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Lead-free Solders in Microelectronics

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Abstract

Practically all microelectronic assemblies in use today utilize Pb–Sn solders for interconnection. With the advent of chip scale packaging technologies, the usage of solder connections has increased. The most widely used Pb–Sn solder has the eutectic composition. Emerging environmental regulations worldwide, most notably in Europe and Japan, have targeted the elimination of Pb usage in electronic assemblies, due to the inherent toxicity of Pb. This has made the search for suitable ''Pb-free'' solders an important issue for microelectronics assembly. Approximately 70 Pb-free solder alloy compositions have been proposed thus far. There is a general lack of engineering information, and there is also significant disparity in the information available on these alloys. The issues involved can be divided into two broad categories: manufacturing and reliability/performance. A major factor affecting alloy selection is the melting point of the alloy, since this will have a major impact on the other polymeric materials used in microelectronic assembly and encapsulation. Other important manufacturing issues are cost, availability, and wetting characteristics. Reliability related properties include mechanical strength, fatigue resistance, coefficient of thermal expansion and intermetallic compound formation. The data available in the open literature have been reviewed and are summarized in this paper. Where data were not available, such as for corrosion and oxidation resistance, chemical thermodynamics was used to develop this information. While a formal alloy selection decision analysis methodology has not been developed, less formal approaches indicate that Sn-rich alloys will be the Pb-free solder alloys of choice, with three to four alloys being identified for each of the different applications. Research on this topic continues at the present time at a vigorous pace, in view of the imminence of the issue. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Solders; Microelectronic packaging; Interconnects; Surface mount; Tin; Lead; Indium

1. Introduction

Soldering is a well-known metallurgical joining method that uses a filler metal, the solder, with a melting point below 425°C [1]. In the immense electronic materials world, solder plays a crucial role in the assembly and interconnection of the silicon die (or chip). As a joining material, solder provides electrical, thermal and mechanical continuity in electronics assemblies. The performance and quality of the solder are crucial to the integrity of a solder joint, which in turn is vital to the overall functioning of the assembly. Solders are used in different levels of the electronic assembly sequence, as shown in Fig. 1. As a die bonding material, the solder provides the electrical and mechanical connection between the silicon die and the bonding pad. It also serves as a path for dissipation of the heat generated by the semiconductor. Bonding of the die to a substrate and its encapsulation is referred to as Level 1 packaging. While the predominant method of providing electrical connection to the silicon chip is through wire bonding, the use of solder bumps on the

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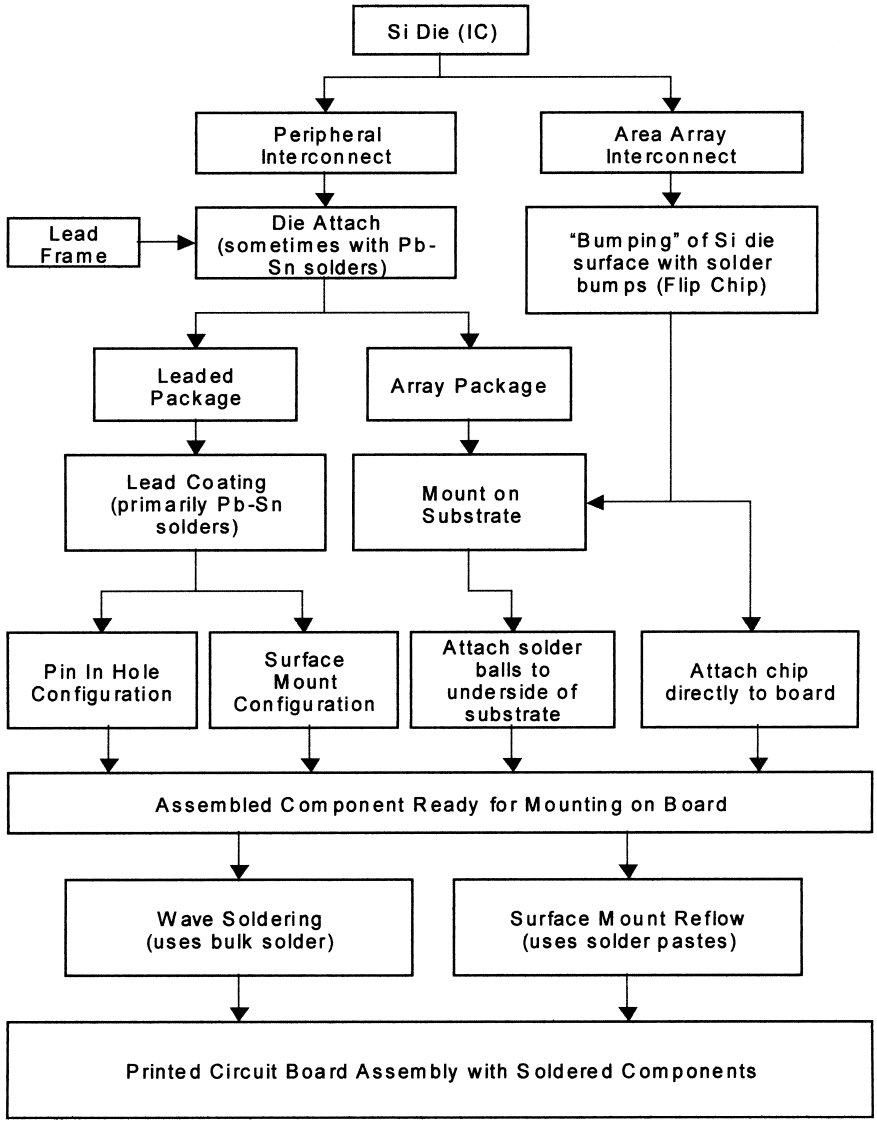

Fig. 1. Overview of silicon IC assembly process.

surface of the Si die, instead of wire bonding, has been gaining acceptance recently, due to the higher number of input/output terminals that can be attached to a given area. The flip chip configuration, a cross section of which is shown in Fig. 2, is such an approach. The Si die is turned 'upside down', hence flip chip, and mounted on an appropriate substrate.

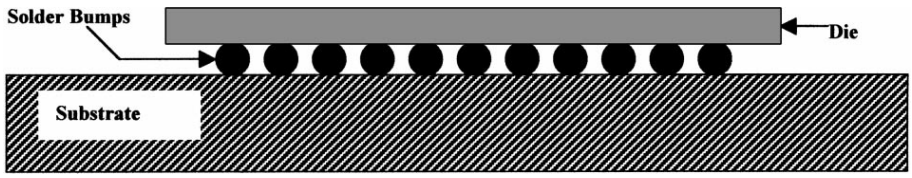

Fig. 2. Cross-section of a flip chip connection.

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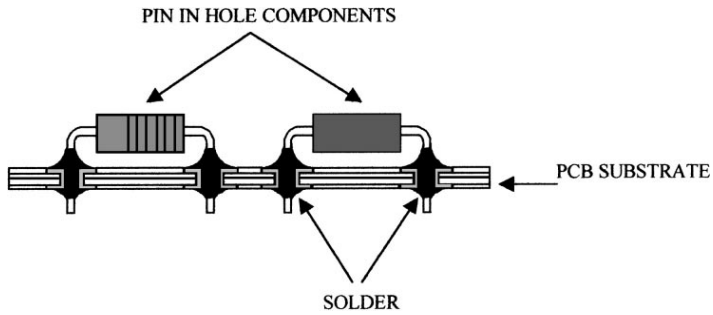

Fig. 3. Cross-section of a pin through hole connection of a microelectronics component on a printed wiring board.

The next level of assembly and interconnect, referred to frequently as Level 2 packaging, is where the component (encapsulated silicon die) is mounted on a printed wiring board (PWB). Solder is the primary means of interconnect in Level 2 packaging. Practically all microelectronic devices (also known as packages) are mounted on PWBs using solders. There are two primary means of attaching electronic components to PWBs — pin-through-hole (PTH) or surface mount technology (SMT), illustrated in Figs. 3 and 4, respectively. Surface mounted electronic components can either be leaded, i.e. with leads, as shown in Fig. 4 or have solder balls that are called ball grid arrays (BGAs), as shown in Fig. 5. The locations where solders are used are also shown.

1.1. Printed circuit board assembly

The assembly and soldering of Printed Circuit Board Assemblies (PCBA) can involve pure surface mount components or mixed technology assemblies where both SMT and PTH are used, either in single- or double-sided PCBA configuration. Soldering of surface mounted devices, commonly called reflow soldering is done by application of solder paste on one of the mating surfaces, usually on soldering pads located on the PCB, and heating the assembly to melt the paste, which upon solidification forms the joint. The solder paste is a mixture of solder powder, flux and other additives forming a thick cream. Additives are included in the paste to promote wetting (surfactants) and to control the property of the paste (tackiness, slump, viscosity, etc.). Reflow soldering is defined as 'the joining of mating surfaces that have been tinned and/or have solder between them, placing them together, heating them until the solder fuses, and allowing them to cool in the joined position' [2].

As shown in Fig. 6, PTH soldering is done by wave soldering, where the assembly is transported over a molten solder bath from which the solder rises and forms solder joints by capillary action. The properties of the solder that are important are invariably process dependent. The formulation and printability of the solder paste are critical parameters for reflow soldering, while viscosity

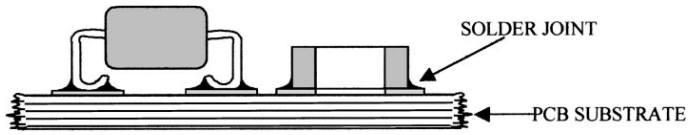

Fig. 4. Cross-section of a surface mount connection of a microelectronics component with leads on a printed wiring board.

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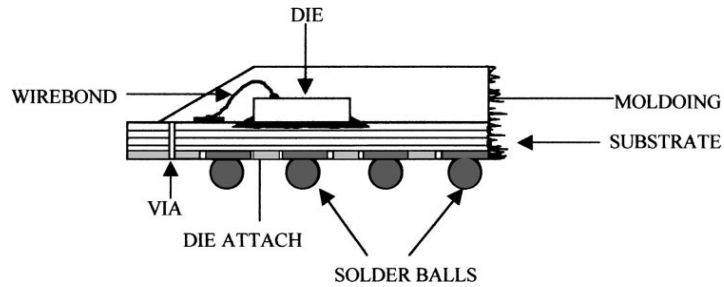

Fig. 5. Cross-section of a ball grid array (BGA) microelectronics component.

and density of the molten solder significantly influences the performance of the wave soldering process.

1.2. Solder usage in Level 1 packaging

Hitherto, solder usage had been restricted primarily to the board level assembly process, i.e. Level 2 packaging, with very little being used in Level 1 packaging. However, with the advent of area array packaging concepts (flip chip and ball grid arrays), usage of solders in Level 1 packaging is increasing sharply. In the 'flip chip' approach the silicon die has an array of solder bumps placed on it, usually by plating or vapor deposition.

For Si dies that have their terminals on the periphery, and are therefore wire bonded, the trend has been to attach the component to the board via the area array concept, by using solder balls, as shown in Fig. 5. The solder balls are attached to the substrate, and the entire assembly is processed through a reflow oven. The solder ball melts and forms a joint between the solder ball pad of the substrate and the ball itself.

1.3. Pb in Sn–Pb solders

In board level packaging the solder used is primarily 63Sn–37Pb, a eutectic composition, or 60Sn–40Pb, a near eutectic composition. With a melting eutectic temperature of 183°C, the Sn–Pb

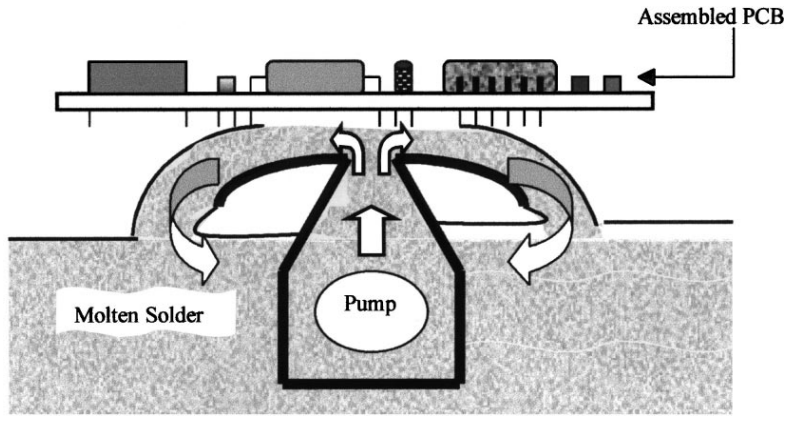

Fig. 6. Wave soldering of a PCBA.

binary system allows soldering conditions that are compatible with most substrate materials and devices. As one of the primary components of eutectic solders, Pb provides many technical advantages, which includes the following to Sn–Pb solders:

1. Pb reduces the surface tension of pure tin, which is 550 mN/m at 232°C, and the lower surface tension of 63Sn–37Pb solder (470 mN/m at 280°C) facilitates wetting [3].
2. 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 [4].
3. 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.

These factors, combined with Pb being readily available and a low cost metal, make it an ideal alloying element with tin. The board level soldering system that is mainly based on eutectic and near eutectic Sn–Pb solders has been well developed and refined with many years of experience. A relatively well-established knowledge base about the physical metallurgy, mechanical properties, flux chemistries, manufacturing processes and reliability of eutectic Sn–Pb solders exists. Board level assembly and soldering equipment are almost exclusively engineered with Sn–Pb solder in mind. A good understanding of the behavior of Sn–Pb solders has enabled current board level technology to assemble and create small geometry solder joints, approaching 75 μm in size, in high volume, and at competitive cost. Nevertheless, there are legal, environmental and technological factors that are pressing for alternative soldering materials and processing approaches. These factors include:

1. Legislation that tax, restrict or eliminate the use of Pb due to environmental and toxicological concerns.
2. The continued trend towards packaging and interconnect miniaturization in 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) [5] 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.
3. 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.
4. The need for cascade soldering of complex assemblies that require different types of solders with different melting temperatures.

