INVESTIGATIONS ON THE PROPERTIES OF Sn-8Zn-3Bi LEAD-FREE AND Sn-37Pb EUTECTIC SOLDER ALLOYS

By

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DEDICATION

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ABSTRAK

Sifat-sifat logam pateri bebas plumbum Sn-8Zn-3Bi dan logam pateri eutektik Sn-37Pb yang bersentuhan dengan substrak kuprum telah dikaji. Sifat-sifat ini termasuk sifat basahan (sudut sentuhan, daya basahan, ketegangan permukaan), sifat terma (DSC, pekali pengembangan terma) dan sifat mekanikal (kekuatan tensil dan ricihan). Sudut sentuhan dan daya basahan diukur dari 5^{o}C sehingga 35^{o}C (Sn-8Zn-3Bi) atau 50^{o}C (Sn-37Pb) melebihi takat lebur/liquidus mereka. Kesan berbagai faktor termasuk flux, kekasaran permukaan, kedalaman celupan dan perimeter sampel terhadap sudut sentuhan dan daya basahan juga telah dikaji.

Keputusan menunjukkan penurunan sudut sentuhan dan ketegangan permukaan apabila suhu bertambah. Sudut sentuhan bagi logam pateri Sn-8Zn-3Bi adalah lebih kurang dua kali daripada Sn-37Pb pada 35^{o}C melebihi suhu takat lebur mereka. Kesan flux dan kekasaran permukaan terhadap sudut sentuhan menunjukkan sudut terkecil, 24^{o}, bila flux MHS37 digunakan dan kekasaran permukaan substrak kuprum lebih kurang 270 nm. Dalam eksperimen neraca basahan, keputusan menunjukkan daya basahan meningkat bila suhu dan perimeter sampel bertambah, manakala daya basahan berkurangan bila kedalaman celupan bertambah. Dalam julat 10^{o}C di atas suhu takat lebur (liquidus) daya basahan untuk Sn-8Zn-3Bi adalah lebih tinggi daripada untuk Sn-37Pb. Situasi berubah bila suhu bertambah melebihi 15^{o}C di atas takat lebur, di mana daya basahan untuk Sn-37Pb menjadi lebih tinggi. Pengukuran pekali pengembangan terma (CTE) untuk aloi logam pateri menunjukkan kedua-dua Sn-8Zn-3Bi dan Sn-37Pb mempunyai nilai yang lebih kurang sama sehingga 80^{o}C dan meningkat sedikit bagi suhu melebihi 80^{o}C. Takat lebur di dapati

masing-masing 195^{o}C dan 184^{o}C bagi Sn-8Zn-3Bi dan Sn-37Pb. Kedua-dua kekuatan tensil dan kekuatan ricihan bagi Sn-8Zn-3Bi adalah lebih tinggi daripada Sn-37Pb.

INVESTIGATIONS ON THE PROPERTIES OF Sn-8Zn-3Bi LEAD-FREE AND Sn-37Pb EUTECTIC SOLDER ALLOYS

ABSTRACT

Properties of Sn-8Zn-3Bi lead-free solder and Sn-37Pb eutectic solder in contact with copper substrates have been investigated. These properties include wetting properties (contact angle, wetting force, surface tension), thermal properties (DSC, CTE) and mechanical properties (tensile and shear strength). Contact angle and wetting force were measured from 5°C above their melting/liquidus temperature up to 35°C (Sn-8Zn-3Bi) or 50°C (Sn-37Pb) above melting temperature. The effect of various factors including fluxes, surface roughness, immersing depth and sample perimeter on contact angle and wetting force are also investigated.

Results obtained show that contact angle and surface tension reduced as temperature increases. Contact angle of Sn-8Zn-3Bi solder is approximately twice of that in Sn-37Pb at 35°C above their melting temperatures. The effect of fluxes and surface roughness on contact angle show the lowest value of contact angle, 24°, when MHS37 flux was used and the surface roughness of copper substrate was around 270 nm. In wetting balance tests, results obtained show the wetting force increased as temperature and sample perimeter increased, while it decreased when immersing depth increased. Within a 10°C above the melting (liquidus) temperature, the wetting force of Sn-8Zn-3Bi was higher than that in Sn-37Pb. The situation changes when temperature increases more than 15°C above melting point, where wetting force of Sn-37Pb became higher. The measurements of coefficient of thermal expansion (CTE) of solder alloys show that CTE of Sn-8Zn-3Bi was similar to CTE of Sn-37Pb up to 80°C and a bit higher above 80°C. The melting temperatures were found are 195°C and

184°C for Sn-8Zn-3Bi and Sn-37Pb, respectively. Both tensile strength and shear strength of Sn-8Zn-3Bi were higher than that of Sn-37Pb.

CHAPTER 1

INTRODUCTION

1.1 Overview

While advances in transistors, resistors, capacitors, diodes, and especially integrated circuits have revolutionized the world, these devices are of very little value as individual components. For these devices to be of use, they must be electrically connected to each other and to mechanical devices. The majority of these electrical connections are made by soldering, Figure 1.1. Not only does solder make electrical connections, it is also used to provide mechanical, thermal connection between the component and its supporting printed circuit board (Towasshiraporn *et al*, 2004).

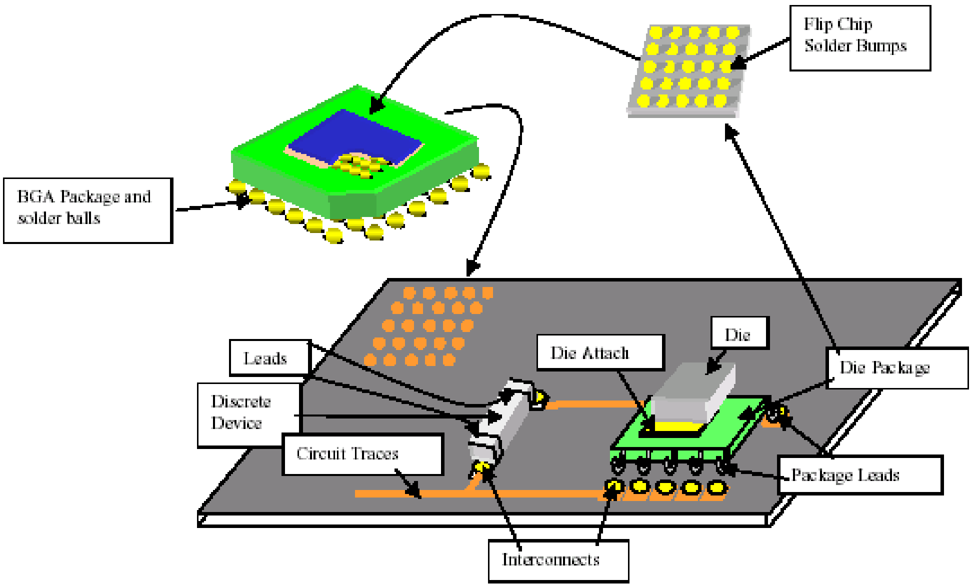

Figure 1.1: Solder Used in Electronic Assemblies

The practice of soldering has been in existence for some time. While there is evidence to suggest that it was used even earlier, many different soldering techniques were widely used throughout the Greek and Roman Empires, as well as in Viking dominated Scandinavia. Archeologists have found jewelry, weapons, tools, and cutlery that have been very skillfully soldered (Mark *et al*., 1997). Throughout the years solder has been used in various applications; however it was the invention of electronic devices in the latter part of 20th century that lead to rapid advances in soldering technologies.

