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Review Article

Development of High-Temperature Solders: Contribution of Transmission Electron Microscopy

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This article briefly reviews the results of recently reported research on high-temperature Pb-free solder alloys and the research trend for characterization of the interfacial reaction layer. To improve the product reliability of high-temperature Pb-free solder alloys, thorough research is necessary not only to enhance the alloy properties but also to characterize and understand the interfacial reaction occurring during and after the bonding process. Transmission electron microscopy analysis is expected to play an important role in the development of high-temperature solders by providing accurate and reliable data with a high spatial resolution and facilitating understanding of the interfacial reaction at the solder joint.

Key Words: Step soldering, Melting temperature, Spatial resolution, Scanning electron microscopy, Transmission electron microscopy

INTRODUCTION

As the human health hazard and environmental problems due to hazardous substances used in electronic packaging became an issue, the European Union enacted the Restriction of Hazardous Substances (RoHS) Directive regarding electrical and electronic products in 2006. Thereafter, a number of countries introduced environmental regulations regarding imported electronic products.

The study of medium-temperature Pb-free solder, represented by Sn-Ag-based solder, to replace Sn-37wt%Pb (hereinafter the notation Sn-37Pb is used, omitting the unit of wt%) for packaging technology is essentially complete. Sn-Ag-Cu solder is a representative alloy and is widely used as a standard solder alloy (Suganuma, 2004). However, little research has examined the high-temperature Pb-free solder used for step soldering, power devices, and flip-chip connections because an exemption for high-melting-temperature-type solders (i.e., lead-based alloys containing 85 wt% or more lead) has been added to the RoHS Directive, and this exemption is permitted owing to the lack of viable Pb-free alternative alloys with similar melting points. Thus, Pb-containing high-temperature solders are still heavily used by many manufacturers. Nevertheless, the development of high-temperature, high-reliability, and eco-friendly Pb-free solder is essential because of not only environmental issues but also processing issues. In particular, in step soldering, the solder used for the first step must have a higher melting temperature than that used for the next step. In addition, Sn-37Pb (melting point T_m=183°C) has been replaced by Sn-Ag-Cu solder (T_m=221°C), and the reflow temperature was accordingly increased by ~40°C, which implies that solders having melting temperatures higher than ~250°C are required for step soldering if Sn-Ag-Cu solder is used in the secondary mounting process.

Vianco defined "ultrahigh-temperature" solder as "solder used in environments having sustained temperatures as high

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as 300°C and momentary temperature excursions to levels as high as 350°C" (Vianco, 2002). High-temperature solders are generally required to have adequate physical properties, including high ductility and thermal conductivity and low electrical resistance, and to be cheap and eco-friendly. In particular, they must have a higher solidus temperature than the secondary reflow temperature (~250°C) of the intermediate T_m solder packaging and have a lower liquidus temperature than the glass transition temperature (~400°C) of polymer-based substrate materials.

Alloys containing Au-, Bi-, Cd-, Sn-, and Zn-based solders reportedly satisfy these conditions. This article considers Bi-, Sn-, and Zn-based high-temperature Pb-free solder candidates, excluding Au-based alloys, which are costly, and Cd-based alloys, which are harmful to the environment.

CANDIDATES FOR HIGH-TEMPERATURE PB-FREE SOLDERS

Sn-Sb solder has melting points of 235°C and 240°C for the representative compositions of Sn-5Sb and Sn-10Sb, respectively, and the melting point rises as the Sb content increases by peritectic reaction (Fig. 1A) (Okamoto, 2012). It has not only excellent wettability and high mechanical properties at room temperature, but also an electrical resistance similar to that of Pb-Sn solder (Geranmayeh & Mahmudi, 2005; El-Daly et al., 2011a, 2011b). However, it has drawbacks such as toxicity due to the presence of Sb and a too-low liquidus line for it to be used for step soldering.

Bi-Ag solder has a melting temperature of 262.5°C at the eutectic composition (Bi-2.5Ag) (Fig. 1B) (Karakaya &