There are several Pb-free solders, such as Sn–Au, Sn–In, Sn–Ag, Sn–Bi, that have been in use in the electronics industry for special applications. Major solder paste vendors have research programs targeted at developing new alloys that can be ‘drop in’ replacements for eutectic Sn–Pb. Many of these new alloys are ternaries and quaternaries, rather than binaries, and information regarding the characteristics of these alloys is frequently proprietary; there is relatively little information available in the open literature.

In this paper a review of the existing literature on the metallurgy of Pb-free solders for microelectronics applications is presented. To this end, the physical, electrical, chemical and mechanical properties, including the physical metallurgy, of alternative solders are discussed. The corrosion behavior of Pb-free solders as applicable to microelectronics is also described. First, a brief

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description of the legislative and regulatory actions advocated to restrict the use of Pb is provided. However, prior to that, in order to avoid confusion, a brief description of the two drastically different usages of the word 'lead' is provided.

1.4. Pb and lead

Due to possible confusion arising from the use of the word 'lead', which could have two different meanings, the chemical symbol Pb is used when the metallic element lead is being referred to. When fully spelt out as 'lead', it stands out for 'a self-supporting path which connects the electrical component to the outside world', as shown in Fig. 4.

2. Health and environmental concerns with lead

2.1. Adverse health effects of lead

Lead and Pb compounds have been cited by the Environmental Protection Agency (EPA) as one of the top 17 chemicals posing the greatest threat to human life and the environment [6]. When Pb accumulates in the body over time, it can have adverse health effects. Lead binds strongly to proteins in the body and inhibits normal processing and functions of the human body. Nervous and reproductive system disorders, delays in neurological and physical development, cognitive and behavioral changes, reduced production of hemoglobin resulting in anemia and hypertension [7] are some of the adverse effects of lead on human health. When the level of lead in the blood exceeds 50 mg/dl of blood, lead poisoning is considered to have occurred [8]. Recent studies have found that a Pb level even well below the established official threshold could be hazardous to a child's neurological and physical development.

The concern about the use of Pb in the electronics industry stems from occupational exposure, Pb waste derived from the manufacturing process, and the disposal of electronic assemblies. Although the consumption of Pb by the electronics industry appears to be minimal [7], the potential for Pb exposure cannot be ignored. A potential source of occupational exposure in electronics is the soldering process, especially the wave soldering operation. Studies have shown that there is little danger of exposure to Pb in hand soldering and tinning operations because Pb is relatively non-volatile at normal soldering temperatures [9]. However, inhalation of Pb vapors or Pb bearing dust generated by dross during the wave soldering operation is a possible danger to workers. Wave soldering generates dross due to surface oxidation at the surface of the molten solder. About 90% of dross formed during wave soldering can be refined to pure metal for reuse [10], but the remaining is a waste product. The Resource Conservation and Recovery Act has classified this waste as hazardous to human health and requires special handling and disposal. The Occupational Safety and Health Administration (OSHA) requires that workers have no more than 50 mg/dl of Pb in their blood [11]. This exposure limit is related to maintaining Pb levels in blood at or below 40 mg/dl, believed to prevent adverse health effects from exposure to Pb throughout a working lifetime. For workers planning to have children, OSHA recommends maintaining blood Pb levels below 30 mg/dl.

2.2. Lead and the environment

Lead and Pb containing compounds are considered environmental hazards because of lead's toxicity [12]. In the electronics industry, the lead generated by the disposal of electronic assemblies

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Table 1
World market for PCB assemblies

Country	Dollar value (in billions)	
	1992	1997 [16]
Japan	6	7.2
USA	5.8	14.6
Asia	3.4	8.7
Europe	3.2	9.7
Rest of the world	1.6	2.0
Total	20	42.2

is considered as hazardous to the environment. The world markets for the assembly and soldering of PCB is shown in Table 1, with Japan and the US being the major suppliers and users of PCB assemblies [13]. This market is expected to double within the next 10 years [13,14]. At the end of the useful life of lead bearing electronic products, they are typically disposed of in solid waste landfills. There are no clear scientific data or studies that clearly describe the mechanism by which lead from disposed electronic products enter the ground water stream, or the animal or human food chain. The only available data that appears to be relevant come from unrelated studies that have described the breakdown of PbO to $PbCO_3$ in the presence of Cl^- and CO_2 [15].

In 1986, a review of the use of lead in electrical and electronics applications actually revealed a dramatic decrease [17]. The use of lead in batteries appeared to be constant. The use of lead for electronic soldering accounts for approximately 40–50% of the total for all soldering uses. It is expected that industries will be required to increase the extent of recycling of lead. But the use of recycled lead for electronics application can be severely limited since recycled lead displays higher α-particle emission than virgin lead. This can have detrimental effects on the performance of integrated circuits because α-particle emission leads to the occurrence of soft errors [18].

2.3. Legislation

In the US, legislation to limit the use of lead has been introduced in both the Senate and the House of Representatives. The Legislation includes: (a) H.R. 2922, the Lead based Paint Hazard Abatement Act of 1991, which would impose a tax on lead, (b) S. 391, the Lead Exposure Reduction Act of 1991, and (c) H.R. 3554, the Lead Exposure Act of 1992 [18]. These bills have not passed yet, but it is likely that some form of legislation will be passed in the future. As can be seen from recent proposals, the use of lead will be restricted and requirements such as notification to EPA for new products containing lead may be imposed. The EPA has released an Advanced Notice of Proposal Rule (APR) entitled ‘Comprehensive Review of Lead in the Environment’ under the Toxic Substance Control Act (TSCA) that has significant regulatory implications [19]. Such requirements could affect product development and new product release schedules. Although it is unlikely that the US will ban the use of lead in electronics in the near future, lead prices will definitely increase due to increasing regulatory requirements, taxes, and fees.

While in the US there has been serious discussion of requiring the electronics industry to do away with Pb in solder alloys, in Europe the same trend has been gaining momentum and acceptance. From 1 January 2004, European nations will be requiring the use of Pb-free solder alloys in all electronic assemblies, according to the *Directive on Waste from Electrical and Electronic Equipment* which would require that ‘the use of lead, mercury, cadmium, hexavalent chromium, and

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halogenated flame retardants' be phased out [20]. This will be a requirement for both domestic and foreign manufacturers. If the US industry does not comply with this requirement, then exports to Europe will become impossible.

While Japan has not banned the use of lead, legislation being proposed there will prohibit lead from being sent to land fills and other waste disposal sites. This leaves manufacturers with the option of either attaining 100% recycling of lead, or using Pb-free solder alloys.

Therefore, developing viable alternative Lead-free solders for electronic assemblies is of paramount importance. Major Japanese corporations have begun to respond to this by announcing their own plans for shifting to Pb-free solders. Seiko Epson Corp. has announced that it will cease using Pb-bearing solders in PCBs for printers and other equipment by March 2002 [21].

3. Performance characteristics of 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 performance, and must also have the desired melting temperature. It must adequately wet common PCB lands, 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.

When trying to identify an alternative to the current Pb–Sn solders that are widely used, it is important to ensure that the properties of the replacement solder are comparable to or superior than Pb–Sn solders. The major performance characteristics of solder that are of importance for second level packaging applications are manufacturability, reliability and environmental suitability. Manufacturability describes how well a Pb-free solder fits into current second level packaging practices without requiring significant changes. Manufacturability involves most of the physical properties of a solder alloy relevant to soldering such as melting temperature, solderability, viscosity, density, thermal and electrical properties, corrosion and oxidation behavior, surface tension, reworkability and cost. Reliability of a solder alloy for the first and second level packaging is mainly dependent to the coefficient of thermal expansion, elastic modulus, yield strength, shear strength, fatigue and creep behavior of the alloy. A Pb-free alloy also needs to be environmentally friendly. The properties of solders that are of importance from a manufacturing and also long-term reliability standpoint are summarized in Table 2. In the next sections, a detailed description and analysis of the desirable performance characteristics of potential Pb-free solders are provided.

Table 2
Important properties of solder alloys

Properties relevant to manufacturing	Properties relevant to reliability and performance
Melting/liquidus temperature	Electrical conductivity
Wettability (of copper)	Thermal conductivity
Cost	Coefficient of thermal expansion
Environmental friendliness	Shear properties
Availability and number of suppliers	Tensile properties
Manufacturability using current processes	Creep resistance
Ability to be made into balls	Fatigue properties
Copper pick-up rate	Corrosion and oxidation resistance
Recyclability	Intermetallic compound formation
Ability to be made into paste	

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Table 3
Metal cost per kg[a]

Element	Cost (2 January 1997) (US$/kg)
Lead	1.10
Zinc	1.08
Copper	2.24
Antimony	2.64
Bismuth	7.15
Tin	8.67
Silver	153.19
Indium[b]	194.59

[a] Metal cost only, does not include fabrication costs, margins, etc.; original data (in US$/lb) was multiplied by 2.2 to obtain cost in kg.
[b] The indium price has been highly variable; 1-year-prior, the price was US$ 230.00/lb.

4. Solder alloy costs

The microelectronics industry is extremely cost conscious. The history of the industry has been to continuously produce higher performance at lower costs. Since cost of the product is the resultant of the cumulative cost of the components, the cost of Pb-free solder alloys can impact the cost of the finished product. Cost competitiveness in the electronics industry is maintained by reducing the cost of individual components to a minimum, in order to maximize the overall cost reduction.

The unit cost of the major elemental metals used in solders is summarized in Table 3. In Table 4, the cost of some solder alloys is listed. On an elemental basis, Pb and Zn are the cheapest metals. Surprisingly, In is more expensive than Ag. All of the Pb-free solder alloys are more expensive than the eutectic Pb–Sn alloy, which costs US$ 5.87/kg. While some of the alloys are in the US$ 7.70–8.80/kg range, other alloys cost between US$ 11.00 and 16.50/kg. The Sn–In–Ag ternary alloy costs US$ 51.63/kg. If cost were the sole deciding factor, it is highly unlikely that the electronics industry would adopt an alternative solder. There has to be a demonstrated benefit in using one or more of the

Table 4
Cost of solder alloys per kg

Alloy	Cost (12 January 1997) (US$/kg)	Patented alloy
63Sn–37Pb	5.87	No
42Sn–58Bi	7.79	No
77.2Sn–20In–2.8Ag	51.63 (113.92)[a]	Yes
85Sn–10Bi–5Zn	8.14	No
91Sn–9Zn	7.99	No
90Sn–7.5Bi–2Ag–0.5Cu	11.42	No
96.3Sn–3.2Ag–0.5Cu	13.27	No
95Sn–3.5Ag–1.5In	16.52 (21.19)[a]	No
96.2Sn–2.5Ag–0.8Cu–0.5Sb	2.21	Yes
96.5Sn–3.5Ag	13.73	No
98Sn–2Ag	11.55	No
99.3Sn–0.7Cu	8.62	No
97Sn–2Cu–0.8Sb–0.1Ag	8.78	Yes
95Sn–5Sb	8.36	No

[a] Based on indium cost in January 1996.

Pb-free solder alloys. For example, a significant improvement in reliability that can offset the cost increase could justify the adoption of a higher cost alternative. However, in the case of Pb-free solders, the driving force is government legislation, which would eventually prohibit the use of the lower cost solder alloy, which happens to have a long track record at this point. It should also be noted from Table 4, that three of the alloys listed are patented alloys, which implies that the number of suppliers could be restricted. The prospect of an entire industry being dependent on one supplier for its solder alloys is not desirable. If this were to happen, the likelihood of future price decrease would be extremely small as there will be no competition.

The price of In has been highly variable. While in January 1997 the price of metallic In was US$ 187/kg, it has been subjected to major fluctuations in the past. The average annual price was US$ 136.4/kg in 1994, US$ 374/kg in 1995, US$ 369.6/kg in 1996, US$ 308/kg in 1997 and US$ 297/kg in 1998 [22]. Indium is recovered almost exclusively as a byproduct of Zn production. No In was recovered from ores in the US in 1998 [21]. The top four In producing countries for 1996 were Canada, China, France, and Japan, accounting for a total of 76% of world consumption [23]. The price of Ag has also fluctuated in the past, although it has been relatively stable over the last 15 years. While price fluctuations of minor components have minimal effect on the alloy cost, price fluctuations of major constituents can be expected to have a more significant effect, thus making In a less attractive choice.

Purely from a cost and availability standpoint, an unpatented solder alloy, with multiple suppliers and a stable price structure, and no geopolitical concerns, would be most desirable.

5. Pb-free solder alloy compositions

A relatively large number of Pb-free solder alloys have thus far been proposed, and are summarized in Table 5, with their elemental compositions. The solder alloys are binary, ternary and some are even quaternary alloys. A total of 69 alloys were identified from the literature. It can be noticed that a very large number of these solder alloys are based on Sn being the primary or major constituent. The two other elements that are major constituents are In and Bi. Other alloying elements are Zn, Ag, Sb, Cu, and Mg and in one case a minor amount of Pb. In reviewing the compositions listed in Table 5, it can be seen that some compositions are variations of one basic composition. For example, there are four Sn–10Bi compositions, with variations in the ternary additive — either Cu or Sb, and with or without Zn. A brief description of Sn, and other major binary systems is provided in this section.

5.1. Tin

The ability of 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 Sn melts at 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. Consequently tin pest can be a problem for applications that operate at extremely low temperature and can be particularly problematic for devices that cycle across the 13°C temperature. Due to its body centered tetragonal crystal structure that is anisotropic, the thermal

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Table 5
Elemental composition of Pb-free solder alloys

Alloys	Sn	In	Zn	Ag	Bi	Sb	Cu	Mg	Fe	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–43Sn+2.5% Fe	43				54.5				2.5	
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–(CASTIN)	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–4Cu–0.5Ag	95.5			0.5			4			
Sn–10In–1Ag–(0–10.5)Bi	78.5	10		1	10.5					
	89	10		1	0					
Sn–20In–2.8Ag	77.2	20		2.8						
Sn–42In	58	42								
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								

Table 5 (*Continued*)

Alloys	Sn	In	Zn	Ag	Bi	Sb	Cu	Mg	Fe	Pb
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							

expansion of tin is also anisotropic [24]. 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 [25]. 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 [26], 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.