Various solder alloys have been used in soldering technology. Since 4000BC, some typical alloy as Chrysocolla (Au glue), Au alloyed with Cu and Cd (dirt)… have been used in Artwork and Jewelry (Frear, 2002), Figure 1.2.

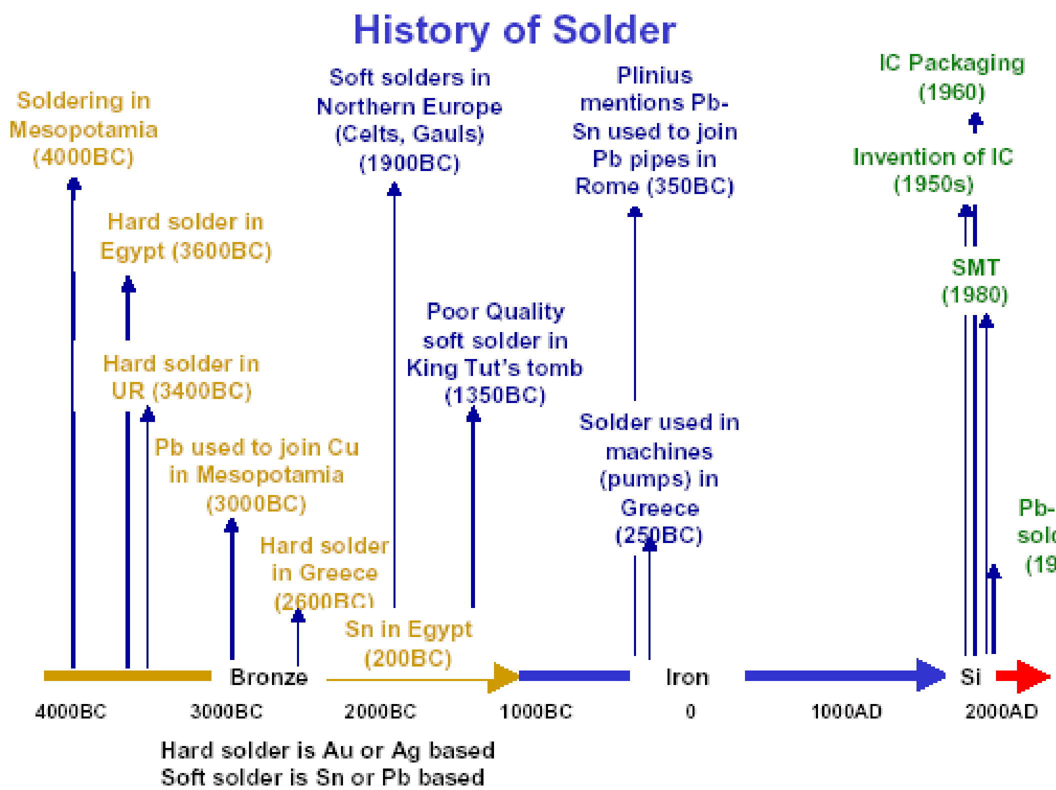

Figure 1.2: History of Solder (Frear, 2002)

In recent decades of years, tin-lead (Sn-Pb) solder has been the most commonly solder alloy used in electronic devices, especially eutectic 63Sn-37Pb and near eutectic 60Sn-40Pb. As one of the primary components of eutectic solder, lead

(Pb) provides many technical advantages, which includes the following to Sn-Pb solders:

- Pb reduces the surface tension of pure tin, which is 550 mN/m at 232^0C, and the lower surface tension of 63Sn-37Pb solder (470 mN/m at 280^0C) facilitates wetting (Vianco, 1993).
- As an impurity in tin, even at levels as low as 0.1 wt.%, Pb prevents the transformation of white or beta (β) tin to gray or 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 (Reed-Hill, 1994).
- 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. (Abtew *et al*, 2000).

These factors, combined with Pb being readily available and a low cost metal, make it an ideal alloying element with tin. However, there are legal, environmental and technological factors that are pressing for alternative soldering materials and processing approaches. These factors include (Abtew *et al*, 2000):

- Legislation that tax, restrict or eliminate the use of Pb due to environmental and toxicological concerns.
- The continued trend towards packaging and interconnect miniaturization in surface mount technology (SMT) that is stretching the physical capability of Sn-Pb solder to provide sound and reliable solder joints. The natural radius of curvature of molten solder, R, as determined by surface tension, ($R = (\gamma/\rho g)^{1/2}$ = 2.2 mm) is already larger than the sizes of the solder joints of SMT devices with less than 0.5 mm pitch. This means that forcing the solder to form joints with a smaller radius of curvature can result in runaway of solder from desired locations due to high internal liquid pressure.

- The need for better paste printing capability that is required for fine pitch SMT. The minimum distance between adjacent soldering pads for optimum paste application is dependent on the edge definition of the print itself. This depends on the granular nature of the paste, which in turn is dependent on the natural radius of curvature.
- The need for cascade soldering of complex assemblies that require different types of solders with different melting temperatures

Therefore, alternative lead free solders need to be considered. Many different solder compositions have been investigated, for example: SnZn (Mavoori *et al*., 1997), SnZnAg (Song *et al*., 2003; Chang *et al*., 2003) SnAg (Choi *et al*., 2000; Chada *et al*., 2000; Shohji *et al*., 2003) SnAgCu (Moon *et al*., 2000; Zribi *et al*., 2001; Nurmi *et al*., 2004). Common to all these new lead free solders that tin remains their basic element in most of them.

The Sn-Zn eutectic solder alloy, that have melting points close to that of the Sn-37Pb solder, have been considered as one alternative because they also possess the advantages of high strength, good creep resistance, and high thermal fatigue resistance (Chiu *et al*., 2002). However, the Sn-Zn system solders show poor wetting during soldering to electrodes (Iwanishi *et al*., 2003), poor oxidation resistance in reflow soldering and may cause soldering failures, such as poor wetting and non-wetting (Shohji et al., 2004). By adding Bi into Sn-Zn solders, the melting point can be decreased, and the greater the amount of Bi rendered, the lower the melting point. Bismuth also helps improve the wettability and corrosion performance of Sn-Zn solders (Chiu *et al*., 2002).

1.2 Objective of Study

Research on properties of lead free solder alloys are expanded with every passing day with the purpose of understanding and improving properties of lead-free solders. In this work, properties of tin-zinc-bismuth (Sn-8Zn-3Bi) lead-free solder are investigated. The solder is expected to have good wetting on copper (Cu) substrate, good mechanical properties which comparable to the eutectic Sn-37Pb solder alloys.

