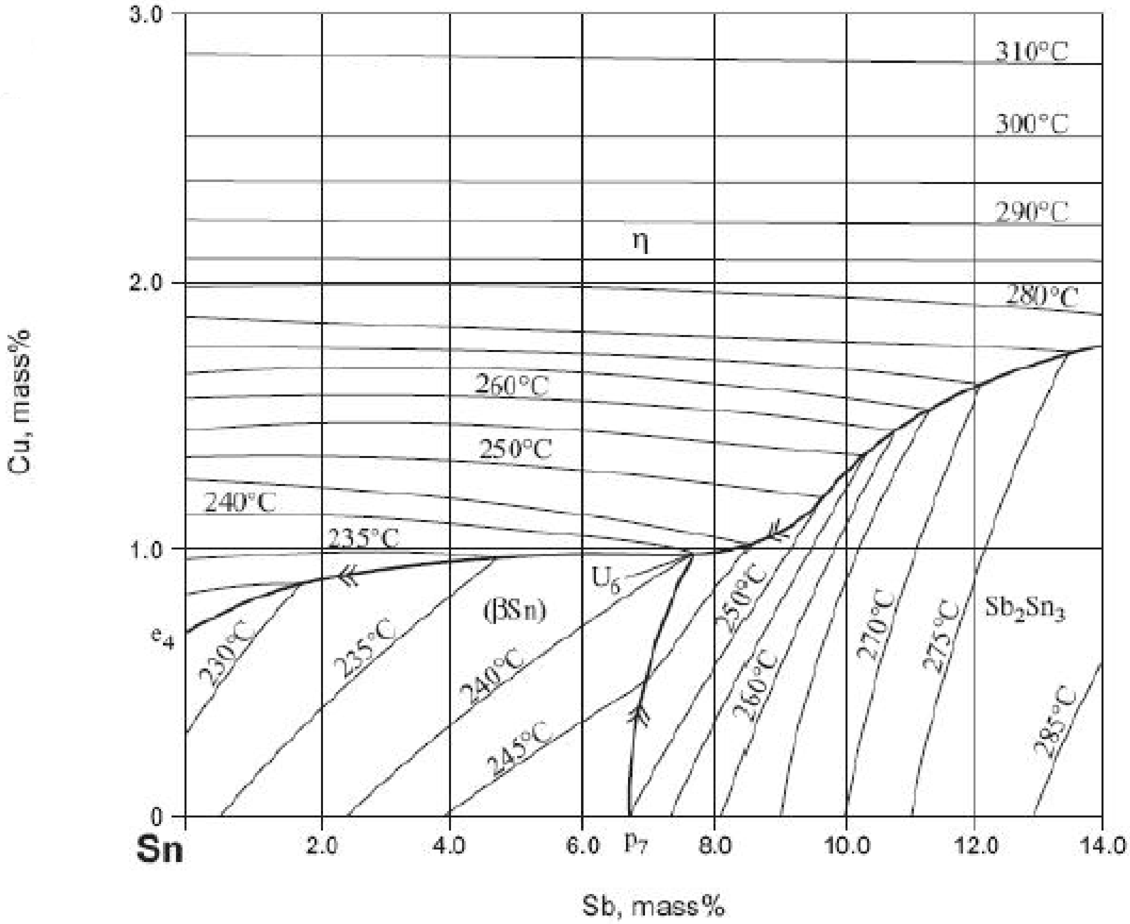

Figure 2. 4: Sn-Sb-Cu ternary phase diagram- liquidus surface of Sn corner (Ghosh, 2007)

2.3.4 Properties of Metal Alloys

2.3.4.1 Mechanical Properties of Metal Alloys

The three properties discussed most often in metallurgy are hardness, ductility and strength. These properties are related to one another. Generally, ductility decreases and the material become more brittle when its strength and hardness increase. As a material becomes more ductile, its strength and hardness are reduced. Normally, strength, hardness and ductility are desirable properties in metal. Generally, a bad characteristic of metal is brittleness (the opposite of ductility). Thus, a main goal of metallurgy science is to find ways to increase the hardness and strength without reducing its ductility (Brandt and Warner, 2005).

a. Hardness of metal alloys

The definition of hardness refer to the resistant of a metal surface to be damaged, dented, worn a way, or deteriorated in any way as a result of a force or pressure against it.

Since hardness relates to several other key properties of metal, especially strength, brittleness and ductility, it is the most important property of metals during studying metallurgy. By measuring the hardness of metal; its strength, brittleness and ductility can be indirectly measured. Hardness and strength can be improved without significantly decrease the ductility when certain alloys are added to metal. Manufacturers often attempt to develop metals that have high hardness and strength without losing too much of the ductility.