Tin is also prone to whisker growth — single-crystal growth resembling fine wire that can extend up to 0.64 mm high [27]. The whiskers are tetragonal β-tin that may grow in response to internal stress in the material or external loads. Rapid whisker growth in tin occurs at about 51°C and is influenced by plating conditions and substrate property. Whiskers do not affect solderability nor do they cause deterioration of the tin coatings. However, longer whiskers may cause electrical shorts in PCBs. Elements such as lead suppress whisker growth in tin. Virtually no whisker growth is encountered in eutectic tin–lead solder [27].

5.2. Sn–Zn

The Sn–9 wt.% Zn alloy appears to be an attractive alternative, with a melting temperature of 198°C that is relatively close to eutectic tin–lead. Its 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 [28]. The solidified microstructure is reported to exhibit large grains with a fine uniform two-phase eutectic colony. Sn–9 wt.% Zn is the eutectic composition for the Sn–Zn system, and the microstructure can be expected to be lamellar, consisting of alternating Sn-rich and Zn rich phases. Compared to the Pb–Zn system, in the Sn–Zn system, both Sn and Zn interact with Cu to form intermetallic phases.

5.3. Sn–Cu

The Sn–Cu binary alloy has a eutectic composition of Sn–0.7 wt.% Cu and a eutectic temperature of 227°C. The solidification reaction consists of Cu precipitated in the form of hollow rods of the intermetallic Cu_6Sn_5. Data that describes the property of this alloy hardly exists. However, because of the high concentration of tin in this alloy, it may be prone to whisker growth or transformation to gray tin may occur. The effect of Cu additions on tin whisker growth, or the $\beta \rightarrow \alpha$ transformation is not clear at this time.

5.4. Sn–Bi

The Sn–Bi alloy has a eutectic composition of 42Sn–58Bi and a relatively low eutectic temperature of 139°C. The room temperature equilibrium phases are Bi and Sn with about 4 wt.% Bi in solid solution [29]. 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.% [30]. 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. [31] for relatively slow cooling rates. Wild [32] 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 occurs. Cracking was not observed during rapid cooling. Cooling rates, however, were not specified in the literature. It has also been reported [24] 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 [32].

5.5. Sn–Ag

The eutectic composition for the Sn–Ag binary system occurs at Sn–3.5Ag. The eutectic temperature is 221°C. The microstructure consists of Sn and the intermetallic Ag_3Sn in the form of thin platelets [33]. McCormack et al. [33] 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 [34]. 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.

5.6. Sn–In

Due to their substantially lower melting temperature and a much lower tendency to scavenge gold, compared to tin–lead solders, In–Sn solders have been used for SMT applications. The indium based solder with the composition of In–48Sn is the one that is commonly used for SMT applications. The eutectic composition is In–49.1Sn, 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 [24]. Mei and Morris [35] 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 [36], and significant microstructural coarsening was observed by Seyyedi [37], after prolonged aging of the solder joints made on a Cu substrate.

6. Melting/liquidus temperature

From a manufacturing perspective the melting temperature, i.e. the liquidus temperature, is perhaps the first and most important factor. The eutectic temperature of Sn–Pb is 183°C, and most of the assembly equipment in use today is designed to operate using 183°C as a base reference. While some variation in the baseline temperature, for example 50°C, can be accommodated by the equipment currently in place, if the melting point of the replacement Pb-free solder is significantly higher, then new equipment will have to be purchased by manufacturers, 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 90 s, during board-level assembly and/or the reflow of solder balls and solder bumps.

For binary and higher systems, a unique 'melting temperature' can be expected only for eutectic compositions or for compositions that melt congruently. Other compositions can be expected to melt over a range of temperatures, with melting beginning at the solidus temperature and being complete at the liquidus temperature. The solidus, liquidus and eutectic temperatures for binary systems are readily available. Melting temperature information for ternary systems are less readily available, and for quaternary systems they can be extremely difficult to obtain, except perhaps from the developers or manufacturers of the particular alloy.

The solidus, T_s, liquidus, T_l, and eutectic temperatures, T_e, for the alloys in Table 5 are presented in Table 6. Temperatures for ternary and quaternary systems were frequently reported in the literature as 'melting temperature', T_m, and therefore are listed as such in Table 6 as well. It is possible that the melting temperature reported is in reality the liquidus temperature, i.e. the temperature at which the solder alloy is completely molten, since it is the liquidus temperature that is of importance to soldering operations in the microelectronics industry. The liquidus, solidus and eutectic temperatures of the Pb–Sn system have been included in Table 6 for purposes of reference to current practice. The melting temperature for some ternary and quarternary systems was not reported. It is not possible to independently determine these, unless ternary and quaternary phase diagrams for these systems are available, or if they are directly measured.

As can be seen from Table 6, the vast majority of the Pb-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 Pb–Sn system. Too high a liquidus or melting temperature means that processing temperatures have to be higher. When using a eutectic Pb–Sn solder with a eutectic temperature of 183°C, the typical solder

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Table 6
Melting points of Pb-free solder compositions[a]

Alloy composition	T_m (°C)	T_s (°C)	T_l (°C)	T_e (°C)	Reference
Sn–37Pb				183	
Sn–40Pb		183	187		
Bi–26In–17Sn	79				[38]
Bi–32In				109.5	
Bi–41.7Sn–1.3Zn	127				[39]
Bi–41Sn–1Ag					
Bi–41Sn–1Pb					
Bi–42Sn				139	
Bi–43Sn (eutectic)				139	
Bi–43Sn+2.5% Fe					
Bi–45Sn–0.33Ag	140–145				[40]
In–3Ag				141	
In–34Bi				110	
In–48Sn (eutectic)				117	
Sn–1Ag–1Sb		222	232		[41]
Sn–1Ag–1Sb–1Zn					
Sn–2.5Ag–0.8Cu–0.5Sb	210–216		217		[42,43]
Sn–2.8Ag–20In	178				[43]
Sn–25Ag–10Sb	233				[44]
Sn–2Ag		221	225		
Sn–2Ag–0.8Cu–0.6Sb	210–216				[39]
Sn–2Ag–0.8Cu–6Zn		217	217		[41]
Sn–2Ag–0.8Cu–8Zn		215	215		[41]
Sn–3.5Ag				221	
Sn–3.5Ag–(<6)Bi		211–221	212		[39,43]
Sn–3.5Ag–1Zn	217				[45,46]
Sn–3.5Ag–1Zn–0.5Cu	216, 217				[28,45]
Sn–3.6Ag–1.5Cu	225				[41]
Sn–4.7Ag–1.7Cu	217				[39,47]
Sn–4Ag		221	225		
Sn–4Ag–7Sb			230		[41]
Sn–4Ag–7Sb–1Zn					
Sn–10Bi–0.8Cu		185	217		[41]
Sn–10Bi–0.8Cu–1Zn					
Sn–10Bi–5Sb		193	232		[41]
Sn–10Bi–5Sb–1Zn					
Sn–4.8Bi–3.4Ag					
Sn–42Bi		139	170		
Sn–45Bi–3Sb		145	178		[41]
Sn–45Bi–3Sb–1Zn					
Sn–56Bi–1Ag	136.5				[39]
Sn–57Bi–1.3Zn	127				[39]
Sn–5Bi–3.5Ag					
Sn–7.5Bi–2Ag–0.5Cu		207	212		[38]
Sn–0.75Cu		227	229		
Sn–0.7Cu (eutectic)				227	
Sn–2Cu–0.8Sb–0.2Ag	266–268				[42]
Sn–3Cu		227	275		
Sn–4Cu–0.5Ag		216	222		[38,48,49]
Sn–10In–1Ag–(0–10.5)Bi	188–197				[39]
Sn–20In–2.8Ag	178–189				[39]
Sn–42In		117	140		
Sn–5In–3.5Ag					
Sn–10In–1Ag–0.5Sb	196–206				[39]
Sn–36In		117	165		
Sn–50In		117	125		
Sn–8.8In–7.6Zn	181–187				[39]

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Table 6 (*Continued*)

Alloy composition	T_m (°C)	T_s (°C)	T_l (°C)	T_e (°C)	Reference
Sn–2Mg (eutectic)				200	
Sn–5Sb		234	240		
Sn–4Sb–8Zn	198–204				[39]
Sn–7Zn–10In–2Sb	181				[46,50]
Sn–8Zn–10In–2Bi	175				[51]
Sn–8Zn–4In					
Sn–8Zn–5In–(0.1–0.5)Ag	187				[39,45]
Sn–9Zn–10In	178				[46,50]
Sn–5.5Zn–4.5In–3.5Bi	185–188				[39]
Sn–6Zn–6Bi	127				[39]
Sn–9Zn (eutectic)				198	
Sn–9Zn–5In	188				[39,46,50,51]

[a] All unreferenced data was obtained from [52].

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:

1. The highest temperature polymeric materials used in microelectronics can endure, without the onset of permanent degradation.
2. 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 s is the current standard reflow time).
3. 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 120 s without onset of degradation, then it becomes possible to use solder alloys with liquidus temperatures around 230°C.

The solidus temperature determines the homologous temperature of the solder alloy. For eutectic Pb–Sn alloys room temperature represents ~0.65 of the homologous temperature. As such, if the solder alloy is subjected to a constant static load, it can be expected to creep. The use of solder alloys with lower solidus temperatures means that the homologous temperature will increase. This can be expected to result in the alloy being subjected to more severe creep conditions. From a 'resistance to creep' perspective, it would be advantageous to use solder alloys with higher solidus temperatures.

(The homologous temperature (T_H) is obtained by dividing the alloy's desired service temperature, in Kelvin, by its melting point, also in Kelvin. It is a measure of the state of activation of the atoms within a metallic alloy. When T_H>0.5, then the atoms within the alloy have sufficient energy to participate in thermally activated processes such as creep and grain growth.)

7. Wetting characteristics

To form a proper metallurgical bond between two metals, wetting must take place. This means that a specific interaction must take place between the liquid solder and the solid surface of the parts to be soldered. The ability of the molten solder to flow or spread during the soldering process is of

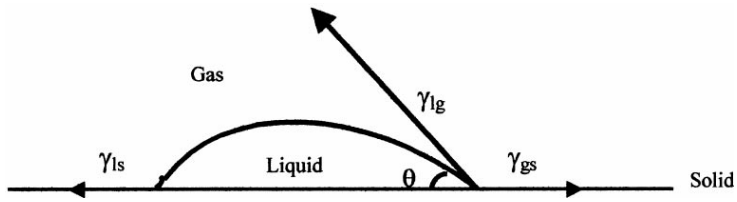

Fig. 7. Diagram of wetting angle.

prime importance for the formation of a proper metallic bond. The term 'wetting' is often used when discussing soldering processes. The phenomenon of spreading is also frequently referred to as wetting. By definition, wetting is a measure of the ability of a material, generally a liquid, to spread over another material, usually a solid [5]. The extent of wetting is measured by the contact angle that is formed at the juncture of a solid and liquid in a particular environment, as shown in Fig. 7. In general, if the wetting or contact angle lies between 0 and 90° the system is said to wet, and if the wetting angle is between 90 and 180°, the system is considered to be non-wetting. The contact angle (θ) is determined from the balance of surface tensions at the juncture, according to the Young–Dupre equation:

$$\gamma_{gs} = \gamma_{ls} + \gamma_{gl} \cos \theta \tag{1}$$

where γ_{gs} is the surface tension of the solid in the particular environment, γ_{ls} is the interfacial energy (surface tension) between the solid and the liquid, and γ_{gl} is the surface tension of the liquid in the same environment.

The most fundamental characterization of wetting is given by considering the thermodynamics of the wetting forces. In terms of free energy, good wetting will occur if there is a net lowering of the total free energy, i.e. the surface energy of the solder is lowered by it forming an interface that is at a lower surface interfacial energy.

7.1. Surface tension

The interfacial forces (surface tension) between the molten solder, flux and substrate influence the degree of wetting, which in turn determines the formation of proper solder joints. As such, surface tension is one of the critical physical properties of solder that determines its wetting behavior. In addition to wetting, the surface tension of the molten solder plays a number of critical roles in SMT assembly. Capillary flow for PTH soldering, self-alignment of surface mounted devices, the capability to keep devices from falling off during second reflow, and the natural radius of curvature are all functions of the surface tension of the molten solder.

The surface tension of a liquid is a thermodynamic quantity and is defined as the amount of work needed to isothermally enlarge the liquid surface area [53]. Thermal equilibrium is seldom reached in actual SMT 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 affect the surface tension of solder. Studies have shown that the surface tension value of solder varies with temperature [54], flux composition [55], and the extent of solder substrate interactions [56]. For these reasons the surface tensions of solder and most other liquid metals under actual processing conditions are not precisely known [57]. There are very few surface tension data available for Lead-free solders. Vincent and

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Table 7
Measured values of surface tension for binary alloys

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

Richards [58] measured the surface tension of a range of binary Pb-free alloys in both air and nitrogen with <20 ppm O_2, at 50°C over their liquidus temperature. The data are shown in Table 7. 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. The data for eutectic Sn–Zn and Sn–Cu do not fit this trend. More accurate characterization of the surface tension values is required.

The surface tension values contained in Table 7 were used to calculate the natural radius of curvature, R, of the alloys, according to Eq. (2), and the results are contained in Table 8.

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

where γ is the surface tension, ρ the density and g is the acceleration due to gravity.

As can be seen from Table 8, only Bi–42Sn has a natural radius of curvature that is less than Pb–Sn. The other alloys have R-values that are greater. The implication of this result is that extra care will have to be taken with these alloys to prevent bridging between contacts as the pitch between contacts keeps getting smaller and smaller.

7.2. Wetting angle

Although surface tension and wetting angle are related, the latter is more specifically related to the particular materials combination under investigation. The wetting angle of Pb-free solders, primarily on Cu substrates, using a variety of fluxes, has been investigated by several researchers, and is summarized in Table 9. The wetting angle is affected by a variety of factors, including surface roughness, time, flux used and effectiveness of the flux and temperature of measurement.