The main objectives of this work are:

1. To study the properties of tin-zinc-bismuth (Sn-8Zn-3Bi) lead free solder based on:
    - Microstructure
    - Wetting properties: Wetting time, wetting force, withdrawal force, surface tension, contact angle
    - Physical properties: Different Scanning Calorimetry (DSC), Coefficient of thermal expansion (CTE)
    - Mechanical properties: Tensile strength, shear strength
2. To study the effect of various factors, including temperature, flux, surface roughness on wetting properties
3. To make comparison between the tin-zinc-bismuth (Sn-8Zn-3Bi) lead free solder and the eutectic tin-lead solder (Sn-37Pb)

CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 Lead-Free Solder Alloys

As the restriction of lead (Pb) in industrial fields has been strongly promoted because of the environmental protection on water resources, the development of lead-free solders is become a critical subject for the new generations in electronic and automobile products. Many different solder compositions have been proposed as a substitute for tin-lead (Sn-Pb) solders, Abtew and Selvaduray (Abtew *et al*., 2000) have reported a relatively large number of lead-free solder alloys, and are summarized in Table 2.1, with their elemental compositions. The solder alloys are binary, ternary and some are even quaternary alloys. It can be noticed that a very large number of these solder alloys are based on tin (Sn), the element tin being the primary or major constituent. The two other elements that are major constituents are iridium (In) and bismuth (Bi). Other alloying elements are zinc (Zn), silver (Ag), antimony (Sb), copper (Cu), magnesium (Mg) and in one case a minor amount of lead (Pb).

In reviewing the compositions listed in Table 2.1, it can be seen that some compositions are variations of one basic composition. For example, there are three Sn-8Zn compositions, with the variations in the mass percent of ternary additive element In (4%, 5% and 10%), and a minor amount of Bi or Ag. The element tin makes an appearance in almost alloys with the composition varies from 17 wt.% (Bi-26In-17Sn) to 99.25 wt.% (Sn-0.75Cu). These lead-free solder alloys composition are based on four basic system, there are tin-silver (Sn-Ag), tin-bismuth (Sn-Bi), tin-iridium (Sn-In) and tin-zinc (Sn-Zn).

Table 2.1: Elemental Composition of Lead and Lead-Free Solder Alloys (Abtew *et al*., 2000)

Alloy	**Sn**	**In**	**Zn**	**Ag**	**Bi**	**Sb**	**Cu**	**Mg**	**Pb**
Sn-37Pb	63								37
Sn-40Pb	60								40
Bi-26In-17Sn	17	26			57				
Bi-32In		32			68				
Bi-41.7Sn-1.3Zn	41.7		1.3		57				
Bi-41Sn-1Ag	41			1	58				
Bi-41Sn-1Pb	41				58				1
Bi-42Sn	42				58				
Bi-43Sn (eutectic)	43				57				
Bi-45Sn-0.33Ag	45			0.33	54.7				
In-3Ag		97		3					
In-34Bi		66			34				
In-48Sn (eutectic)	48	52							
Sn-1Ag-1Sb	98			1		1			
Sn-1Ag-1Sb-1Zn	97		1	1		1			
Sn-2.5Ag-0.8Cu-0.5Sb	96.2			2.5		0.5	0.8		
Sn-2.8Ag-20In	77.2	20		2.8					
Sn-25Ag-10Sb	65			25		10			
Sn-2Ag	98			2					
Sn-2Ag-0.8Cu-0.6Sb	96.6			2		0.6	0.8		
Sn-2Ag-0.8Cu-6Zn	91.2		6	2			0.8		
Sn-2Ag-0.8Cu-8Zn	89.2		8	2			0.8		
Sn-3.5Ag	96.5			3.5					
Sn-3.5Ag-6Bi	90.5			3.5	6				
Sn-3.5Ag-1Zn	95.5		1	3.5					
Sn-3.5Ag-1Zn-0.5Cu	95		1	3.5			0.5		
Sn-3.6Ag-1.5Cu	94.9			3.6			1.5		
Sn-4.7Ag-1.7Cu	93.6			4.7			1.7		
Sn-4Ag	96			4					
Sn-4Ag-7Sb	89			4		7			
Sn-4Ag-7Sb-1Zn	88		1	4		7			
Sn-10Bi-0.8Cu	89.2				10		0.8		
Sn-10Bi-0.8Cu-1Zn	88.2		1		10		0.8		
Sn-10Bi-5Sb	85				10	5			
Sn-10Bi-5Sb-1Zn	84		1		10	5			
Sn-4.8Bi-3.4Ag	91.8			3.4	4.8				
Sn-42Bi	58				42				
Sn-45Bi-3Sb	52				45	3			
Sn-45Bi-3Sb-1Zn	51		1		45	3			
Sn-56Bi-1Ag	43			1	56				
Sn-57Bi-1.3Zn	41.7		1.3		57				
Sn-5Bi-3.5Ag	91.5			3.5	5				
Sn-7.5Bi-2Ag-0.5Cu	90			2	7.5		0.5		
Sn-0.75Cu	99.25						0.75		
Sn-0.7Cu (eutectic)	99.3						0.7		
Sn-2Cu-0.8Sb-0.2Ag	97			0.2		0.8	2		
Sn-3Cu	97						3		
Sn-10In-1Ag-10.5Bi	78.5	10		1	10.5				
Sn-10In-1Ag	89	10		1					
Sn-20In-2.8Ag	77.2	20		2.8					
Sn-42In	58	42							

Table 2.1: Continued

Alloy	Sn	In	Zn	Ag	Bi	Sb	Cu	Mg	Pb
Sn-5In-3.5Ag	91.5	5		3.5					
Sn-10In-1Ag-0.5Sb	88.5	10		1		0.5			
Sn-36In	64	36							
Sn-50In	50	50							
Sn-8.8In-7.6Zn	83.6	8.8	7.6						
Sn-2Mg (eutectic)	98							2	
Sn-5Sb	95					5			
Sn-4Sb-8Zn	88		8			4			
Sn-7Zn-10In-2Sb	81	10	7			2			
Sn-8Zn-10In-2Bi	80	10	8		2				
Sn-8Zn-4In	88	4	8						
Sn-8Zn-5In-(0.1-0.5)Ag	86.5	5	8	0.5					
Sn-9Zn-10In	81	10	9						
Sn-5.5Zn-4.5In-3.5Bi	86.5	4.5	5.5		3.5				
Sn-6Zn-6Bi	88		6		6				
Sn-9Zn (eutectic)	91		9						
Sn-9Zn-5In	86	5	9						

*All compositions are in %wt.

2.1.1 The Element Tin

The ability of tin (Sn) to wet and spread on a wide range of substrates, using mild fluxes, has caused it to become the principal component of most solder alloys used for electronic applications.

