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Introductory Chapter: Overview of Recent Progress in Soldering Materials

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1. Introduction

Sn-Pb solders have a long history and are widely used in the electronics industry due to their low cost, good solderability, low melting temperature and satisfactory mechanical properties. However, due to recent legislation and market pressures, Pb is being removed from electronic products [1].

Many lead-free solders have been studied as replacements for Sn-Pb solders. Of these, Sn-Ag-Cu-based materials are the most promising candidates owing to their overall properties, including mechanical and reflow properties, wettability and reliability.

Nowadays, electronic devices have become smaller and more complicated. However, the reliability of soldered components remains a critical issue. The need for high electric current density and the decreasing scale of solder-substrate interfaces of the latest advanced electronic products are everyday challenges for those in solder-related industries.

This book concerns solders and focuses on material characterizations, solder composition, and the methods used to make alloys and determine their structures, physical properties and applications. Physical properties, the factors that control them, and theoretical verification are key elements of solder research and will be reviewed in detail. Corrosion of solders is included in the coverage of the properties related to solder composition and mechanical properties.

2. Composition

To improve Sn-based solders for specific applications, various alloying elements have been studied, e.g., Ag, Bi, Al, Cu, In, Sb, Zn and so on. The selection of alloying elements is generally

used to tackle problems regarding to pure Sn, to control the formation of intermetallic compounds (IMC), to keep the melting point at eutectic or near eutectic, to improve corrosion resistance and improve mechanical properties and so on [1, 2].

Several publications have already reported on these elements used to form various alloy compositions. Examples of basic compositions are Au-Sn, Bi-Sn, Sn-Ag, Sn-Cu, Sn-In and Sn-Zn. However, the properties of these binary alloy systems are far away from any applications [3]. In the next development, ternary solders are proposed, such as Sn-Ag-Cu, Sn-Ag-Bi and Sn-Zn-Bi solders. However, the formation of brittle failure behavior of IMC during soldering of both phases remains a problem. Now, trending in solder research is composite solders.

3. Joints

The interconnectivity of device components is very important in terms of electrical and mechanical properties. Most of these components are connected by solder joints. Solder joint is a very interesting subject to study in detail, and many new problems arise as electronic devices change almost daily.

Within this joint, IMCs are an important issue and must receive proper attention. Formation of an IMC layer at the solder/substrate interface after reflowing used to indicate a good joint between the solder and the substrate.

However, IMCs continue to achieve higher working temperatures and longer times. Thick IMC negatively affect the long-term reliability of solder joints due to their brittle nature [4, 5]. Even worse, to accommodate microelectronic components, current smaller and thinner sizes of solder joints are needed. The formation of smaller joints indirectly means that the volume fraction of the formed IMC layer tends to increase.

To inhibit interfacial IMC growth, several types of substrate finishes have been developed. The most popular surface finish for Cu substrates for high-end electronic applications is electroless nickel electroless palladium immersion gold (ENEPIG). ENEPIG is a tri-layered structure consisting of a layer each of electroless Ni, electroless Pd and immersion Au. The electroless Ni layer serves as an efficient diffusion barrier between the solder and the Cu pad, which can effectively inhibit the growth of interfacial IMCs [6].

Another approach to reducing the growth of IMCs uses composite solders. Inert reinforcements i.e. TiO_2 , Al_2O_3 , CeO_2 , Fe_2NiO_4 , TiC , TiO_2 , ZnO , ZrO_2 and a carbon base i.e. graphene and carbon-nanotube are among the popular materials to be used in composite solders. These inert particles (mostly of nanosize) are nonreacting with the molten solder during the reflow process, which helps to refine the IMC's structure and consequently improve the mechanical and other properties [7–9]. Composite solders have therefore attracted considerable attention. For a full review of nanocomposite solders, the reader is referred to Shen and Chan [7].

4. Nanoindentation

Many physical/mechanical characterizations of solder joint have been proposed. However, since the miniaturization of devices reduces solder joint size, the effectiveness of characterization also needs to follow this trend. Nanoindentation hardness testing, using nanometer-sized indents, is another popular tool that is accorded with smaller component properties. It is used to estimate the physical and mechanical properties of materials [6]. An example of nanoindentation testing involves curve marks and plotting of the force that is applied to solder materials (**Figure 1**) [9].

Figure 1. Areas of the nanoindentation marks on the cross-sectioned surface of (a) SAC305 and (b) the hysteresis plot of the loading and unloading indenters for SAC305, adapted from Ref. [9].

5. Corrosion

Material selections for solder are not normally designed for corrosion resistance. If this material is in contact with a corrosive environment, it could cause failure of the circuit. Once the corrosion has occurred, mechanical and electrical failures make the product stop. The corrosion properties of Sn-based lead-free alloys in corrosive environments have not been widely reported, even though it is important in many automotive, aerospace, maritime and defense applications [10]. Corrosion mainly originates either within the circuit (flux corrosion) or from the environment [11, 12].

5.1. Flux corrosion

Flux corrosion is related to the solder flux residue produced during soldering and remains corrosive even after the soldering operation has completed. Solder flux residue acts as a corrosion promoter in the presence of ionic substances and a resin component. Aggressive ions, such as Cl^- or Br^- in flux, will increase the corrosion activities. Flux residue resin also accumulates dust during operation and later provides a hydrophilic surface which forms a medium for the ions to react with the solder materials [12, 13].

The failure analysis of flux corrosion has been reported by several authors. Jellesen et al. [12], for instance, used a drop of solution (DI water or flux solution) on a micro tactile switch under DC bias. This reportedly helped to prove that the corrosion originated from flux contamination and condensation (**Figure 2**).

Figure 2. SEM micrograph of a failed switch due to severe corrosion and migration. (1) Silver, (2, 3) excessive deposits of Sn—major corrosion species, (4) carbon from the plastic housing and (5) flux residues, adapted from Ref. [12].

Figure 3. SEM image of a corroded Cu/Sn-9Zn/Cu butt joint after tensile strength measurement, adapted from Ref. [14].

5.2. Environment corrosion

Air moisture or aggressive mediums contained in natural environments are another source of solder corrosion. The most reported studies involved Cl^- and OH^- ions. Many alloy compositions and new elements have been introduced to improve corrosion resistance without reducing other properties.

Research on the corrosion of solders includes various aspects of solder characterizations. Examples include open circuit potential, galvanic cell, polarization, electrochemical impedance spectroscopy and so on.

One interesting corrosion study is the combined effect of corrosion on mechanical properties. Corrosion-mechanical studies are varied, e.g., the effect of immersion time of Cu/Sn-9Zn/Cu [14] (**Figure 3**). The focus here is more on the preferential dissolution of Zn and Sn. The formation of corrosion products and grooves proves the cause of joint failure. Later, the formation of cracks is the final stage that causes the mechanical properties of solders.

6. Conclusion

Lead-free solder characterization, properties, mechanism and applications of the latest developed solder materials are briefly reviewed in this introductory chapter. Further discussion on certain topics can also be found in this book. This review will hopefully assist readers in obtaining an overview of this exciting and promising field.

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