Table 8
Natural radius of curvature R, of Pb-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	2.7	2.61
Sn–40Pb (near eutectic)	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

Table 9
Wetting angle of lead-free solders

Solder alloy	Wetting angle (°)	Temperature (°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	[45,60]
	37+/−7	215		
Sn–9Zn (eutectic)			Poor	[39]
Sn–5Sb	37			[61]
	36+/−3	260	On Cu, rosin flux	[62]
	34<x<51		With A611, A260HF and B2508 flux on OFHC Cu substrate	[49]
Sn–20In–2.8Ag	44+/−8	220	RMA Alpha Flux, on OFHC Cu substrate	[44]
			Wetting time and wetting force matrices (flux versus temperature)=comparable to Sn–37PB	[63]
Sn:50In	63+/−6	215	All Cu substrate using A611 flux	[45]
	41+/−9	230		
	33+/−5	245		
Sn–3Cu	31			[60]
Sn–4Cu–0.5Ag	34<x<51		With A611, A260HF and B2508 flux on OFHC Cu substrate	[49]
Sn–10Bi–0.8Cu	32	250	Flux: Kester #197	[41]
	42	340	Flux: Kester #197	[41]
Sn–10Bi–0.8Cu–1Zn	33	250	Flux: Kester #197	[41]
	38	295	Flux: Kester #197	[41]
	27	340	Flux: Kester #197	[41]
Sn–10Bi–5Sb	39	250	Flux: Kester #197	[41]
	48	340	Flux: Kester #197	[41]
Sn–10Bi–5Sb–1Zn	50	250	Flux: Kester #197	[41]
		295	Flux: Kester #197	[41]
	29	340	Flux: Kester #197	[41]
Sn–4.8Bi–3.4Ag	33+/−4	230	Flux: RMA Alpha 611	[62]
	31+/−4	245	Flux: RMA Alpha 611	[62]
	33+/−4	260	Flux: RMA on Cu	[62]
Sn–1Ag–1Sb	38	250	Flux: Kester #197	[41]
	43	340	Flux: Kester #197	[41]
Sn–1Ag–1Sb–1Zn	41	250	Flux: Kester #197	[41]
	41	295	Flux: Kester #197	[41]
	42	340	Flux: Kester #197	[41]
Sn–2.5Ag–0.8Cu–0.5Sb	44+/−8		On OFHC Cu substrate, using RMA	[43,62]
			Flux: Alpha 611 similar to Sn–Pb	[42]

The data reported by Loomans et al. from Table 9 is most useful for comparing the wetting angle of the different alloys, because they were all measured while using the same flux. Of the six alloys whose wetting angle was measured, the Sn–10Bi–0.8Cu alloy has the lowest wetting angle of 32°, at 250°C. The addition of 1 wt.% Zn to this alloy does not affect the wetting angle significantly. As the temperature is increased, the wetting angle is expected to decrease. However, the data reported by Loomans et al. does not support this expectation. It is found that while the wetting angle decreases with increasing temperature for some systems, the reverse is found for other systems. It is interesting to note that for the alloy systems measured by Loomans et al. when Zn was absent as an alloying agent, the wetting angle increased when the measurement temperature was increased. In other words, the alloys wet the copper substrate better at 250°C than at higher temperatures such as 340°C. However, the addition of 1 wt.% Zn halts this trend in all systems with the wetting improving at higher temperature, or remaining approximately the same.

The data reported by Artaki et al. show the wetting angle for the Sn–48Bi–3.4Ag alloy being relatively independent of temperature. Vianco et al. [64] measured the wetting angle of two solder alloys — Oxygen-Free High Conductivity (OFHC) Cu substrates, using three different fluxes, thus showing the effect choice of flux can have on the wetting angle, which was reported to vary between 34 and 51°.

The data on wetting angles of Pb-free solder alloys is quite disparate, and meaningful comparison of the performance of the alloys is difficult. This is because the temperature of measurement, preparation of the Cu substrates, fluxes used, and other experimental variables vary with each investigator.

There is a need to establish a standard procedure for measuring the wetting angles of Pb-free solder alloys, and IPC is probably the most suited organization to undertake this on behalf of the electronics industry. The manner in which temperature and alloying agents affect the wetting angle is not adequately understood at this time and definitely warrants further investigation.

7.3. Wetting force

In addition to the sessile drop method for determining the contact angle, and thus extent of wetting, a 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 forces indicating smaller wetting angles 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. This is an important parameter for actual manufacturing operations. Typical processing times for completing soldering operations are 60–90 s. Solders that might have very good wetting characteristics, i.e. low wetting angles or high wetting forces, but require long incubation periods, such as 2–5 min for maximum wetting to be attained might be suitable from a scientific perspective, but would be commercially not viable due to loss of productivity. The time to wetting can therefore dictate the industrial acceptability of solders.

The maximum wetting force (F_{max}) and time to wetting (T_w) of three Pb-free solders and eutectic Pb–Sn solder, with Cu substrates, were measured at 240°C using an aqueous clean flux (Kester #2224-25) and a no-clean flux (Alpha Metals Lonco SL5-65) [59]. The Pb-free solders used in this study were Sn–3.5Ag, Sn–58Bi, and Sn–9Zn. The results are shown in Table 10a and b, which represent data for an aqueous clean flux and a no-clean flux, respectively.

Table 10
Wetting force on bare Cu coupons, 240°C

Alloy	T_m (°C)	$F_{max\ (avg)}$ (mN)	$T_{w\ (avg)}$ (s)
(a) 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
(b) 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	–

Table 11
Wetting force on bare Cu coupons, at 62°C above melting point

Alloy	T_m (°C)	$F_{max\ (avg)}$ (mN)	$T_{w\ (avg)}$ (s)	T_{exp} (°C)
(a) Aqueous clean flux				
Sn–37Pb	183	4.792	0.385	245
Sn–3.5Ag	221	4.822	0.400	283
Sn–58Bi	139	3.518	0.608	201
Sn–9Zn	199	1.772	0.625	261
(b) No-clean flux				
Sn–37Pb	183	3.486	1.570	
Sn–3.5Ag	221	4.013	0.785	
Sn–58Bi	139	2.410	4.092	
Sn–9Zn	199	−4.300	X	

All three Pb-free solder alloys had wetting forces (F_{max}) significantly lower than eutectic Pb–Sn. 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 did not wet the Cu substrate at all when the less aggressive no-clean flux was used. While there are major variations in the time to wetting, they are all 3 s or less; from a manufacturing perspective, the variation in T_w is not a concern. The same measurements were repeated at a temperature of 62°C above the melting point, and the results are shown in Table 11a and b.

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 soldering alloy with a 140°C melting temperature could be reflowed at around 180–190°C, which is much lower than the 220–240°C range for eutectic Pb–Sn solders. 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.

The wetting force data reported are consistent with the wetting angle information reported by others, and summarized in Table 9. The Sn–9Zn solder alloy has poor wetting characteristics when in contact with copper. The extent of interaction of wetting angle or wetting force, is dependent on the type of flux used. The use of a more aggressive flux results in better interaction, as reflected by the consistently higher wetting forces. This is due to the fact that the more aggressive flux (aqueous clean, in this case, as compared to no-clean) is also more effective in removing surface oxidation layers.

While the overall trend of the results is not significantly different, there are some changes. It can be seen that the wetting force of the Sn–3.5Ag alloy is comparable to, if not better, than that of eutectic Pb–Sn. The wetting force displayed by the Sn–9Zn alloy is still significantly lower than the others, with dewetting occurring when a no-clean flux is used.

In a study to determine the effect of stored surface energies on the wetting force, the behavior of eutectic Pb–Sn solder was compared with a 77.2Sn–20Zn–2.8Ag Pb-free solder [65]. The results are shown in Fig. 8. Copper coupons were cold rolled, the extents of cold work being 10, 20, 30, 40, and 50% to store energy in the coupons, following which the wetting force was measured. The wetting force was found to increase linearly with the extent of cold working, over the cold work range tested. This trend was the same for both solder alloys, although the ternary Sn–In–Ag alloy had wetting forces that were typically 0.6–0.7 mN lower than that for the Pb–Sn alloy. Concomitant with the increase in wetting force, the time to wetting (T_w) was also found to decrease. However, all values of T_w were 0.4 s or less, and therefore has no influence on industrial soldering operations. Collazzo's

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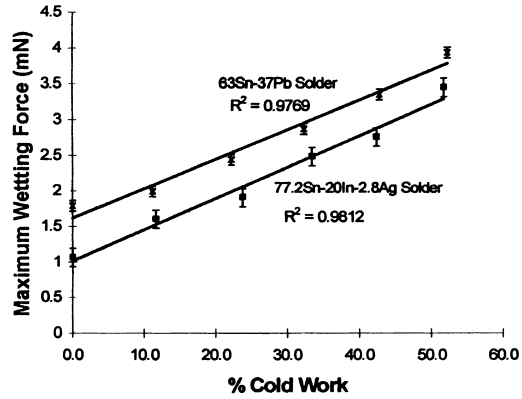

Fig. 8. Effect of stored surface energies on the wetting force.

research shows that in cases where the wetting force might be inadequate, cold working of the lead frames might be an avenue of increasing this interaction.

Romm and Abbott [66] compared the wetting behavior of eutectic Pb–Sn and a Pb-free Sn–Ag–Cu–Sb alloy on leads that had Sn–Pb, Ni–Pd and Ni–Pd–Au finishes. They also measured the force required to pull the leads off, and did 3000 cycles of temperature cycling (−65 to 150°C) tests. The purpose of their work was to determine the effects of the Pb-free finishes and compare it to the Pb–Sn lead finish, rather than to test Pb-free solder alloys themselves. However, for the combinations tested, it was reported that there was no correlation between the wetting angle and the reliability or mechanical strength of the solder joint. All combinations were reported to have passed the temperature cycling tests with no failures.

8. Solder–substrate interactions

During soldering, molten metal (solder) comes into contact and reacts with the Cu pads on the substrate or PCB. The nature of this interaction is dependent on the composition of the solder, and how each of the constituents interacts with the Cu pad. Whether or not the Cu pad is coated, which it frequently can be, also affects the nature of the interaction with the constituents of the solder. Of fundamental significance here is the long-term reliability of the solder joint, which is directly dependent on the quality of the bond formed between the solder and the Cu pad.

There can be a number of intermetallic compounds formed at the substrate and solder interface during soldering. However, only the intermetallic compounds that forms first during the soldering process has a significant effect on wetting and solderability. When intermetallic compounds are formed at the solder substrate interface, the interfacial energy should consequently be lowered indicating that wetting has taken place, resulting in the reduction of the net free energy at the interface. Both wetting and intermetallic compound formation are driven by interfacial energy and in soldering the formation of intermetallic compounds is a consequence of good wetting. However, not all wetting of a solid surface by a liquid will result in the formation of intermetallic compounds.

The formation of intermetallic compounds between the solder and the Cu substrate is desirable for the formation of a good solder joint. However, the type(s) of intermetallic compounds formed, their growth rates, and their effect on long term reliability of the solder joint has been the subject of research for a very long time. The research thus far has been focused on the effect of Cu–Sn

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intermetallic compounds and their effects on solder joint strength and long term reliability, because Sn–Pb solders were used almost exclusively. Since Sn, In and Bi are the major constituents of Pb-free solder alloys, this discussion of solder–substrate interaction and intermetallic compound formation will begin with the interaction of these three elements with Cu before discussing the interaction between the other constituents.

8.1. Cu–Sn

From the phase diagram for Cu–Sn, the intermetallic phases that are stable below 300°C are the ε and η phases. The ε phase has a composition range between 25.7 and 27.1 wt.% Sn, and corresponds very closely to the composition Cu_3Sn. The η phase has Sn concentration of between 44.8 and 45.5 wt.%, and corresponds to the composition Cu_6Sn_5. Both phases have been identified in investigations of Pb–Sn solder–Cu substrate interactions [67–69]. The growth of these phases are reported to follow the Arrhenius relationship, with the activation energy for Cu_6Sn_5 being between 0.41 and 0.5 eV and for Cu_3Sn being between 1.06 and 1.27 eV, in the 90–170°C range [70]. This indicates that the growth of Cu_6Sn_5 would be faster than Cu_3Sn under these temperature conditions. These data were obtained by reacting a 60%Sn–40%Pb solder paste on single crystal Cu substrate. The copper used in microelectronics is normally in one of the following three forms: (a) rolled copper for lead frames, (b) rolled copper foil used for lead traces, and (c) electroplated copper traces or pads. The activation energies for the formation and growth of the Cu_6Sn_5 and Cu_3Sn on these types of copper can be expected to be different from that of single crystal copper, and needs further research.

8.2. Bi–Cu

The Bi–Cu binary system exhibits eutectic behavior with a eutectic composition of 99.5 wt.% Bi, and a eutectic temperature of 270°C. Bi does not form intermetallic compounds with Cu.

8.3. Cu–In

At temperatures below 300°C, three intermetallic phases form. The δ phase has In concentrations between 28 and 31 wt.%, the In concentration in the η phase ranges between 35 and 39 wt.%, and for the ϕ phase the range is between 41 and 42 wt.%. No reports on growth rates and activation energy requirements were found.

8.4. Sn–Zn

The Sn–Zn system exhibits eutectic behavior, with a eutectic composition of Sn–9Zn, and a eutectic temperature of 198°C. The solid solubility of Sn in Zn is less than 0.05 wt.%. The maximum solid solubility of Zn in Sn has been estimated as being ~2 wt.% [71]. Since the Zn-rich phase is essentially pure Zn, intermetallic compounds of Zn–Cu can be expected to form when Sn–Zn solders are used on copper substrates.

8.5. Ag–Sn

On the Sn-rich side this system exhibits eutectic behavior, with a eutectic composition of Sn–3.5Ag and a eutectic temperature of 221°C. The Sn rich intermetallic phase (ε) has a nominal

composition of Ag_3Sn, with the concentration of Sn varying between 25.5 and 26 wt.%. The solid solubility of Ag in Sn is less that 0.1 wt.%.

8.6. Minor constituents

Though not major constituents, Pb-free solders can contain minor amounts of Zn, Ag, Sb, and Mg. The Cu–Zn system forms three intermediate phases with relatively broad ranges of stoichiometry; none of these can be termed as intermetallic compounds. The Ag–Cu system exhibits eutectic behavior that is very similar to Pb–Sn, with no formation of intermetallic compounds or phases. Sb forms two intermediate phases with Cu. The ε phase has Sb concentration between 18.3 and 19.7 wt.%. The second intermediate phase has a composition range between 32.5 and 33.4 wt.% Sb and corresponds to the compound Cu_2Sb.