Elemental tin has the melting temperature of 231°C. Tin exists in two different forms with two different crystal structures in the solid state. White or β-tin has a body-centered tetragonal crystal structure and is stable at room temperature. Gray tin or α-tin, which has a diamond cubic crystal structure, is thermodynamically stable below 13°C. The transformation of β-tin to α-tin, also referred as *tin pest*, takes place when the temperature falls below 13°C, and results in a large increase in volume, which can induce cracking in the tin structure. Due to its body centered tetragonal crystal structure that is anisotropic, the thermal expansion of tin is also anisotropic. Therefore, when tin is exposed to repeated thermal cycling, plastic deformation and eventual cracking at grain boundaries can occur. This effect has been observed in thermal cycling over a range as small as 30-75°C. Thus, thermal fatigue can be induced in tin or tin-rich phases of solder alloys even when no external mechanical strain is imposed.

The addition of alloying agents has been reported to be effective in suppressing this phase transformation, thus ameliorating the problems associated with tin pest. According to Lewis (Lewis, 1961), the addition of greater than 0.5 wt.% Sb, 0.1 wt.% Bi, or over 5 wt.% Pb is effective in eliminating tin pest. However, the mechanisms via which these alloying agents contribute towards elimination of tin pest are not clear at this time. Taking the example of the Sn-Pb system, the solid solubility of Pb in Sn at 13°C is less than 0.3 wt.%. A 5 wt.% Pb-Sn alloy will be a two-phase alloy consisting of the Sn-rich and the Pb-rich phases. It is not clear if the Pb addition actually suppresses the $\beta \rightarrow \alpha$ transformation in the Sn-rich phase, or if the Pb-rich phase 'absorbs' the volume expansion by plastically deforming, with the net result of an absence of the manifestation of tin pest on the macroscopic structure (Abtew *et al.*, 2000).

2.1.2 Tin Silver Solder Alloys

The eutectic composition for the tin-silver (Sn-Ag) binary system occurs at Sn-3.5Ag and the eutectic temperature is 221°C (Figure 2.1). The microstructure consists of Sn and the intermetallic Ag_3Sn in the form of thin platelets (McCormack *et al.*, 1993). McCormack *et al.* described the solidified microstructure of the binary eutectic Sn-3.5%Ag as consisting of a β-Sn phase with dendritic globules and inter-dendritic regions with a eutectic dispersion of Ag_3Sn precipitates within a β-Sn matrix. Addition of 1% Zn has been shown to improve the solidification microstructure of this alloy by eliminating the large β-Sn dendritic globules and introducing a finer and a more uniform two-phase distribution throughout the alloy (McCormack *et al.*, 1995). The addition of Zn suppresses the formation of β-Sn dendrites and results in a uniform dispersion of Ag_3Sn. Similar to the Sn-0.07Cu alloy, this solder may be prone to whisker growth due to its high tin composition. However, there is no information available in the literature with regard to whisker growth in Sn-Ag (Abtew *et al.*, 2000).

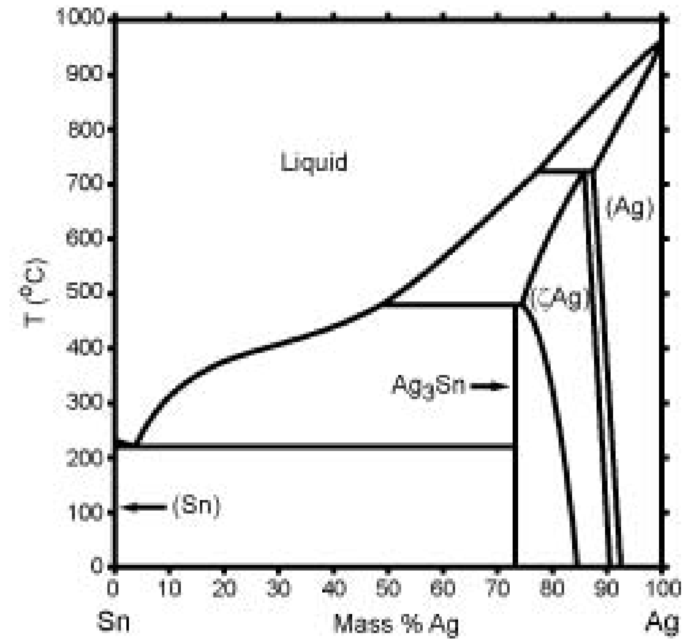

Figure 2.1: Tin-Silver Phase Diagram

2.1.3 Tin Bismuth Solder Alloys

The tin-bismuth (Sn-Bi) system has a eutectic composition of 42Sn-58Bi and a relatively low eutectic temperature of 139°C (Figure 2.2). The room temperature equilibrium phases are Bi and Sn with about 4 wt.% Bi in solid solution (Morris *et al.*, 1993). Since tin has very low solubility in Bi at the eutectic solidification temperature of 130°C, the Bi phase is essentially pure Bi. However, the maximum solubility of Bi in Sn is about 21 wt.% (Kabassis *et al.*, 1986). As the alloy cools, Bi precipitates in the Sn phase. At moderate cooling rates, the eutectic Sn-Bi microstructure is lamellar, with degenerate material at the boundaries of the eutectic grains. This microstructure is similar to the one theoretically predicted by Croker *et al*. (Croker *et al*., 1973) for relatively slow cooling rates. Wild (Wild, 1971) observed cracks on slowly cooled eutectic Sn-Bi solder joints. Slow cooling resulted in the formation of large grains. Tin precipitates from the solder matrix along the boundaries of these large grains through which cracking occur. Cracking was not observed during rapid cooling. Cooling rates, however, were not specified in the literature. It has also been reported (Glazer, 1995) that recrystallization of the alloy produced an expansion of up to 0.0007 in./in. The expansion results in embrittlement, which may be due to strain hardening caused by deformation that occurs to accommodate the expansion (Wild, 1971).