Since Vickers microhardness has many advantages for testing the pewter alloys sample, it is used to study in this project to measure hardness. The advantages of the Vickers hardness test are that extremely accurate readings can be taken, and just one type of indenter is used for all types of metals and surface treatments. The Vickers method is capable of testing the softest and hardest of materials, under varying loads (Brandt and Warner, 2005).

b. Tensile Strength

Tensile strength can be defined as the resistance of a material to a slowly applied force. Usually the tension samples are machined into form of a dog bone shape (Levi et al., 1995). The tensile strength of metals and alloys can be evaluated by using tensile test. In this test, a metal sample is pulled to failure in a relatively short time at a constant rate. The force data obtained can be converted to engineering stress data and a plot of engineering stress versus engineering strain can be created. The mechanical properties of metals and alloys that can be obtained from the engineering tensile test are (Smith and Hashemi, 2004):

1. Modulus of elasticity
2. Yield strength at 0.2 percent offset
3. Ultimate tensile strength
4. Percent elongation at fracture
5. Percent reduction in area at fracture

2.3.4.2 Physical Properties of Metal Alloys

The main interests to scientists and engineer are the ways in which any material interacts and responds to various form of energy. This provides the essential base for design and innovation. The force fields (gravitational, electric, magnetic), electromagnetic radiation (heat, light, X-rays), and high-energy particles are the energy acting on a material. Generally, the responses of a material referred to as its physical properties, are governed by the structural arrangement of atoms/ions/molecules in the material. In this project, the physical properties of pewter alloys will be focused on their densities and melting point behaviors. The densities will be measured by using digital density meter. The melting point will be measured by using differential scanning calorimetry analysis (DSC).

a. Density

Density, r , defined as the mass per unit volume and, for solids, is usually expressed in g/cm^3 or lb/ft^3.

$$\text{Density}, r = \frac{\text{Mass}}{\text{Volume}} \qquad \text{(Campbell, 2008)}$$

Density clearly depends on the mass of the atoms, their size and the way they are packed. Metals are dense because they have heavy atoms and close packing. Furthermore, this property increases with increasing atomic numbers in each subgroup of the periodic table.

On alloying, because the mass of solute atoms differs from that of solvent, and also because the lattice parameter changes on alloying, the density of metal changes. The parameter change may often be deduced from Vegard's law, which assumes that the lattice parameter of a solid solution varies linearly with atomic concentration, but numerous deviations from this ideal behavior do exist (Smallman and Ngan, 2007).

b. Melting Point Behaviors of Metal Alloys

The melting temperature (Tm) is a physical property which can be measured by differential scanning calorimetry analysis (DSC) (El-Daly et al., 2009). As the melting point increases, the activation energy for self-diffusion also increases. This relationship exists because the higher-melting-temperature metals tend to have stronger bonding between their atoms (Campbell, 2008).

2.3.5 Strengthening Mechanism in Metal Alloys

The mechanism of both crystalline and amorphous materials such as yield strength, ductility, and toughness can be strengthened by strain (work) hardening, grain-boundary strengthening, solid solution strengthening, precipitation hardening, and dispersion strengthening. These mechanisms of strengthening restrict dislocation motion that makes the material stronger. The ability of a metal to deform depends on the ability of dislocations to move (Hertzberg, 1996).

The strengthening mechanism plays an important role to realize the function of intermetallic compound and eutectic structure in lead free pewter alloys.

According to Buschow (1977), intermetallic compounds are chemical compounds of metals with each other. Intermetallic compounds are produced by direct reaction of their components upon heating or by double decomposition reactions. The formation of intermetallic compounds is observed during the separation of an excess of a component from metallic solid solutions or as a result of positional ordering of the atoms of the components in solid solutions.

According to Vnuk et al., (1980), the Sn-rich matrix in broken-lamellar eutectic appears to contribute significantly in solid solution strengthening. Thus, the solid solution strengthening plays an important role to mechanical properties improvement of lead free pewter alloys.

In this chapter; since the pewter alloys were produced by casting, only three strengthening mechanisms, grain-boundary strengthening, solid solution strengthening and strain hardening will be described.

2.3.5.1 Grain-Boundary Strengthening

The yield stress of the polycrystals increased linearly with increasing misorientation across the grain boundary. The result state that a simple grain boundary has little inherent strength and that the strengthening due to grain boundaries results from mutual interference to slip within the grains.

A general relationship between yield stress and grain size was proposed by Hall and by Petch.

$$s_o = s_1 + kD^{-1/2} \qquad (2.1)$$

Where s_o : the yield stress

s_1 : the "friction stress", or resistance of crystal lattice to dislocation movement

k : the "locking parameter", which measure the relative hardening contribution of the grain boundaries

D: grain diameter

The Hall-Petch equation was applied on yield-point measurement in low-carbon steel. This expresses the grain-size dependence of the flow stress at any plastic strain out to ductile fracture and also to express the variation of brittle fracture stress with grain size and the dependence of fatigue strength on grain size. This equation also was based on the concept that grain boundaries act as barriers to dislocation motion (Dieter, 1988). According to CALLISTER (2007), a fine-grained material (one that has small grains) is harder and stronger than one that is coarse grained, since the former has a greater total grain boundary area to impede dislocation motion. It should also be mentioned that grain size reduction improves not only strength, but also the toughness of many alloys.

2.3.5.2 Solid Solution Hardening

A solid solution forms when, as the solute atoms are added to the host material, the crystal structure is maintained, and no new structures are formed (Callister, 2007).