8.7. Ternary compounds

The earlier discussion focused on the formation of binary compounds between one of the constituents of the solder and Cu substrates. In the case of Pb–Sn solders, ternary compound formation does not occur due to the lack of interaction between Pb and Cu. Pb is practically insoluble in solid Cu, and the system exhibits eutectic behavior on the lead-rich side, and liquid immiscibility at intermediate concentrations. However, when two or more of the constituents of a solder interact with Cu to form intermetallic compounds or intermediate phases, the possibility of ternary compound formation exists [72]. This area needs significant research efforts in the future if the long-term reliability of Pb-free solder joints is to be established.

9. Mechanical properties

When an electronic device is in operation, the solder connections are subjected to mechanical stresses and strains. The primary cause of these stresses and strains arise from the fact that the electronic component and the board have different coefficients of thermal expansion. An example of how these stresses are generated, in the case of flip chip packages, between the silicon die and the substrate, is shown in Fig. 9. If room temperature represents the unstrained conditions, then as the temperature of the system rises, the board expands more than the component, resulting in the solder ball connection being subjected to shear strain. As the system is switched ‘on’ and ‘off’, it is subjected to thermal cycling, resulting in the solder connection being subjected to cyclic shear stresses. The resultant shear strain will be determined by the shear modulus of the particular solder material.

The solder connections are thus subjected to cyclic loading, and depending upon its fatigue life, the number of cycles before fatigue failure begins will be determined. Plastic deformation of the solder connection is also possible, if the shear strain due to differential thermal expansion exceeds the shear strain for yielding.

The solder joint can also be subjected to tensile loading, typically when the board or substrate is bent, as shown schematically in Fig. 10. This can happen during mechanical handling of the product, and sometimes when the finished product is clamped in the text fixtures for testing after assembly. The tensile properties such as yield strength, UTS and elastic modulus are therefore necessary to determine the extent of tensile deformation the solder connection can withstand without failure.

Some of the environments where electronic devices are used are subjected to vibration, notable examples being automotive and aeronautical applications. The devices can experience a very large

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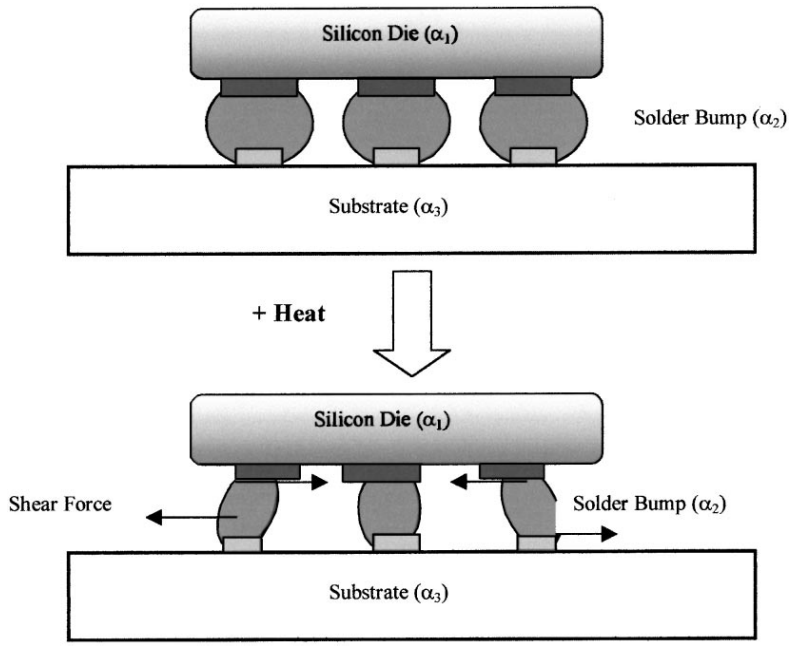

Fig. 9. Solder joints subjected to shear strain during thermal cycling due to CTE mismatch between the Die (α_1), the solder (α_2) and the substrate (α_3).

number of vibrations, with the direct result of the solder joint being subjected to cyclic loading. For such applications the fatigue life of the solder joint as a function of the loading characteristics becomes critical.

When the device is actually operating, the differential thermal expansion can result in a constant static loading being applied on the solder connection. Since even room temperature represents a homologous temperature that is greater than 0.6 for most solders, this result in the solder connection being loaded under conditions where it can be susceptible to creep, i.e. exposure to constant load at elevated temperatures.

9.1. Tensile properties

The data available for the elastic modulus, yield strength, ultimate tensile strength and ductility in terms of percent elongation are summarized in Table 12. The elastic modulus varies from a low of

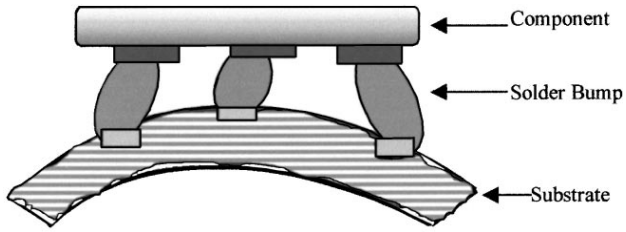

Fig. 10. Solder Bumps (joints) subjected to tensile loading due to substrate flexing (bending) during handling of the assembly.

Table 12
Tensile properties of Pb-free solders

Solder composition units	Elastic modulus (GPa)	Reference	Yield strength (MPa)	Reference	Ultimate tensile strength (Mpa)	Reference	Percent elongation	Reference
Sn–37Pb	39, 30.5	[38]			19 at 20°C, 4 at 100°C	[73]		
Bi–41Sn–1Ag							40% at 25°C	[74]
Bi–41Sn–1Pb					73 at 0.4/s strain rate, cast processing	[38]		
					55 at unspecified strain rate and processing	[38]		
					71 at unspecified strain rate and bulk processing	[38]		
Bi–42Sn	42	[38]	41	[38]			73–150% at strain rate $0.005<X<0.0033$	[59]
							4.9% at −65°C, 20% at 25°C, 159% at 85°C	[74]
In–48Sn (eutectic)	23.6	[38]						
	19.5	[38]						
Sn–2.5Ag–0.8Cu–0.5Sb	29.4	[42]			39.5	[42]	42.4%	[42]
Sn–3.5Ag	50	[38]	48	[38]	42.8 at 5°C/min cooling	[39]	42.5% at 5°C/min	[39]
					55 at 0.022 strain rate, cast processing	[38]		
					37 at 0.000033 strain rate, cast processing	[38]		
					20 at 0.00015 strain rate, cast, aged 25°C	[38]		
					56 at 0.0008 strain rate, cold rolled sheet	[38]		
					37 at 20°C	[73]		
Sn–5Ag			34	[38]				
Sn–3.5Ag–<6Bi					71.7 at 5°C/min cooling	[39]	15% at 5°C/min cooling	[39]
							40% at 0.00015/s strain rate	[59]
							25% at 0.033/s strain rate	[59]
							31% at 0.000033/s strain rate	[59]
Sn–3.5Ag–1Zn					52.2 at 5°C/min cooling	[39]	27.5% at 5°C/min cooling	[39]
Sn–3.5Ag–1Zn–0.5Cu					48.3 at 5°C/min cooling	[39]	7.0% at 5°C/min cooling	[39]
Sn–42Bi							16.6%	[59]
Sn–5Bi–3.5Ag					71.7 at 5°C/min cooling	[39]	15% at 5°C/min cooling	[39]
Sn–20In–2.8Ag	38.6 at 20°C	[44]			46.9 at unspecified cooling rate	[39]	47% at unspecified cooling rate	[39,44]

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Table 12 (*Continued*)

Solder composition units	Elastic modulus (GPa)	Reference	Yield strength (MPa)	Reference	Ultimate tensile strength (Mpa)	Reference	Percent elongation	Reference
					46.9	[44]		
Sn–30In			17	[38]				
Sn–42In							38% at 5/s strain rate	[59]
Sn–60In			4.5	[38]				
Sn–5In–3.5Ag					62.1 at 5°C/min cooling	[39]	20% at 5°C/min cooling	[39]
Sn–8Zn–4In					50.3 at 5°C/min cooling rate	[39]	25% at 5°C/min cooling rate	[39]
Sn–8Zn–5In(0.1–0.5)Ag					52.4 at 5°C/min cooling rate (0.1%Ag)	[39]	40% at 5°C/min cooling rate (0.1% Ag)	[39]
Sn–9Zn–10In					55.2	[46]		
Sn–9Zn (eutectic)					64.8 at 5°C/min cooling rate	[39]	45% at 5°C/min cooling rate	[39]
					103	[46]		
Sn–9Zn–5In					62.1	[46]		
Sn–5Sb					31 at 20°C	[73]	25% at 20°C	[73]
					20 at 100°C	[73]	31% at 100°C	[73]

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19.5 GPa for the In–48Sn eutectic alloy, to a high of 50 GPa for the Sn–3.5Ag alloy. The elastic modulus of Sn–37Pb eutectic solder is 39 GPa. The Bi–42Sn alloy has an elastic modulus of 42 GPa, which is close to Sn–37Pb. Alloys with a lower elastic modulus are preferred because the stress induced in the solder joint will be lower for a given strain, based on Hooke's law.

The yield strength, ultimate tensile strength and ductility (% elongation) can be expected to be microstructure and strain rate dependent. The microstructure in turn, is chemical composition and thermal history dependent, including cooling rate and aging. The data for UTS and ductility reflect this dependence on microstructure and strain rate. The Sn–3.5Ag alloy has UTS of 55 MPa at a strain rate of 0.022/s. When aged, and tested at 0.0015/s strain rate, the UTS drops to 20 MPa. Without aging, when the strain rate is reduced from 0.022 to 0.000033/s, the UTS also drops, from 55 to 37 MPa. Since all solder alloys operate at homologous temperatures in excess of 0.5, they can be expected to age over the lifetime of the electronic system. Hence, strength values, after subjecting samples to aging conditions representative of microelectronics assemblies, are necessary for determining the ability of the solder to withstand deformation over its lifetime. It is also important that the experimental strain rate reflect the strain rate in microelectronics assemblies. When comparing the UTS values of solder alloys that had all been cooled at a rate of 5°C/min, the Sn–5Bi–3.5Ag system has the highest strength — 71.7 MPa. The UTS of most solder alloys are in the 40–50 MPa range. The UTS for the Sn–40Pb alloy is 19 MPa at 20°C and 4 MPa at 100°C.

Judging from the data, all of the Pb-free solders appear to have UTS values significantly greater than the near eutectic Sn–40Pb. However, the UTS are strongly microstructure dependent, and the data needs to be interpreted with great caution. Since the data contained in Table 12 is a compilation from various sources, the effects of strain rate, microstructure and purity of the alloys also needs to be taken into consideration. Of particular relevance to microelectronics is the loss of strength as temperature increases. A significant loss of strength at higher temperatures would result in the alloy being more susceptible to creep deformation and fatigue failure. The Sn–40Pb alloy's UTS drops from 19 to 4 MPa when the temperature is raised from 20 to 100°C — representing a 79% loss in tensile strength. The Sn–5Sb alloy loses 35% of its tensile strength for the same rise in temperature.

The ductility of the Pb-free solder alloys are also processing and testing condition dependent. The data for Bi–42Sn demonstrates this very well. The elongation varies from 73 to 150% as the strain rate varies from 0.005 to 0.0033/s. Similarly, while the elongation is 4.9% at −65°C, it is 159% at 85°C. Overall, the ductility of the alloys fall within the 15–40% range, with the Sn–5Bi–3.5Ag alloy having the lowest ductility of 15%. Inspection of the data reveals the general trend of increased ductility with lower UTS values. Without doubt, the microstructure will play a major role in influencing this trend.

9.2. Shear properties

As stated earlier, during its service life, solder joints in microelectronics systems experience shear loading most of the time. The shear properties, namely the shear modulus and shear strength, for solder alloys for which data were available are tabulated in Table 13. Surprisingly, both shear modulus and shear strength data were not available for the alloys — only one or the other was available for each of the alloys, with the exception of Sn–42Bi. The shear moduli available are 7.5 and 7.8 GPa, for Sn–42Bi and Bi–41Sn–1Ag, respectively. In the absence of experimental values for the shear modulus (G), it can be calculated if the elastic modulus, E, and Poisson's ratio, v, are known according to Eq. (3) [75].

$$G = \frac{E}{2(1+v)} \tag{3}$$

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Table 13
Shear properties

Solder composition	Shear modulus (GPa)	Reference	Shear strength (MPa)	Reference
Sn–40Pb			34 at 20°C; 21 at 100°C	[76]
Bi–41Sn–1Ag	Approx. 7.8 at 25°C, 0.5% strain, 1 Hz, 2000 cycles	[74]		
Bi–42Sn	15.8[a]		35 at strain rate 0.0033/s<X<0.005/s	[59]
			55 at strain rate 0.4/s	[77]
			23.7 at strain rate 0.4/s	[78]
			26 at strain rate 0.001/s	[59]
			26 at 0.00062 strain rate, 25°C	[38]
			28 at 0.0015 strain rate, 60°C	[38]
			9 at 0.004 strain rate, 100°C	[38]
In–48Sn (eutectic)	8.87[a]		14 at 0.083/s strain rate on Cu substrate, 25°C	[38]
			11.5 at 0.00081/s strain rate on Cu substrate, 40°C	[38]
			7 at 0.083/s strain rate on Cu substrate, 75°C	[38]
			3.5 at 0.083/s strain rate on Cu substrate, 100°C	[38]
Sn–3.5Ag	18.8		38 at 20°C; 23 at 100°C	[76]
			27 at 0.004/s strain rate, Cu lap shear joint, 25°C	[38]
			39 at 4/s strain rate, Cu ring and plug, 25°C	[38]
			14 at 0.004/s strain rate, Cu lap shear joint	[38]
			55+/−1, ring in plug test	[63]
Sn–4.8Bi–3.4Ag			81+/−11, for ring in plug test	[63]
Sn–42Bi	Approx. 7.5 at 25°C, 0.5% strain, 1 Hz at 2000 cycles	[74]	20 at 0.0001/s strain rate, aged 3 days (Cu)	[50]
			30 at 0.0001/s strain rate, aged 30 days (Cu)	[50]
			30 at 0.001/s strain rate, aged 3 days (Cu)	[50]
			32 at 0.001/s strain rate, aged 30 days (Cu)	[50]
Sn–5Bi–3.5Ag			35 at strain rate 0.0033/s<X<0.005/s	[59]
Sn–20In–2.8Ag	14.5[a]		33.1 at 20°C	[44]
Sn–5Sb			37 at 25°C; 21 at 100°C	[76]
			28 at 20°C; 14 at 100°C	[73]
Sn–2.5Ag–0.8Cu–0.5Sb	11.1[a]			

[a] Values calculated according to Eq. (3).