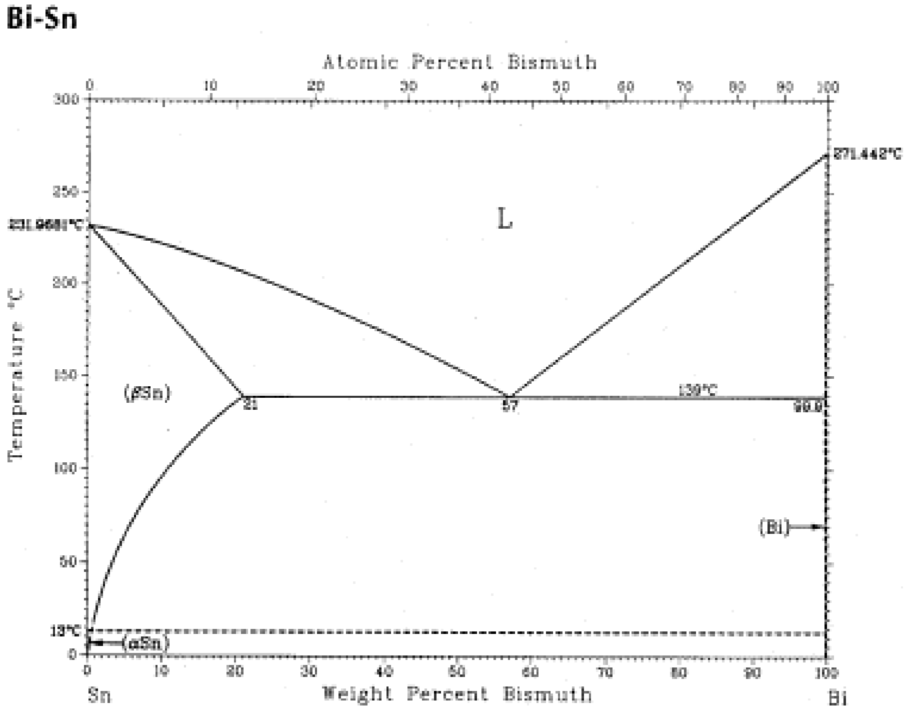

Figure 2.2: Tin-Bismuth Phase Diagram

2.1.4 Tin Indium Solder Alloys

The indium-based solder with the composition of In-48Sn is the one that is commonly used for surface mount technology (SMT) applications. The eutectic composition is In-48Sn, and the eutectic temperature is 117°C. The two phases that form are intermetallic phases–an In-rich, pseudo-body-centered tetragonal phase, β, which has 44.8 wt.% Sn, and a hexagonal Sn-rich phase, γ, with 77.6 wt.% Sn (Glazer, 1995). Mei and Morris (Mei et al., 1992) described the microstructure of In-48Sn solder on a Cu substrate as having lamellar features. The Sn-rich phase is composed of equiaxed grains. The In-rich phase contains Sn precipitates. A similar structure with less irregularity was observed by Freer and Morris on a Ni substrate (Freer et al., 1992), and significant microstructural coarsening was observed by Seyyedi (Seyyedi, 1993), after prolonged aging of the solder joints made on a Cu substrate.

2.1.5 Tin Zinc Solder Alloys

The Sn-9Zn eutectic solder alloy appears to be an attractive alternative, with a melting temperature of 198°C that is relatively close to eutectic tin-lead solder (Figure 2.3).

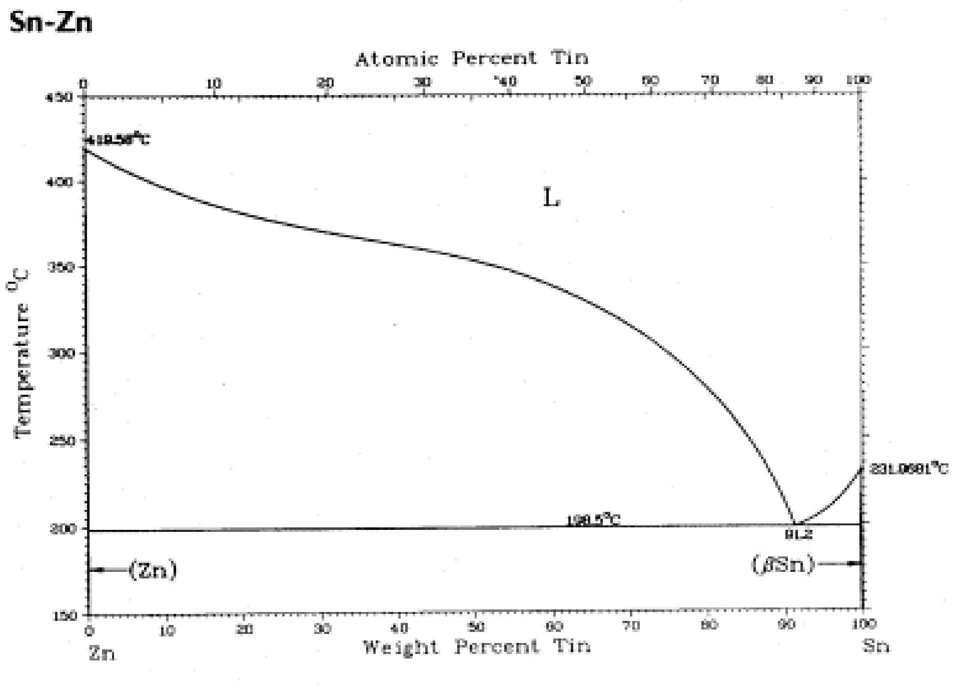

Figure 2.3: Tin-Zinc Phase Diagram

Tin-zinc eutectic structure consists of two phases: a body centered tetragonal Sn-matrix phase and a secondary phase of hexagonal Zn containing less than 1% tin in solid solution (McCormack et al., 1994). Sn-9Zn is the eutectic composition for the tin-zinc system, and the microstructure can be expected to be lamellar, consisting of alternating Sn-rich and Zn rich phases. Compared to the Sn-Pb system, in the Sn-Zn system, both Sn and Zn interact with Cu to form intermetallic phases (Abtew et al., 2000).

2.1.6 The Sn-8Zn-3Bi Solder Alloy

Sn–Zn eutectic alloy has recently been considered as a potential candidate for lead-free solder material because of its low melting point (198 .C), excellent mechanical properties and low cost. However, the Sn–Zn alloy suffers problems of poor wetting, easy oxidation and dross formation (Song *et al*., 2005). Alloying element Bi has been chosen to improve the wetability.

The addition of Bi could decrease surface tension of the liquid solders, and accelerate their spreading out on Cu substrates (Zhou et al., 2005). The tin-zinc-bismuth system has no intermetallic phase (see Figure 2.2, 2.3, 2.4), and lower melting temperature compared to Sn-8Zn solder.

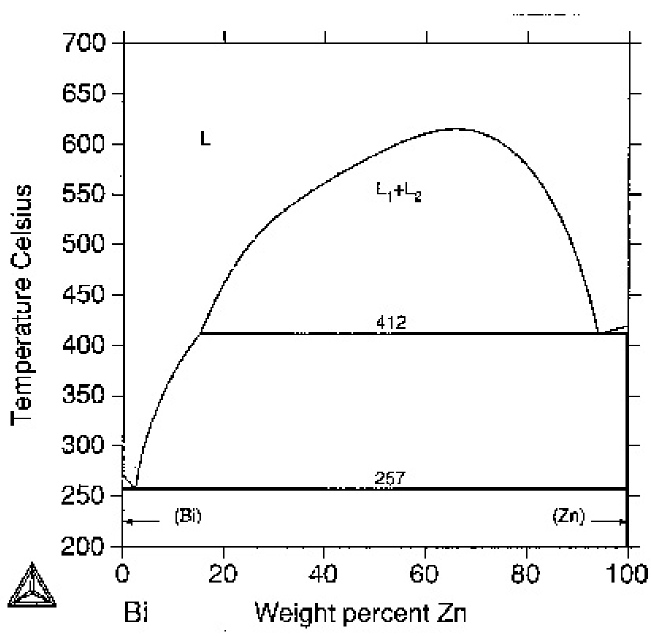

Figure 2.4: Bismuth-Zinc Phase Diagram

2.2 Properties of Solder Alloys

2.2.1 Melting Temperature

Table 2.2: Melting (Liquidus) Temperatures of Lead and Lead-Free Solder Alloys (Abtew *et al*., 2000)

