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Review paper

A review: On the development of low melting temperature Pb-free solders

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ABSTRACT

Pb-based solders have been the cornerstone technology of electronic interconnections for many decades. However, with legislation in the European Union and elsewhere having moved to restrict the use of Pb, it is imperative that new Pb-free solders are developed which can meet the long established benchmarks set by leaded solders and improve on the current generation of Pb free solders such as SAC105 and SAC305. Although this poses a great challenge to researchers around the world, significant progress is being made in developing new solder alloys with promising properties. In this review, we discuss fundamental research activity and its focus on the solidification and interfacial reactions of Sn-based solder systems. We first explain the reactions between common base materials, coatings, and metallisations, and then proceed to more complex systems with additional alloying elements. We also discuss the continued improvement of substrate resistance to attack from molten Sn which will help maintain the interface stability of interconnections. Finally, we discuss the various studies which have looked at employing nanoparticles as solder additives, and the future prospects of this field.

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1. Introduction

The soldering process has been a fundamental aspect in the realisation of all electronic products since the commencement of the electronic age, and it is anticipated that it will remain the primary assembly and interconnection technology for some time to come. As the durability and reliability of solder joints is absolutely essential to the functionality and lifespan of an electronic product, it is key that the solders used are optimised in terms of their physical and chemical properties to provide robust interconnections. It has long been recognised that solder joints embody a potential

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point of weakness in all electronic products: regardless of the ever increasing sophistication of modern electronic systems, they will not function if their component interconnections fail. To date, the most successful solders have been based on Sn–Pb alloys, and indeed their unique combination of chemical, physical, thermal, and mechanical properties have provided durable and reliable functionality for many decades [1]. However, due to the environmental and health concerns associated with the use of Pb, legislation in the European Union and elsewhere has moved to restrict its use. Despite much resistance on the grounds of cost and reliability concerns, the transition from traditional Sn–Pb eutectic alloys to Pb-free solder alloys is occurring [1–3]. As Pb is one of the least expensive elements on Earth, its replacement will have an intrinsic cost increase while the incidental costs of developing viable alternatives are non-trivial. However, the overriding concern is one of reliability, and whether the new Pb-free alloys can live up to the performance level of their traditionally used counterparts.

In this development process, the new solder alloys will be compared with traditional eutectic or near-eutectic Sn–Pb systems, and will be expected to perform equally well or better in most respects. Thus, new elemental additions to Sn-based systems should fulfil the following basic requirements [4–6]:

- Reduce the surface tension of pure Sn to improve the wettability.
- Enable quick formation of intermetallic compounds (IMCs) between the solder and substrate by diffusion.
- Improve upon the ductility of Sn.
- Prevent the transformation of β-Sn to α-Sn, which causes unwanted volume change and degrades structural integrity and reliability of solder.
- Keep the melting temperature around 183 °C with eutectic or near-eutectic composition, in instances where the liquid phase can transform into two or more solid phases.
- Improve mechanical properties (e.g. creep, thermo-mechanical fatigue, vibration and mechanical shock, sheared and thermal ageing).
- Prevent the occurrence of excessive tin whisker growth.

The Pb-free solder alloys fulfilling these requirements are more likely to be multi-component alloys rather than a binary composition like Sn–Pb, given the greater range of possibilities with the former. A striking problem with Pb-free Sn-based alloys is that the liquidus and solidus temperatures are generally either too high or too low or far apart [1]. Additionally, the mechanical properties and wettability of such alloys are a concern and must be improved upon. The addition of further alloying elements provides an opportunity to control and tune these thermal and mechanical properties, although this task is non-trivial and requires much research and development. To date, various alloying elements have been studied, including Ag, Bi, Cd, Cu, In, Sb, Zn, Al [5,7]. A key point in this work is to ensure that the melting temperature of the solder alloy is not too high, as higher temperatures would compromise their applicability in constructing electronics packaging, which often include polymeric materials with low heat tolerance. If this condition is not met along with those listed above, a substantial and unreasonable change in soldering practice would be required [8]. From these considerations, the basic systems of Sn–Cu, Sn–Ag, and Sn–Ag–Cu have emerged as the front runners in the replacement of Sn–Pb solders. However, these high-Sn-content alloys (of around 95–99.3 wt.% [3]) have proved to be problematic in terms of void formation, large undercooling during solidification, overly rapid IMC formation and spalling of interfacial IMCs during high temperature storage. These concerns are listed, along with the emergent solder alloys, in Table 1 [9,10].

There is a continuous effort to understand the mechanism of the interfacial interactions – including the formation and growth of IMCs – occurring at solder/substrate interfaces. IMC layer formation consists of several distinct physical processes, such as nucleation, growth and coarsening. Among these processes, IMC nucleation is one of great importance as the particular sequence of IMCs formed has a significant effect on the morphology and evolution of IMC layers, consequently affecting the reliability of soldered assemblies [5]. The IMC growth problem becomes acute for applications where an electronics package will experience severe temperature gradients and cyclic mechanical loading through vibration or shock [9–11]. The interfacial IMC formation between component/solder/substrate and its failure after aging is shown schematically in Fig. 1. One frequently utilized way to influence the interfacial reactions and the properties of product layers in a given system is to alloy either metallization (conductor) or solders with small amounts of additional elements. It is noted that the presence of impurities in the interconnection system may also have marked effects on the properties and growth of IMC layers

Table 1
Example of Pb-free solder alloys melting range between 109 and 226 °C and concerns.

Alloy system	Composition	Melting range (°C)	Application remarks
Melting temperature below 180 °C			
Bi–In	Bi–33In (eutectic)	109	Bi content, melting point too low for some applications
Sn–In	Sn–52In	118	In adds to cost. Specialized applications for wetting ceramics and glasses
	Sn–50In	118–125	
Sn–Bi	Sn–58Bi (eutectic)	138	Low melting point eutectic solder. Potential segregation problems. Low melting phase with Pb traces
Melting temperature range 180–200 °C			
Sn–Bi–In	Sn–20Bi–10In	143–193	Replacement candidates for near-eutectic SnPb alloys. Potential segregation and cracking problems with increasing Bi content. Low melting phase with Pb traces
Sn–Zn–Bi	Sn–8Zn3Bi	189–199	Zn imparts poor corrosion resistance and reduced wettability
Sn–Zn	Sn–9Zn (eutectic)	198.5	
Melting temperature range 180–230 °C			
Sn–Ag	Sn–3.5Ag (eutectic)	221	Primary replacement candidates for neareutectic SnPb alloys. High melting point
	Sn–2Ag	221–226	
Sn–Ag–Cu	Sn–3.8Ag–0.7Cu (SAC387) (near eutectic)*	217	
	Sn3.9Ag0.6Cu	~217	
	Sn–1Ag–0.5Cu (SAC 105)	~217	
	Sn–3Ag–0.5Cu (SAC305)	~217	
	Sn–4Ag–0.5Cu (SAC405)	~217	
Sn–Cu	Sn–0.7Cu (eutectic)	227	Low cost. Plumbing alloy. Poor mechanical properties. Application for wave soldering

* The exact eutectic composition is unknown.