For the alloys for which elastic modulus data were available, the shear modulus was calculated, assuming a value of 0.33 for v, and are included in Table 13. The dependence of the shear strength on the strain rate and test temperature is evident, with the shear strength decreasing at lower strain rates and/or higher test temperatures, with the temperature effect being more predominant than the strain rate effect. The loss in shear strength in going from 20 or 25°C to 100°C is summarized in Table 14. There is significant loss in the shear strength at higher temperatures, with the loss being mostly in the 40–50% range. For the In–48Sn alloy the loss in shear strength is 75%. The strong dependence of tensile strength and shear strength data on test temperature and strain rate is reasonable because the solder alloys are typically at a homologous temperature greater than 0.5 even under room temperature conditions. Thermally activated processes such as diffusion and creep have sufficient

Table 14
Loss in shear strength with temperature increase

Alloy composition	Shear strength (MPa)			Loss (%)
	20°C	25°C	100°C	
Sn–40Pb	34.0		21.0	38
In–48Sn		14.0	3.5	75
Sn–3.5Ag		27.0	14.0	48
	38.0		23.0	39
Sn–5Sb	37.0		21.0	43
	28.0		14.0	50

activation energy to occur. A slow strain rate thus permits creep relaxation, resulting in higher ductility and lower strength values. Higher test temperatures also have the same effect on the strength and ductility data.

9.3. Creep

Creep is a measure of the time required for a material to fail when it is under a constant load at an elevated temperature [79]. It involves deformation mechanisms, such as grain boundary sliding, vacancy diffusion, etc., which requires thermally driven diffusion processes. Therefore, creep deformation becomes critical when the temperature exceeds half the absolute melting temperature of the material [79,80]. Since for most soldering alloys, room temperature is well above half their absolute melting temperature, creep is considered as the most important solder deformation mechanism in SMT [81].

When a material is subjected to a constant load at high temperature, it exhibits three regions of creep behavior, namely, primary, secondary and tertiary creep. The steady-state secondary creep region is the most relevant because it has the simplest and most reproducible behavior and deformation mechanisms that have great engineering significance [29]. The simplest form of the creep equation in the steady-state secondary creep region is [24]:

$$\frac{d\gamma}{dt} = A\tau^n \exp\left(\frac{\Delta H}{RT}\right) \tag{4}$$

where $(d\gamma/dt)$ is the shear strain rate, τ is the shear stress, n is the stress exponent, and ΔH is the activation energy. ΔH and n are specific to the dominant creep mechanism. The constant A is microstructure dependent. R is the universal gas constant and T is the absolute temperature (K). For Sn–Pb solder, the value of n varies from 2 to 7 depending on the microstructure and the dominant creep mechanism. Similarly, the activation energy is related to the rate controlling process for secondary creep [29] and gives insight into the creep mechanism of the material.

In eutectic Pb–Sn solder, the rate controlling mechanism at strain rates below 10^{-5}/s is lattice self-diffusion [24], which appears to be the case for Sn–Bi also. Primary, secondary and tertiary creep was observed for 42Sn–58Bi [29]. Mei and Morris observed that at 65°C solder joints of eutectic Sn–Bi are more creep resistant than eutectic Pb–Sn solder joints formed under the same conditions [29]. The total strain to failure, however, was only 20–25%, which is less than what was found for eutectic Sn–Pb. According to the results of stress relaxation tests conducted by Wild [32], stress relaxation occurred more rapidly in Sn–Bi solder joints than in eutectic Pb–Sn solder joints at both room temperature and 60°C.

Tests conducted by Freer and Morris [36] to evaluate the creep behavior of eutectic In–Sn solder indicated rapid and extensive deformation leading to early failure. Primary creep was not observed; however, a steady state creep region and a tertiary creep region in which extensive deformation took place was encountered. Further, no microstructural changes like coarsening and recrystallization similar to Pb–Sn, was observed. Test results from Darveaux and Banerji [82] indicated that the Sn–3.5Ag alloy exhibited considerably more strain before failure than eutectic Sn–Pb under their test conditions. The test results also suggested the acceleration factor in a thermal cycling test may be greater for Sn–3.5Ag than for eutectic Sn–Pb under the same conditions.[1]

9.4. Fatigue

Fatigue, a measure of resistance to failure due to cyclic loading, can be isothermal or 'thermal'. Isothermal fatigue is where imposed cyclic displacement occurs at a constant temperature. Thermal fatigue, on the other hand, is a condition where cyclic displacement occurs due to a change in temperature, because of the joining of two materials with dissimilar coefficients of thermal expansion. Fatigue in solder joints leads to crack initiation and crack propagation; the fatigue life of a solder joint is determined by the number of stress cycles it endures before a crack is initiated and propagates. Even when the cyclic stress is well below the yield stress of the material, fatigue failure can occur due to defects and irregularities in the microstructure that may serve as crack initiation sites. Defects in the microstructure of a material serve as stress concentration sites that promote inhomogeneous deformation resulting in rapid growth of cracks. One way of enhancing the fatigue life of a material is by altering its resistance to crack initiation or crack propagation. Failure in solder alloys involves both fatigue and creep. For eutectic tin–lead solder, the failure mode in creep and in fatigue appears to be the same. However, the relationship between thermal fatigue life and creep data is not well understood [83]. As solders are increasingly expected to perform in a very dynamic service environment where strain distributions change with time, the capability to understand the fatigue resistance behavior of Pb-free solders is very important.

There is a scarcity of fatigue resistance data for most of the Pb-free alloys. The few data that exist lack accurate characterization of the test conditions, initial microstructure or the failure mechanisms. Furthermore, the available data is more from laboratory tests focused on isothermal fatigue tests that are far from actual surface mount soldering applications. According to Lea [81], eutectic Sn–Pb has the lowest fatigue resistance. The fatigue resistance of some Pb-free solders ranked in increasing order were: 64Sn–36In, 42Sn–58Bi, 50Sn–50In, 99.25Sn–0.75Cu, 100Sn, 96Sn–4Ag, and 95Sn–5Sb.

The test that mimics surface mount applications relatively well was conducted by Strauss and Smernos [84]. Their findings indicated that eutectic Sn–Bi performed better than eutectic Sn–Pb in thermal cycling of through hole components, from −40 to 70°C at 16 min/cycle. Marshall and Walter [85] conducted thermal cycling tests on a Cu pin soldered into a 0.060 in. diameter plated through hole encased in a zinc housing filled with polypropylene. The stress on the joint was created by the expansion of the polypropylene when exposed to high temperatures. The test conditions were −30 to 100°C with 60 min dwells and ramp rate of 6.5°C/min The test results indicate that Ag-containing solders are superior to eutectic Sn–Pb and far superior to In–Sn solders.

[1] The acceleration factor relates the number of test cycles to the number of field or service cycles.

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10. Thermal properties

10.1. Coefficient of thermal expansion

A typical microelectronics assembly is made up of a large variety of materials, most notably, metals, polymers, polymer based composites and sometimes ceramics. During its service life the device goes through heat cycles because every time the device is powered, heat is generated due to IR heating. Localized temperatures on the Si die itself can be as high as 300°C. If all of the components within the device have identical coefficients of thermal expansion (CTE), and heat transfer is instantaneous, then they will expand and contract at the same rate, and no thermally induced stress will arise. Unfortunately, this is not the case and thermally induced stresses do arise. Few data on CTE for Pb-free solders are available and these are summarized in Table 15. CTE data for Si, Cu (used as lead frames), epoxies (the most common encapsulating material) and FR-4 (the most common PCB material) have also been included for reference purposes. Most of the solder alloys have CTE in the low 20×10^{-6}/K range with the exception of Bi–42Sn, which has a CTE of 15×10^{-6}/K.

10.2. Thermal conductivity

The heat generated by the die must be dissipated in order for the device to continue reliable operation. While the main pathway for heat dissipation is through the encapsulation material, the solder joints are also thought of as one pathway for heat dissipation. In high interconnect BGA devices that have more than 400 solder balls, it is a common practice to incorporate thermal solder balls, that do not serve any electrical function, to serve as a heat dissipation medium. The thermal conductivity of the solder is therefore a property of interest. The thermal conductivity data that were available for solder alloys are summarized in Table 16. The room temperature thermal conductivity is approximately 50 W/mK. At higher temperatures the thermal conductivity decreases, as shown by the data for Sn–3.5Ag. Since transport via electron excitation is the primary mechanism for thermal conduction in metals, this result is not surprising.

Table 15
CTE data for Pb-free solders

Solder composition	CTE ($\times10^{-6}$/K)	Reference
Bi–42Sn	15.0 at 20°C	[38]
	14.0	[63]
In–48Sn (eutectic)	20.0 at 20°C	[38]
	2.0 at 20°C	[15]
Sn–3.5Ag	22.0	[38]
	30.0	[38]
	23.0	[63]
Sn–4.8Bi–3.4Ag	23.0	[63]
Sn–20In–2.8Ag	28.0 at 20°C	[44]
Sn–37Pb	21.0	[86]
In–3Ag	20.0	[87]
Si	2.6	
Cu	16.0–18.0	
Epoxies	60.0–80.0	
FR-4	11.0–15.0	

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Table 16
Thermal conductivity data for Pb-free solders

Solder composition	Thermal conductivity (W/mK)	Reference
Bi–42Sn	21.0 at 85°C	[38]
In–48Sn (eutectic)	34.0 at 85°C	[38]
Sn–3.5Ag	33.0 at 85°C	[38]
	54.3 at 23.9°C (w/o contact resistance)	[44]
	36.2 at 23°C (w/o contact resistance)	[88]
	28.2 at 222.9°C	[88]
	28.6 at 246°C	[88]
	29.2 at 256°C	[88]
Sn–3.5Ag–1Zn	33.0 at 85°C	[38]
Sn–20In–2.8Ag	53.5 at 30°C	[44]
In–3Ag	73.0	[87]

11. Electrical properties

When the microelectronics device is functioning, the solder also serves as an electrical interconnect, i.e. all the electrical currents going into and out of the silicon device must pass through the solder connection.

In order to function adequately as an electrical interconnect, the electrical resistivity is the property of interest. The electrical conductivity of the solders chosen must be sufficiently high to permit current flow for the geometry chosen, without IR heating. While this is very much a function of how the solder joint is designed, as the push for miniaturization continues, the electrical resistivity of the solder will continue to become more important. Solder interconnects can also be expected to undergo a certain amount of IR heating due to current flow. In addition, they can also be expected to experience a certain amount of heating due to the heat generated by the silicon device. As such, it is expected that temperatures at the solder joint can be as high as 125°C. The temperature coefficient of resistivity (TCR) therefore also becomes a property of interest. Ideally, the TCR should be as close to zero as possible, up to 125°C.

For most electronics applications, the resistivity of solder is relatively low and its effect on the overall functionality of the circuit is insignificant. Because of the dependence of resistivity on microstructure, grain size, dislocation density, etc., measured values differ significantly among both pure metals and alloys of the same composition [24]. Room temperature resistivity values of common solders and packaging materials used for microelectronics applications are provided in Table 17. The electrical resistivity of the Bi–Sn alloy is notably higher than the other alloys, all of which have electrical resistivities that are similar. The high resistivity value for Bi–Sn can be

Table 17
Room temperature resistivity values for some Pb-free solders and microelectronics packaging materials [24]

Solder alloy	Resistivity (μΩ cm)	Lead frames	Resistivity (μΩ cm)	Elements	Resistivity (μΩ cm)
63Sn–37Pb	10, 14.4, 15	52Ni–48Fe	43.2	Ag	1.59
96.5Sn–3.5Ag	10, 12.3	42Ni–58Fe	57	Bi	115
58Bi–42Sn	30, 34.4, 34	Cu–0.6Fe–0.05Mg–0.23Sn	2.65	Sn, Pb	10.1
50Sn–50In	14.7, 30			Cu	1.73
48Sn–52In	14.7				

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attributed to the high electrical resistivity of the elemental Bi, which is 115 μΩ cm, as compared to 10.1 μΩ cm for Sn.

There is a lack of resistivity (and impedance) data measured under AC conditions, especially at high frequency. As clock speeds of electronic products increase, the AC impedance characteristics will become more important than DC resistivity. This is particularly true at higher frequencies where the skin effect can dominate electrical conductivity, and the surface characteristics of the solder joint becomes more important than the bulk.

12. Chemical properties

Three major chemical properties can affect the usage and long-term reliability of solders. They are: (a) solubility of Cu in the solder, (b) resistance to corrosion, and (c) oxidation behavior.

12.1. Cu solubility

When large baths of solder are used, such as in wave soldering, the solder bath tends to pick up Cu from the copper leads being soldered. When a critical Cu concentration in the bath is reached, the bath needs to be replaced. As such, the Cu pick up rate, and extent of Cu concentration in the bath before the bath needs to be replaced are important parameters and cost factors in soldering operations. The ability of solder baths to pick up Cu is directly dependent on the solubility of Cu in the major constituents. The data in this section is summarized from Hansen and Anderko [52], Elliot [89] and Shunk [90].

The solubility of Cu in Pb is extremely low. The eutectic point in the Cu–Pb system is at 0.06 wt.% Cu. The solid solubility (at T<327°C) of Cu in Pb is less than 0.007 wt.%. However, the solubility of Cu in liquid Pb is greater than 0.06 wt.%, though not appreciably. While the solid solubility of Cu in Sn is practically zero, the Cu–Sn eutectic point in the tin-rich side of the phase diagram occurs at a Cu concentration of 0.7 wt.%, and at 270°C. As the temperature increases, the solubility of Cu in Sn increases appreciably. At 300°C, the maximum solubility of Cu in Sn is estimated at 2.5 wt.%. The Cu pick up by Pb–Sn solder baths can therefore be attributed to the Sn content in the Pb–Sn solders.