Alloy composition	T_m (°C)	T_s (°C)	T_l (°C)	T_e (°C)
Sn-37Pb (eutectic)				183
Sn-40Pb		183	187	
Bi-26In-17Sn	79			
Bi-32In (eutectic)				109.5
Bi-41.7Sn-1.3Zn	127			
Bi-42Sn			139	
Bi-43Sn (eutectic)				139
Bi-45Sn-0.33Ag	140-145			
In-3Ag			141	
In-34Bi			110	
In-48Sn (eutectic)				117
Sn-1Ag-1Sb		222	232	
Sn-2.5Ag-0.8Cu-0.5Sb		210-216	217	
Sn-2.8Ag-20In	178			
Sn-25Ag-10Sb	233			
Sn-2Ag		221	225	
Sn-2Ag0.8Cu-0.6Sb	210-216			
Sn-2Ag-0.8Cu-6Zn		217	217	
Sn-2Ag-0.8Cu-8Zn		215	215	
Sn-3.5Ag (eutectic)				221
Sn-3.5Ag-(<6)Bi		211-221	212	
Sn-3.5Ag-1Zn		217		
Sn-3.5Ag-1Zn-0.5Cu	216-217			
Sn-3.6Ag-1.5Cu	225			
Sn-4.7Ag-1.7Cu	217			
Sn-4Ag		221	225	
Sn-4Ag-7Sb			230	
Sn-10Bi-0.8Cu		185	217	
Sn-10Bi-5Sb		193	232	
Sn-42Bi		139	170	
Sn-45Bi-3Sb		145	178	
Sn-56Bi-1Ag	136.5			
Sn-57Bi-1.3Zn	127			
Sn-7.5Bi-2Ag-0.5Cu		207	212	
Sn-0.75Cu		227	229	
Sn-0.7Cu (eutectic)				227
Sn-2Cu-0.8Sb-0.2Ag	266-268			
Sn-3Cu		227	275	
Sn-4Cu-0.5Ag		216	222	
Sn-10In-1Ag-(0-10.5)Bi	188-197			
Sn-20In-2.8Ag	178-189			
Sn-42In		117	140	
Sn-10In-1Ag-0.5Sb	196-206			

Table 2.2: Continued

Alloy composition	**T_{melt} (°C)**	**T_{solid} (°C)**	**T_{liquid} (°C)**	**$T_{eutectic}$ (°C)**
Sn-36In		117	165	
Sn-50In		117	125	
Sn-8.8In-7.6Zn	181-187			
Sn-2Mg (eutectic)				200
Sn-5Sb		234	240	
Sn-4Sb-8Zn	198-204			
Sn-7Zn-10In-2Sb	181			
Sn-8Zn-10In-2Bi	175			
Sn-8Zn-5In-(0.1-0.5)Ag	187			
Sn-9Zn-10In	178			
Sn-5.5Zn-4.5In-3.5Bi	185-188			
Sn-6Zn-6Bi	127			
Sn-9Zn (eutectic)				198
Sn-9Zn-5In	188			

The melting/liquidus temperature perhaps the first and most important factor of alternative lead-free solder alloys. The melting temperature of eutectic Sn-37Pb solder is 183°C, and most of the assembly equipment in use today is designed to operate using 183°C as a base reference (Abtew *et al.*, 2000). Some variation in the baseline temperature, for example 50°C (Abtew *et al.*, 2000), can be accommodated by the current equipment. If the melting point of the replacement lead-free solder is significantly higher than that in eutectic Sn-Pb solder, new equipment will have to be purchased, leading to significant capital expenditure and product cost increases.

Another reason for maintaining the melting point at a temperature close to 183°C is the prevalent usage of thermoset polymers in microelectronics packaging. Epoxy resins are used for encapsulation, substrates and attaching the silicon die to carriers or substrates, i.e. the die attach material. To some extent silicones are also used. It is important that these and other materials do not degrade during the soldering operations. Currently, the highest temperatures that these polymeric materials are exposed to is approximately 230°C for 90s (Abtew *et al.*, 2000), during board-level assembly and/or the reflow of solder balls and solder bumps.

Abtew and Selvaduray (Abtew *et al*., 2000) also reported melting/liquidus temperature of lead-free solder alloys, and are summarized in Table 2.2 above, melting temperature of Sn-Pb solder alloys are also given for reference. Temperatures for ternary and quaternary systems were frequently reported in the literature as "melting temperature", T_m. It is possible that the melting temperature reported is in reality the liquidus temperature, the temperature at which the solder alloy is completely molten (Abtew *et al*., 2000), since it is the liquidus temperature that is of importance to soldering operations in the microelectronics industry.

As can be seen from Table 2.2, the vast majority of the lead-free solder alloys have melting points or liquidus temperatures in the low 200°C range, though there are a few alloys with significantly lower melting temperatures, primarily among the Bi and In systems. The Sn-Cu systems have liquidus temperatures that are significantly higher than the 183°C eutectic temperature of the Sn-Pb system. Too high a liquidus or melting temperature means that processing temperatures have to be higher. When using a eutectic Sn-37Pb solder with a eutectic temperature of 183°C, the typical solder reflow temperature is 220°C, which represents a margin close to 40°C. The highest liquidus temperature that would be acceptable would be dependent on the following factors (Abtew *et al*., 2000):

- The highest temperature polymeric materials used in microelectronics can endure, without the onset of permanent degradation.
- The efficiency of heat transfer to ensure that the solder alloy melts, forms a joint, and resolidifies within a reasonable time so that productivity can be maintained (90 seconds is the current standard reflow time).
- The extent to which the temperature profile variations inside the ovens used for soldering can be controlled with precision.

Depending upon the answers to the factors mentioned earlier, it is possible to use solder alloys with higher liquidus temperatures. If a 20°C margin is sufficient, and the polymeric materials can withstand a maximum temperature of 250°C for about 120s without onset of degradation, then it becomes possible to use solder alloys with liquidus temperatures around 230°C (Abtew *et al*., 2000).

2.2.2 Wetting Characteristic

By definition, wetting is a measure of the ability of a material, generally a liquid, to spread over another material, usually a solid (Abtew *et al*., 2000). The extent of wetting is indicated by the contact angle.

Figure 2.5 shows the schematic diagram of a drop of liquid solder resting on a flat horizontal metallic surface in the flux atmosphere. This angle $\boldsymbol{\theta}$ formed between the liquid and the solid is called the *dihedral angle* (contact angle). Vector $\boldsymbol{\gamma}_{LF}$ is the surface tension between the liquid and its vapor phase, the interfacial tension $\boldsymbol{\gamma}_{LS}$ is the force between the liquid solder and the base metal, and $\boldsymbol{\gamma}_{SF}$ is the interfacial tension between the solid base metal and the vapor phase.