There are two types of solid solution formation; substitutional and interstitial solid solution. For substitutional solid solutions, the solute and solvent atoms are nearly the same size, and the solute atoms simply substitute for solvent atoms on the crystalline lattice. For interstitial solid solutions, the solute atoms size are much smaller than those of solvent atoms and fit within the spaces between the existing solvent atoms on the crystalline structure. The presenc of the substitutional and interstitial alloying elements strains the crystalline lattice of the host solvent structure (Figure 2.2). This increases in strain and distortion creating barriers to dislocation movement. The solid solution hardening is due to some hardening and strengthening of the alloys by the distortion energy. A moving dislocation is either attracted or repelled by the solute; however, both situations result in a strength increment. When the dislocation is attracted to a solute, additional force required to pull the dislocation away from it is the cause of added strength. Otherwise, if the dislocation is repelled by a solute, additional force is required to push the dislocation past the solute atom.

Studies of solid-solution hardening indicate that the hardening depend on the differences in elastic stiffness and atomic size between the solvent and solute. In general, larger differences result in greater hardening but the larger difference in size between solute and solvent atoms, the more restricted is their mutual solubilities. The solvent phase becomes saturated with the solute atoms and reaches its limit of homogeneity when the distortion energy reaches a critical value determined by the thermodynamics of the system (Campbell, 2008).

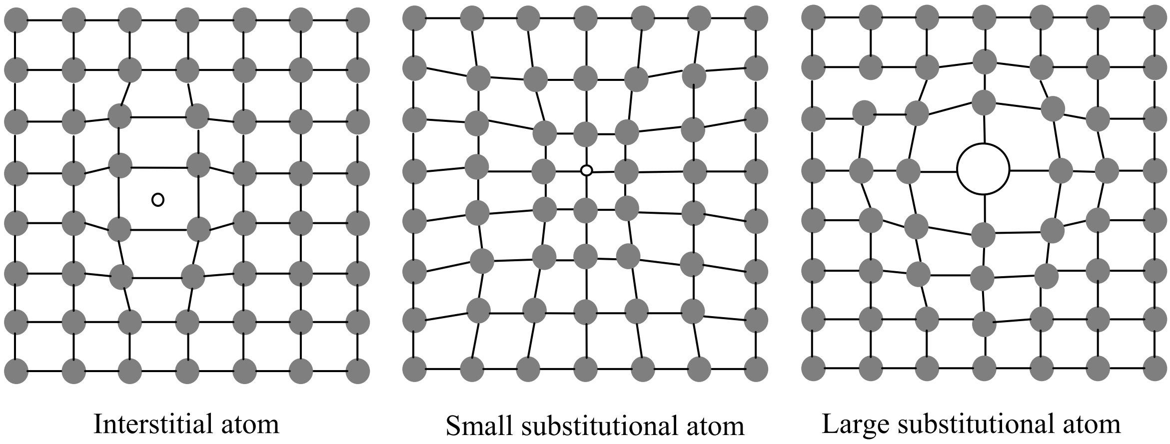

Figure 2. 5: Lattice distortion caused by solute additions (Campbell, 2008).

2.3.5.3 Strain Hardening

Strain hardening (also referred to as work hardening or cold working) is the strengthening of a metal by plastic deformation. This strengthening occurs because of dislocation movements within the crystal structure of the material (Degarmo et al., 2003). Any material with a reasonably high melting point such as metals and alloys can be strengthened in this fashion. Some materials cannot be work-hardened at normal ambient temperatures, such as indium, however others can only be strengthened via work hardening, such as pure copper and aluminum (Smith and Hashemi, 2006). The reason for strain hardening is the increase of dislocation density with plastic deformation. The average distance between dislocations decreases and dislocations start blocking the motion of each other. Ductile metals become stronger when they are deformed plastically at temperatures well below the melting point.

The percent of cold work (%CW) is often used to express the degree of plastic deformation.

$$\%CW = \left(\frac{A_0 - A_d}{A_0}\right) 100 \qquad (2.2)$$

Where A_0 is the original cross-section area, A_d is the area after deformation

2.4 Application of Pewter

Pewter is a bright, shiny alloy that is very similar, if not identical, in appearance to silver. The low melting point of pewter and its excellent flowing and mould-filling properties make pewter casting easy. Pewter possesses high fluidity at casting temperatures and can be cast easily by gravity, and centrifugal, or press die casting techniques, as well as by the lost wax process. Pewter was used in many applications because of these properties.

The main use of pewter is for domestic decorative items such as candlesticks and plaque or for drinking vessels like tankards and goblets. A wide variety of such articles is available, some exhibiting modern art forms characteristic of their country of origin, others copying historical articles of pewterware. Similar alloys are used for centrifugal casting of figures such as knights, soldiers or jewellery in rubber moulds.

2.4.1 Pewter Drinking Vessels

Tankards and mugs for quaffing of beer and ale constitute the most important category of pewter drinking vessels. They are already represented by a large number of examples dating from the 1670s to the 1820s. During this date, pewter drinking vessels were not used only in taverns, but also occasionally in homes. When not used