While the Cu–In phase diagram indicates practically zero solid solubility of Cu in In, on the In-rich side, the eutectic point is at 153°C and 0.5 wt.% In. As the temperature goes up, the solubility of Cu in In rises appreciably, with the solubility at 300°C being approximately 3.5 wt.%. The Bi–Cu system also exhibits eutectic behavior, with the eutectic point occurring at 270°C and 99.85 wt.% Bi. The solubility of Cu in Bi at 300°C is 0.4 wt.%, which is less than the solubility of Cu in Sn or In.

Therefore, Pb-free solders with Bi as the primary constituent can be expected to pick up less Cu than either Sn-based or In-based solders. The addition of ternary and quaternary alloying agents can affect the solubility significantly. The above was based on estimates from binary phase diagrams, and should not be considered as a substitute for experimental determination.

12.2. Corrosion

Depending upon the particular design of the electronic component, and the manner in which it is mounted in a substrate or printed wiring board, the solder connection can be exposed to the atmosphere. This is the case with most SMT, PTH and BGA configurations. The solder is thus not only exposed to air, but also moisture and other corrosives such as chlorine and sulfur compounds.

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Table 18
Standard emf of metals [91]

Metal	Standard emf (V)	Metal	Standard emf (V)
Au	+1.50	Sn	−0.136
Ag	+0.799	Pb	−0.126
Cu	+0.337	In	−0.342
Ni	−0.250	Zn	−0.763
Pd	+0.987	Mg	−2.37

The ability of the solder to be able to withstand atmospheric corrosion is therefore relevant to the long-term reliability of solder joints.

In addition, solder alloys are electrically connected with other metallic components in the electronic device, most notably the copper conductors. Therefore, there is also the potential for galvanically induced corrosion of the solder, which could exacerbate any atmospheric corrosion that might be occurring.

However, there is no corrosion test data available for most of the Lead-free solders. The corrosion behavior of 52In–48Sn soldered on Au substrate in the presence of 15–25 ppb Cl_2 at 85°C and 85% relative humidity was studied by Abtew [87]. A high level of corrosion activity was observed between the solder and Au pad interface. The corrosion product was identified as $In(OH)_3$. Vincent and Richards [58] tested Bi, Zn, Ag, Cu, and Sb with Sn eutectic in an environment containing 200 ppm NO_2, 100 ppb H_2S, 20 ppb Cl_2 at 30°C and 70% relative humidity. Good results were reported on all alloys except Sn–9Zn where precipitates of $ZnCl_2$ were observed.

Differences in the electromotive force (Δemf) between the phases present in the alloy are frequently a good indication of the corrosion potential. If Δemf between the phases present in the solder alloy is large, corrosion is likely to take place because the electrochemical coupling in the presence of moisture is high. Data that indicate differences in emf between the different phases of the Pb-free alloys was not available. Corrosion of solder alloys, in the presence of a suitable electrolyte can occur either due to the potential difference between the major phases in the alloy or galvanic coupling between one or more phases of the alloy and other parts of the microelectronics device. Some metals that are frequently used in microelectronics are Cu, Au, Ag, Ni and Pd. The standard emf for these metals and metals used in solder alloys are listed in Table 18.

Cu is the material used most frequently for leads and pads on BGA substrates and printed wiring boards. Ni, Au, Pd and combinations thereof are frequently used as surface coatings on Cu to inhibit atmospheric oxidation of Cu. While the Au layer is extremely thin (∼10 nm) and generally dissolves in the solder, the Ni layer is much thicker, and stays intact after soldering is complete. As can be seen from Table 19, all of the elements used in solder alloys are anodic with respect to the metals that they are joining. In has a greater potential difference with respect to Cu when compared to Sn and Pb, implying a greater galvanic driving force for the corrosion of In. Zn is even more anodic.

Table 19
Δemf values for metals commonly used in microelectronics

Metals used in solder	Metals used in microelectronics				
	Au	Ag	Cu	Ni	Pd
Sn	1.636	0.935	0.473	−0.114	1.123
Pb	1.626	0.925	0.463	−0.124	1.113
In	1.842	1.141	0.679	0.092	1.329
Zn	2.263	1.562	1.10	0.513	1.75

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Table 20
Standard free energy of formation of oxides (molar basis)

Compound	$\Delta G^0_{f,T}$ (kJ/mol)			
	298 K	400 K	500 K	600 K
Bi_2O_3	−497.0	−469.5	−443.0	−414.9
In_2O_3			−541.4	−515.0
SnO_2	−520.4	−499.5	−479.4	−457.6
PbO	−188.8	−178.8	−168.7	−159.5
Sb_2O_3	−624.3	−596.6	−569.8	−543.0
ZnO	−318.6	−312.8	−298.5	−288.9
Ag_2O	−10.5	−3.8	2.5	8.8
CuO	−129.4	−119.7	−111.0	−101.7

The Δemf for combinations of metals that are commonly used in microelectronics devices and in solder alloys was calculated, and are tabulated in Table 19. As can be seen from Table 20, with the exception of Ni, all of the other metals used in microelectronics galvanically couple with solder alloys in a manner that would promote the oxidation of the solder alloy. While Ni is anodic with respect to Sn and Pb, it is cathodic with respect to In. Furthermore, since Ni is a coating on the Cu pads or Cu lead frames and is electrically conductive, it cannot be expected to inhibit the nature of the galvanic coupling between the Cu and the constituents of the solder alloys.

12.3. Oxidation of solder alloys

Depending upon the environments in which solders are placed, there exists the potential for them to react with oxygen in the environment, resulting in the formation of an oxide layer. The likelihood of a metal forming an oxide and the stability of the oxide formed is represented by the standard Gibbs free energy of formation (ΔG^0_f) of that oxide. The ΔG^0_f values for the major constituents in solder alloys are summarized in Tables 20 and 21.

Values of ΔG^0_f have been calculated for the temperature range of 298–600 K since typical solder reflow temperatures are in the 530 K range and temperature cycling during reliability testing is done up to 420 K. Table 20 lists ΔG^0_f values on a molar basis whereas Table 21 lists them on a gram atom of oxygen basis. The latter more accurately compares the potential for the metal to be oxidized.

Table 21
Standard free energy of formation of oxides (per gram atom O basis)

Compound	$\Delta G^0_{f,T}$ (kJ/g atom O)			
	298 K	400 K	500 K	600 K
Bi_2O_3	−165.7	−156.5	−147.7	−138.3
In_2O_3			−180.5	−171.7
SnO_2	−260.2	−249.7	−239.7	−228.8
PbO	−188.8	−178.8	−168.7	−159.5
Sb_2O_3	−208.1	−198.9	−189.9	−181.0
ZnO	−318.6	−312.8	−298.5	−288.9
Ag_2O	−10.5	−3.8	2.5	8.8
CuO	−129.4	−119.7	−111.0	−101.7

As can be seen from Table 21, the relative stability of the oxides does not change over the 298–600 K range. ZnO is the most stable oxide followed by SnO, Sb_2O_3, In_2O_3, PbO, Bi_2O_3, and CuO. Any Ag_2O that might be formed will decompose at temperatures of around 400 K and higher.

Knowledge of the ΔG_f^0 of the oxide formed permits the determination of the conditions necessary to prevent oxide formation. This can be achieved by one of the two means: (1) maintaining a partial pressure of oxygen below a certain critical level; or (2) maintaining a reducing atmosphere (e.g. H_2) such that oxide formation can be avoided. The critical oxygen partial pressure can be calculated as follows. Let the generalized oxidation reaction be as shown in Eq. (5).

$$x\mathrm{M} + \tfrac{1}{2}y\mathrm{O}_2 = \mathrm{M}_x\mathrm{O}_y \tag{5}$$

The equilibrium constant, K, is given by

$$K = \frac{1}{(P_{O_2})^{y/2}} \tag{6}$$

$$\Delta G_f^0 = -RT \log K = RT \log(P_{O_2})^{y/2}$$

$$\log(P_{O_2})^{y/2} = \frac{\Delta G_f^0}{RT}$$

$$\frac{y}{2}\log(P_{O_2})^{y/2} = \frac{\Delta G_f^0}{RT}$$

$$\log(P_{O_2})^{y/2} = \frac{2}{y}\frac{\Delta G_f^0}{RT}$$

The critical oxygen partial pressure is therefore

$$P_{O_2} = \exp\left(\frac{2}{y}\frac{\Delta G_f^0}{RT}\right) \tag{7}$$

For SnO_2, the oxide formation reaction is

$$\mathrm{Sn} + \mathrm{O}_2 = \mathrm{SnO}_2 \tag{8}$$

and the critical oxygen partial pressure for oxide formation is given by

$$P_{O_2} = \exp\left(\frac{\Delta G_f^0}{RT}\right) \tag{9}$$

The critical oxygen partial pressures for the compounds listed in Table 20 were calculated and are listed in Table 22. As can be seen from the values contained in Table 22, while there are differences in the critical oxygen partial pressures for onset of oxidation, they are extremely low, below 10^{-24} atm, and even the most sophisticated vacuum equipment available today would not be able to attain such low vacuum levels.

While it may not be possible to control the onset of oxidation with industrial equipment suitable for mass production, the extent to which oxidation proceeds can be controlled by restricting the oxygen content in the environment in which soldering is done so that the oxidation can be kept to a minimum, is possible. An alternative approach frequently taken is to maintain reducing atmospheres,

Table 22
The critical oxygen partial pressures for the compounds

Compound	P_{O_2} (atm)			
	298 K	400 K	500 K	600 K
Bi_2O_3	9.11×10^{-59}	1.4×10^{-41}	1.47×10^{-31}	8.58×10^{-25}
In_2O_3	5.17×10^{-70}	4.37×10^{-50}	2.08×10^{-38}	1.35×10^{-30}
SnO_2	6.8×10^{-92}	6.49×10^{-66}	8.87×10^{-51}	1.53×10^{40}
PbO	6.96×10^{-67}	2.17×10^{-47}	5.85×10^{-36}	1.75×10^{-28}
Sb_2O_3	1.24×10^{-73}	1.23×10^{-52}	2.17×10^{-40}	3.18×10^{-32}
ZnO	2.3×10^{-112}	2.32×10^{-82}	4.62×10^{-63}	5.36×10^{-51}
Ag_2O				
CuO	4.71×10^{-46}	5.56×10^{-32}	6.79×10^{-24}	1.98×10^{-18}

such as H_2, to prevent oxidation. The relevant reaction, for SnO_2 is shown in Eq. (10).

$$SnO_2 + 2H_2 = Sn + 2H_2O \tag{10}$$

The standard Gibbs free energy change for this reaction is given by

$$\Delta G^0_{rxn} = 2\Delta G^0_{f,H_2O} - \Delta G^0_{f,SnO_2} \tag{11}$$

Where $\Delta G^0_{f,H_2O}$ is the standard Gibbs free energy of formation of H_2O, and $\Delta G^0_{f,SnO_2}$ is the standard Gibbs free energy of formation of SnO_2.

The equilibrium constant, K is

$$K = \frac{(P_{H_2O})^2}{(P_{H_2})^2} \tag{12}$$

and,

$$\Delta G^0_{rxn} = -RT\ \log K = -RT\ \log\left(\frac{P_{H_2O}}{P_{H_2}}\right)^2 = -2RT\ \log\left(\frac{P_{H_2O}}{P_{H_2}}\right) \tag{13}$$

The extent to which a hydrogen atmosphere will be effective in preventing oxidation is strongly dependent on the moisture content of the atmosphere. The minimum tolerable moisture content to hydrogen partial pressure ratio is given by (P_{H_2}/P_{H_2O}). These values for the compounds listed in Table 20 were calculated and are listed in Table 23. It can be seen that when Sn and Zn are used, the

Table 23
P_{H_2}/P_{H_2O} ratios

Compound	P_{H_2}/P_{H_2O}			
	298 K	400 K	500 K	600 K
Bi_2O_3	2.4×10^{-12}	1.6×10^{-9}	3.6×10^{-8}	2.6×10^{-7}
In_2O_3	4.0×10^{-6}	2.8×10^{-5}	9.5×10^{-5}	2.1×10^{-4}
SnO_2	3.4×10^{5}	2.3×10^{3}	1.5×10^{2}	2.0×10^{1}
PbO	1.1×10^{-7}	1.3×10^{-6}	5.7×10^{-6}	1.8×10^{-5}
Sb_2O_3	2.5×10^{-4}	5.3×10^{-4}	9.3×10^{-4}	1.4×10^{-3}
ZnO	5.9×10^{15}	3.8×10^{11}	2.0×10^{8}	3.3×10^{6}
Ag_2O				
CuO	4.1×10^{-18}	2.5×10^{-14}	5.3×10^{-12}	1.7×10^{-10}

Table 24
Piling-bedworth ratio and melting point[a]

Metal	Oxide	Pilling-bedworth ratio	Melting point of oxide (°C)
Al	Al_2O_3	1.38	2045
Ti	TiO_2	1.76	1830
Sn	SnO_2	1.19	1127
Pb	PbO	1.29	888
Bi	BiO_3	1.23	860
In	In_2O_3	1.23	–

[a] In_2O_3 volatilizes at 850°C.

partial pressure of H_2O must be kept at very low levels. Oxidation of the In and Sb based alloys can be prevented relatively easily by using a hydrogen atmosphere.

The thermodynamics of oxide formation determines whether or not an oxide film will form spontaneously for a given set of environmental conditions. However, the kinetics is also important, in order to understand the extent to which oxide films will form, and the tenacity of the oxide films. If the film formed is 'protective', regardless of how favorable the thermodynamics are, oxide film growth will diminish rapidly. This is the case with aluminum. Non-protective films can continually spell, resulting in the oxidation reaction continuing for extended periods of time. In order for an oxide film to be 'protective' of the metal on which it forms, it should meet the following requirements [92]:

1. The volume ratio of oxide to metal should be close to 1
2. The film should have good adherence
3. The melting point of the oxide should be high
4. The oxide film should have a low vapor pressure
5. The oxide film should have a CTE nearly equal to that of the metal
6. The film should have high temperature plasticity to prevent fracture
7. The film should have low conductivity and low diffusion coefficients for metal ions and oxygen.