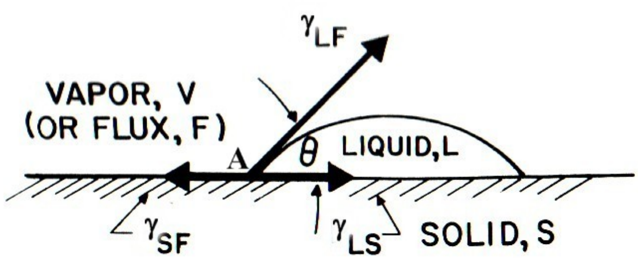

Figure 2.5: Diagram of Contact Angle

From the vector diagram, we get (Young-Dupre equation):

$$\mathrm{Cos}\theta = \frac{\gamma_{SF} - \gamma_{LS}}{\gamma_{LF}} \qquad (2.1)$$

Here γ_{SF} is the force that spreads the liquid on the solid, i.e., the spreading or wetting force. Spreading or wetting will occur if γ_{SF} is larger than the combination of γ_{LS} and $\gamma_{LF} Cos\ \theta$.

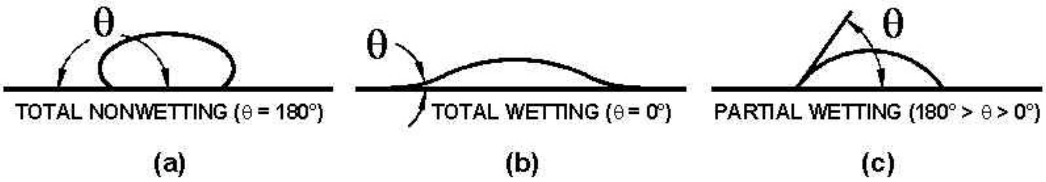

Figure 2.6: Relation between Contact Angle and Degree of Wetting

The two extreme conditions would be total nonwetting, where θ is equal to 180° (Figure 2.6.a), and total wetting, where θ is equal to 0° (Figure 2.6.b). Partial wetting will occur when θ is smaller than 180° and larger than 0° (Figure 2.6.c).

The range of θ (0-180) can be divided into three ranges as follows:

1. $\theta > 90°$. The condition of $\theta > 90°$ indicates the lack of wetting affinity between the liquid surface and the solid surface. The system is considered to be non-wetting.
2. $90° > \theta > M$. This indicates a condition of marginal wetting. Usually $M \leq 75°$ (Manko, 1979), and unless special conditions exist, this type of wetting is not acceptable. M is a purely arbitrary limit set by experience and fulfills the specific requirements of the individual solder system.
3. $\theta < M$. This indicates the condition of good wetting. M has the same value as in 2 above. If extremely high quality is required, the value of M can be taken less than 75°.

2.2.2.1 Surface Tension

The interfacial forces (surface tension) between the molten solder, flux and substrate influence the degree of wetting. Surface tension is one of the critical physical properties of solder that determines its wetting behavior.

The surface tension of a liquid is a thermodynamic quantity and is define as the amount needed to isothermally enlarge the liquid surface area (Wassink, 1989). Thermal equilibrium is seldom reached in actual surface mount technology soldering because the soldering operation is completed before the equilibrium temperature is reached. Furthermore, dissolution of the substrate in the molten solder, the oxidation of the flux, the soldering environment, etc., also affects the surface tension of solder.

Studies have shown that the value of surface tension of solder varies with temperature (Moser *et al*., 2001), alloy composition (Moser *et al*., 2002), flux composition (Goldman *et al*., 1976), and the extent of solder substrate interactions (Deighan *et al*., 1982).

Vincent and Richards (Vincent *et al*., 1993) measured the surface tension of a range of binary lead-free alloys in both air and nitrogen with <20 ppm O_2, at 50°C over their liquidus temperatures. The data are shown in Table 2.3.

Table 2.3: Measured Values of Surface Tension

Alloy	**Surface tension (mN/m)**	
	Air	**Nitrogen (<20ppm O_2)**
Bi-42Sn	319	349
Sn-9Zn	518	487
Sn-40Pb	417	464
Sn-3.5Ag	431	493
Sn-0.7Cu	491	461
Sn-5Sb	468	495

Generally, surface tension values tend to be lower in air than in an inert atmosphere since oxidation lowers the free energy of the liquid surface (Abtew *et al*., 2000). The measured values of eutectic Sn-Zn and Sn-Cu do not fit this trend.

Table 2.4: Natural Radius of Curve, R, of Lead-Free Solder Alloys

Alloy	**Density (g/cm^3)**	**R_{air} (mm)**	**$R_{nitrogen}$ (mm)**
Bi-42Sn	8.74	1.93	2.02
Sn-9Zn	7.27	2.70	2.61
Sn-40Pb	8.90	2.19	2.31
Sn-3.5Ag	7.39	2.44	2.61
Sn-0.7Cu	7.29	2.62	2.54
Sn-5Sb	7.25	2.57	2.64

The surface tension values contained in Table 2.3 were used to calculate the natural radius of curvature, R, of the alloys, according to equation 2.2 (Abtew *et al*., 2000), and the results are contained in Table 2.4.

$$R = \left(\sqrt{\frac{\gamma}{\rho g}} \right)^{1/2} \qquad (2.2)$$

Where γ is the surface tension, ρ is the density of solder, and g is the acceleration due to gravity.

As can be seen in Table 2.4, only Bi-42Sn has a natural radius of curvature that is less than Sn-Pb. The R-values of other alloys are greater than that of Sn-Pb.

2.2.2.2 Contact Angle

Although contact angle and surface tension are related, contact angle is more specifically related to the particular materials combination under investigation. Contact angle of solders is affected by variety of factors, including surface roughness (Lin *et al*., 2003), time, flux used (Vianco *et al*., 1992) and effectiveness of the flux (Abtew *et al*., 2000), and temperature of measurement (Loomans *et al*., 1994). Contact angle of lead free solders, primarily on copper substrates, using a variety of fluxes, has been investigated by several researchers, and is summarized in Table 2.5.

The data reported by Loomans et al. from Table 2.5 is most useful for comparing the contact angle of different alloys because they were all measured while using the same flux. Of the six alloys whose contact angle was measured, the Sn-10Bi-0.8Cu alloy has the lowest contact angle of 32°, at 250°C. The addition of 1 wt.% Zn to this alloy does not affect the contact angle significantly (Loomans *et al*., 1994).

Vianco et al. measured contact angle of two solder alloys with Oxygen-Free High Conductivity (OFHC) Cu substrates, using three different fluxes, thus showing the choice of flux can have effect on contact angle, which was reported to vary between 34 and 51° (Vianco *et al*., 1993).