The Pilling–Bedworth Ratio (PB Ratio) is a useful measure of the extent to which oxide films can be protective and represents the first condition listed here. The Pilling–Bedworth Ratio for Sn, Pb, Bi, In, Al and Ti were calculated and are listed in Table 24 along with the melting point for the oxide. Al and Ti are included here as references because they are classic examples of metals whose oxides form a protective coating.

The Pilling–Bedwoth Ratios for Sn, Pb, Bi and In are similar, and are somewhat lower than Al and Ti. Based upon the fact that the PB ratios are all greater than 1, the oxide films will be under compression offering some measure of protection against further oxidation once the film is formed. The growth kinetics of the oxide films can therefore be expected to follow a parabolic rate law. This is consistent with the results reported by Kuhman et al. [93] who investigated the growth of oxide films on molten Sn–40Pb and In–58.8Sn solder alloys.

13. Toxicity

The extent to which Pb-free solders themselves are 'environmentally friendly' is also relevant. There are two basic requirements here: toxicity and recyclability. While a solder might be Pb-free, if it contains other toxic metallic elements such as Cd, then the whole motivation behind the drive for

Table 25
The threshold limit value of solder metals

Metal	OSHA	ACGIH
Pb	0.05 mg Pb/m^3	0.15 mg Pb/m^3
Sn	None	None
In	None	0.1 mg In/m^3
Bi		
Sb	500 mg Sb/m^3	0.5 mg Sb/m^3
Zn		

Pb-free solder development will be violated. Of particular importance here are the acceptable concentrations in ground water, and potable water, and the leachability of the solder alloys. The alloys used must also be recoverable and recyclable, without significant increase in cost. As stated earlier, solders used in reflow soldering operations pick up copper and must be replaced periodically. This 'discarded' solder is recycled by removing the copper content. At the very least, the major constituent(s) in Pb-free solders should have Cu solubility sufficiently low to permit their expedient removal.

The main driving force for elimination of Pb is its toxic nature. Of concern here is not just the toxicity of Pb, but the fact that when disposed of in landfills, Pb can eventually be leached out and can contaminate underground water sources and subsequently find its way into the human ecosystem in an ingestible form. In choosing alternatives for Pb, it must be ascertained ahead of time that the alternative(s) will not pose a similar hazard. Larger amounts of lead are necessary to cause toxic effects by ingestion than by inhalation [94], because absorption takes place easily from the respiratory tract. For industry, lead intake by inhalation is of far greater concern than by ingestion. Indium is reported to be a poison by subentarieam route, and affects the liver, heart, kidney and blood [95]. Antimony is also reported to be poisonous to humans [96]. Similarly, bismuth is also reported to be poisonous to humans, though considered to be one of the less poisonous of the heavy metals [97].

The threshold limit values, according to OSHA the American Conference of Governmental Industrial Hygienists (ACGIH), where available, are listed in Table 25. The data contained in Table 25 represent the concentration of the metal to which workers can be exposed for a normal 8 h day, 40 h work-week without ill effects. The toxicity issues are basically two-fold: (a) exposure of the general public and (b) occupational exposure.

When exposure of the general public is concerned, the factor of primary concern is whether the metal will be leached by ground water and to what extent it will be leached. For occupational exposure, inhalation and other exposure in the work place is of importance. From the data available, for risks associated with occupational exposure, Sn, In, Bi and Zn do not appear to be hazardous, according to OSHA. Sb, while having an OSHA value of 0.5 mg/m^3, is 10 times less hazardous than Pb. If one were to rely on ACGIH values, In actually has a lower threshold value than Pb, implying higher toxicity levels for occupational exposure.

14. Other manufacturing issues

In the previous sections, the properties of an array of Pb-free solders have been presented. In cases where experimental data were not available, estimates were made based on fundamental

considerations. The availability of engineering data, although a prime consideration, is still only one of the factors that are important for the deployment of Pb-free solders. The engineering data are crucial for the design engineer, to enable the design of interconnects, and to estimate its lifetime. The manufacturing engineer, on the other hand, has to deal with a different set of issues. Solder is used by the microelectronics industry in three basic forms: (a) bulk solder for operations such as wave soldering, (b) solder paste for operations such as surface mount reflow, and (c) solder balls or solder columns for applications such as ball grid array, column grid array and flip chip packages. Solder paste contains solder balls that are typically 4–8 μm in diameter, formulated with flux. Solder balls are typically 0.3–0.75 μm in diameter. While bulk solder production is metallurgically relatively straightforward, ball production does require more sophisticated techniques, and the alloy must be amenable to being fabricated into balls of these sizes. As the drive to miniaturization continues, it is expected that there will be requirements to produce balls that are even smaller in diameter, especially for BGA and flip-chip applications.

As mentioned earlier, fluxes are used to remove surface oxide layers and contamination prior to soldering. Therefore, the availability of suitable fluxes that meet current regulations is also a parameter of concern for manufacturing. The most prevalent fluxes in use today fall into either the 'no-clean' or 'aqueous' category. No-clean fluxes reportedly do not leave residues that can be harmful to the assembly at a later date, leading, for example, to corrosion. Aqueous fluxes are those whose oxides can be washed with aqueous solutions. Fluxes requiring solvents for removal of residues are no longer acceptable.

Fluxes in use today are designed to remove oxide layers on copper. This objective will not change as the transition from Pb–Sn solders to Pb-free solders is made. However, current generation fluxes have also been designed to be compatible with Pb–Sn solders, and how this compatibility will change when the metallurgy of the solders themselves changes is not clear at this time. This could be an issue especially when strong oxidizers such as Zn are included as alloying agents. As the results obtained by Tojima [59] showed that the Zn bearing solder alloy had very poor wettability on copper, possibly due to oxidation of the Zn.

15. Discussion

The information on Pb-free solders that are available thus far falls primarily in the category of basic properties. Two further items that are necessary before concrete steps towards across-the-board adoption of Pb-free solders are still missing, namely (a) data on actual performance and reliability testing, and (b) a systematic materials selection procedure that is based on decision theory. After surveying several customers (users of solders), Witt found that the most critical of the desired properties were manufacturability and reliability [98].

The basic properties and engineering data are measured primarily in the laboratory with bulk materials. Such materials are generally defect-free and very homogeneous. The alloy used in practical applications can have a variety of inhomogeneities embedded within them and the extent to which a particular alloy is 'forgiving' can have a major impact on its long term reliability.

Solder balls that are used in BGA applications frequently have voids within them. Current opinion within the microelectronics packaging and interconnect community is that a void to volume ratio of 20% is tolerable, though there is no well-founded reasoning behind this, except perhaps the minimum requirement for electrical conduction. However, when the solder ball is stressed, the stress concentration factor along the periphery of the void will be three times the applied stress, if the void is spherical. Non-spherical voids can be expected to result in even greater stress concentrations. As

the trend towards miniaturization continues, it becomes increasingly important to be able to manufacture void free solder balls, in order to improve both mechanical and electrical reliability.

The actual operating conditions (room temperature and above) represent homologous temperatures of 0.5 and above for solder alloys. As such, while in service the microstructure of the solder alloy can be expected to be 'evolving' as well. Furthermore, depending upon the particular type of microelectronics assembly process (SMT, PTH, Mixed, etc.) in which the solder alloy is used and the thermal mass of the entire assembly, the cooling rates of the solder alloy will be different under different conditions, thus leading to variations of the microstructure. A systematic investigation of the microstructure dependence of the mechanical properties of Pb-free solder alloys, while necessary, has yet to be initiated. Long term reliability testing, reflecting actual assembly and use conditions are also required. Acquisition of such data will contribute significantly towards convincing manufacturers that Pb-free solders can be an acceptable alternative to Pb–Sn solders

Some of the Pb-free solder alloys being proposed at this time have reflow temperature requirements that are higher, by 20–30°C, than the current Pb–Sn eutectic solder. As to whether this increase in temperature could have a deleterious effect on components and boards that are being soldered is uncertain at this time. Component substrates and boards are typically polymeric, with epoxy resins and BT resins being the most predominant. These have a well-established track record of being able to endure the time–temperature conditions of current assembly processes. An increase in the temperature of the assembly process has the possibility of causing degradation of the polymeric materials, thus leading to reliability issues during its service life.

Solder alloys routinely come into contact with a number of polymeric materials, the interaction with which can have important consequences. Flip-chip configurations currently employ a silicone 'under-fill' material, which fills the open spaces between the silicon die and the substrate. Its primary intent is to reinforce the package and provide it with better mechanical endurance. The wetting characteristics between this under-fill material and the solder ball array, through which it must flow, are important issues that needs to be understood for the under-fill to not only flow evenly and fill up the cavity, but also for it to do so in a void-free manner. While strong wetting characteristics are desired between flip-chip under-fills and Pb-free solders, in the case of solder mask, another polymeric material, poor wetting characteristics are actually preferred. The solder mask is applied specifically for the purpose, as the name implies, to mask off areas not to be soldered. If the solder is able to wet the solder mask, then it is able to 'jump' the solder mask and form a bridge to adjacent solder connections. As miniaturization of microelectronics devices proceeds, these issues will become more critical. These are but a few of the myriad practical issues that need to be resolved in order for Pb-free solders to become a reality, and all indications are that it has to become a reality within the next 5 years.

Of the 60 Pb-free solder alloys that have been proposed so far, approximately 10 alloys seem to have been investigated to varying extents. When there are this many candidates to replace the single alloy that is practically universally used today, it is necessary to develop a systematic manner by which materials selection can be done. While the materials selection and decision analysis communities do have a number of different strategies for materials selection, such an approach is somewhat lacking in the microelectronics industry for choice of Pb-free solders.

One attempt at alloy selection was undertaken by Bastecki [99] who identified the requirement of Pb-free solder as consisting of the following technical and practical factors: (a) cost, (b) melting point, (c) toxicity, (d) solderability, (e) repeatability, (f) availability, and (g) compatibility with Pb. After going through a process of reasoning, Bastecki concluded that certain alloys should be excluded, and some should be retained. These results are shown in Table 26, along with the reason

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Table 26
Lead-free solder alloy selection matrix [99]

Alloys		Melting range (°C)	Metal cost/kg (US$)	Reasons for exclusions
Excluded	Remaining			
Sn63–Pb37(std.)		183	5.87	Pb content
Sn42–Bi58		138	7.79	Bi content, melting point too low for some applications
Sn77.2–In20–Ag2.8		179–189	51.63	In content, cost/avail
Sn85–Bi10–Zn5		168–190	8.14	Zn/Bi content (poor wetting, broad freezing range)
Sn91–Zn9		199	7.99	Zn content (poor wetting)
Sn90–Bi7.5–Ag2–Cu0.5		186–212	11.42	Bi content, four-part alloy, broad freezing range
	Sn96.3–Ag3.2–Cu0.5	217–218	13.27	
Sn95–Ag3.5–In1.5		218	16.52	In content
Sn96.2/Ag2.5–Cu0.8–Sb0.5		213–218	12.21	Four-part alloy, no real benefit over binary alloys
	Sn96.5–Ag3.5	221	13.73	
	Sn98–Ag2	221–226	11.55	
	Sn99.3–Cu0.7	227	8.62	
Sn97–Cu2–Sb0.8–Ag0.2		226–228	8.78	Four-part alloy, no real benefit over binary alloys
	Sn95–Sb5	232–240	8.36	

for exclusion of specific alloys. It is worth noting that the Pb-free alloys that were retained for further consideration were all Sn-rich alloys.

Witt also evaluated a series of Pb-free solder alloys and came to the conclusion that Sn–Ag allowed the most promise for reflow applications while Sn–0.7Cu was most suitable for wave soldering. The solder alloy selection procedures followed by Bastecki and Witt took into account both technical and practical issues. However, the number of factors taken into account was somewhat limited, and a more comprehensive approach, employing a more formalized decision-theory based approach is probably called for.

Nevertheless, both Bastecki and Witt arrived at similar conclusions. The alloys they identified are all Sn-rich and are also not patented. The fact that these alloys are not patented is advantageous to solder alloy manufacturers and users. The Sn-rich alloys identified have Sn contents varying from 95 to 99.3 wt.%. Given that current Pb–Sn solders contain approximately 62 wt.% Sn, this will represent an increase in consumption of Sn by 50% or more. The fact that Sn production and prices have been stable over the last 15 years leads one to the conclusion that concern over Sn availability is not necessary.

16. Conclusions

Pending environmental legislation worldwide has provided an impetus towards the development of Pb-free solders. A relatively large number, approximately 70, of Pb-free solders have been proposed so far, by a combination of researchers and manufacturers. While a few of the alloys are patented, most are not. The majority of the alloys are based on Sn, In, and Bi being the primary component, with Sn being by far the most dominant. Materials selection studies thus far, albeit on a

limited scale, indicate that the Sn rich compositions are the most likely candidates. A major impediment to adoption of In based solder compositions is the volatility of In prices.

A common feature of all Pb-free alloys is the lack of uniformity in the data available, thus making it very difficult to carry out meaningful evaluations and selections. Of the data available, the greater portions have been acquired under laboratory conditions. These tend to be basic data. For successful adoption of any of these alloys, long-term reliability data are extremely important. These will include, among others, properties such as ability to withstand thermal fatigue, corrosion, change in mechanical properties with thermal aging and ability to withstand mechanical strains. While these properties are of interest to the design engineer, the manufacturing engineer has concerns that are somewhat different. These include cost, manufacturability, availability, melting point, and temperature effects on polymeric components.

The adoption of a Pb-free solder poses a major challenge for a number of reasons. Today there is a universally accepted solder, Pb–Sn, which needs to be replaced not for technical reasons but for environmental reasons, and there are numerous contenders. The selection of an acceptable replacement will prove to be a true exercise in engineering materials selection where not only do engineering and scientific data need to be taken into consideration, but also other issues such as manufacturability, environmental friendliness, and even geopolitical factors. If this effort results in the adoption of a single alloy, the impact on the electronics assembly industry worldwide will be significant.

The range of information required before an informed decision can be made is indeed enormous. The number of research papers published on this topic thus far is limited, and they have tended to focus on a few alloy systems, notably the Sn–Bi, In–Sn and Sn–Ag systems. A more wide-ranging investigation, which will include performance under realistic service conditions, is necessary. Given the quantity of information available, the construction of a database to document the research results is also required. The construction of such a database has been initiated at San Jose State University.

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