Lin et al. measured contact angle of three alloys on Cu substrate with different surface roughness. Values of contact angle measured vary from 30° to 50°, and it depended on the surface roughness of substrates. However, effect of surface roughness on contact angle is not yet clear. In some case, contact angle decreased when surface roughness increases, in the other case, it was increased (Lin *et al*., 2002).

The data on contact angles of lead-free solder alloys is quite disparate, therefore a meaningful comparison of the alloy's performances is difficult. This is because the measuring temperature, preparation of the Cu substrates, fluxes used, and other experimental variables vary with each investigator. Therefore, it is need to establish a standard procedure for measuring the contact angles of lead free solder alloys.

Table 2.5: Contact Angle of Lead-Free Solders

Alloy	**Contact angle (°)**	**Temp. (°C)**	**Remarks**	**Reference**
Bi-42Sn	43+/-8	195	Cu substrate using A611 flux, addition of 1 wt% Cu, Sb, or Zn has little effect on solder spread	Jackson *et al*., 1994
	37+/-7	215		Jackson *et al*., 1994
Sn-9Zn			Poor wetting	Hua *et al*., 1997
Sn-5Sb	37			Pan *et al*., 1994
	36+/-3	260	On Cu, rosin flux	Vianco *et al*., 1993
	34<x<51		A611, A260HF and B2508 flux on OFHC[*] Cu substrate	Vianco *et al*., 1992
Sn-20In-2.8Ag	44+/-8	220	RMA Alpha flux, on OFHC Cu substrate	Artaki *et al*., 1994
Sn-50In	63+/-6	215	A611 Flux	Jackson *et al*., 1994
	41+/-9	230		
	33+/-5	245		
Sn-3Cu	31			Felton *et al*.
Sn-4Cu-0.5Ag	34<X<51		A611, A260HF and B2508 flux on OFHC Cu substrate	Vianco *et al*., 1992
Sn-10Bi-0.8Cu	32	250	Flux: Kester #197	Loomans *et al*., 1994
	42	340	Flux: Kester #197	Loomans *et al*., 1994
Sn-10Bi-0.8Cu-1Zn	33	250	Flux: Kester #197	Loomans *et al*.
	38	295	Flux: Kester #197	Loomans *et al*., 1994
	27	340	Flux: Kester #197	Loomans *et al*., 1994
Sn-10Bi-5Sb	39	250	Flux: Kester #197	Loomans *et al*., 1994
	48	340	Flux: Kester #197	Loomans *et al*., 1994
Sn-10Bi-5Sb-1Zn	50	250	Flux: Kester #197	Loomans *et al*., 1994
	29	340	Flux: Kester #197	Loomans *et al*., 1994
Sn-4.8Bi-3.4Ag	33+/-4	230	Flux: RMA Alpha 611	Vianco *et al*., 1993
	31+/-4	345	Flux: RMA Alpha 611	Vianco *et al*., 1993
	33+/-4	260	Flux: RMA on Cu	Vianco *et al*., 1993
Sn-1Ag-1Sb	38	250	Flux: Kester #197	Loomans *et al*., 1994
	43	340	Flux: Kester #197	Loomans *et al*., 1994
Sn-1Ag-1Sb-1Zn	41	250	Flux: Kester #197	Loomans *et al*., 1994
	41	295	Flux: Kester #197	Loomans *et al*., 1994
	42	340	Flux: Kester #197	Loomans *et al*., 1994
Sn-2.5Ag-0.8Cu -0.5Sb	44+/-8		On OFHC Cu substrate, using RMA Flux Alpha 611	Vianco *et al*., 1993
Sn-3.5Ag-(1-5)Bi	43>X>31	245	RMA flux,	Vianco *et al*., 1999
Sn-3.5Ag	31<X<42	280	RMA flux, rough Cu	Lin *et al*., 2002
Sn-3.2Ag-0.5Cu	30<X<50	280	RMA flux, rough Cu	Lin *et al*., 2002
Sn-3.5Ag-0.75Cu	34<X<44	280	RMA flux, rough Cu	Lin *et al*., 2002

(*): Oxygen-Free High Conductivity

2.2.2.3 Wetting Force

The wetting force balance that measures the force of interaction when a solid substrate is dipped into a liquid and then extracted is also utilized to determine the extent of wetting. The wetting force can be correlated to the contact angle, with higher wetting force indicating smaller contact angle and therefore better wetting. While both techniques permit measurement of the extent of wetting, the wetting force balance also permits measurement of the time required to attain the maximum extent of wetting for a particular combination. The wetting time is an important parameter for actual manufacturing operations. Typical processing times for completing soldering operations are 60-90s (Abtew *et al*., 2000). The solders may have good wetting characteristic (high wetting force, low contact angle), but require long periods to attain the maximum wetting force might be suitable from a scientific perspective, but would be commercially not viable due to loss of productivity.

Similar to contact angle, the data on wetting force of lead-free solder alloys is also disparate. Tojima (Tojima, 1999) has compared the maximum wetting force (F_{max}) and time to wetting (t_w) of three lead-free solders and eutectic Sn-37Pb solder. The data were measured at 240°C, with Cu substrates, using an aqueous clean flux (Kester #2224-25) and a no-clean flux. Three lead-free solders used were Sn-3.5Ag, Sn-58Bi, and Sn-9Zn. The results are shown in Table 2.6.

All three lead-free solder alloys had wetting forces (F_{max}) lower than the eutectic Sn-37Pb. While the choice of flux also had a major impact on the wetting forces measured, the trend remains the same. The Sn-9Zn alloy had particularly low F_{max} values, and it did not wet the Cu substrate at all when the less aggressive no-clean flux was used.

Table 2.6: Wetting Force of Lead-Free Solders on Cu Substrate

Alloy	**T_m (°C)**	**F_{max} (mN)**	**t_w (sec)**
Aqueous clean flux			
Sn-37Pb	183	5.025	0.457
Sn-3.5Ag	221	4.816	1.557
Sn-58Bi	139	3.814	0.486
Sn-9Zn	199	1.931	1.029
No-clean flux			
Sn-37Pb	183	4.396	1.100
Sn-3.5Ag	221	2.594	3.057
Sn-58Bi	139	2.570	1.714
Sn-9Zn	199	- 5.790	-

The same measurements were repeated at a temperature of 62°C above the melting point, and the results are shown in Table 2.7. The measurements at 62°C above the melting point were done because the reflow temperature for each alloy would be dependent on its melting temperature. A solder alloy has the melting temperature of 140°C could be reflowed at around 180-190°C, which is much lower than the 220-240°C range of reflow temperature for eutectic Sn-37Pb solder (Abtew *et al.*, 2000). By measuring the wetting force of the alloys at a constant temperature value above the melting point, it was thought that the wetting force on Cu could be more accurately characterized, for manufacturing purposes.

It can be seen that the wetting force of the Sn-3.5Ag alloy is comparable to, if not better, than that of eutectic Sn-37Pb. The wetting force displayed by the Sn-9Zn alloy is still significantly lower than the others, with non-wetting occurring when a no-clean flux is used.