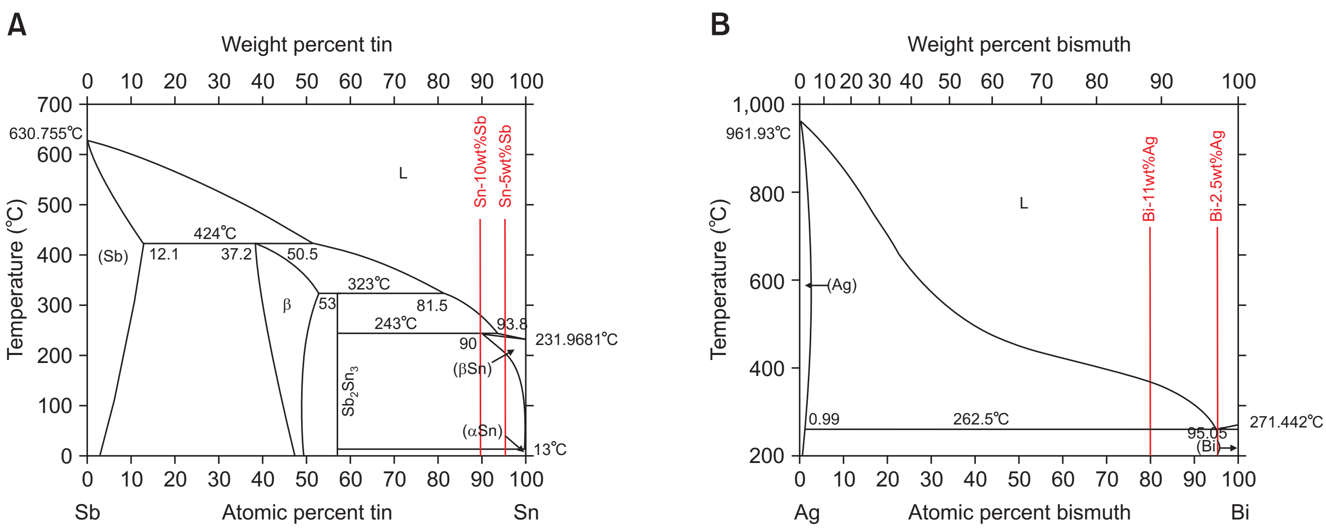

Fig. 1. Binary phase diagrams of Sn-Sb (A) and Bi-Ag (B). Red lines denote typical solder compositions.

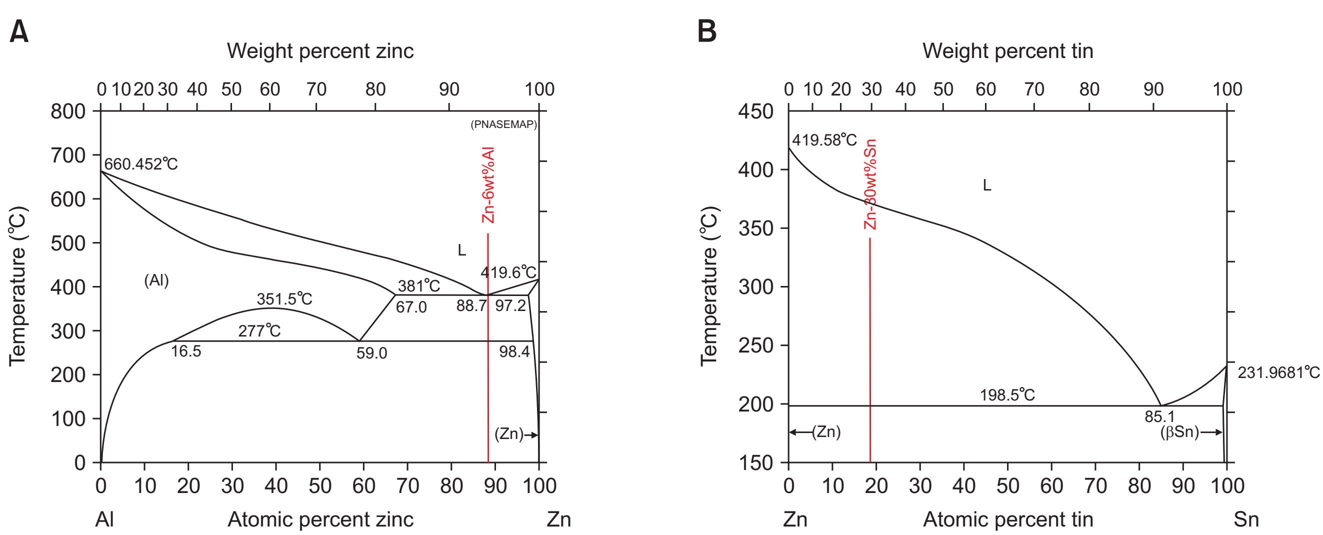

Fig. 2. Binary phase diagrams of Zn-Al (A) and Zn-Sn (B). Red lines denote typical solder compositions.

Table 1. Advantages and disadvantages of high-temperature Pb-free solder candidates

Type	Advantage	Disadvantage
Sn-Sb	Good wettability, good creep properties	Low liquidus line, toxic
Bi-Ag	Adequate melting range	Low conductivity, bad electrical resistance
Zn-Sn	Good ductility, high tensile strength, low cost	Highly corrosive, liquid phase (199°c) at process temperature
Zn-Al	Easy to use in field applications, low cost	Highly corrosive, poor wettability

Thompson, 1993). Research on this solder alloy system is still incomplete, owing mainly to its inferior thermal and electrical conductivity as well as poor workability. A recent study reported that the electrical resistivity of the Bi-11Ag alloy is 86.5 μΩ/cm, which is much lower than that of the Bi-2.5Ag eutectic alloy, 116.5 μΩ/cm (Song et al., 2007a). Song et al. (2007b) have examined rare-earth-material-doped Bi-Ag solders with various Ag concentrations. They suggested that the addition of small amounts of rare earth elements may enhance the wettability of Bi-Ag solder on Cu substrates and the shear strength of the solder joints (Song et al., 2007b).

Zn-based solders can be divided into Zn-Al and Zn-Sn types. A Zn-Al alloy with a eutectic melting point of 381°C (Zn-6Al), as shown in Fig. 2A (Murray, 1983), has been studied because the melting range of Zn-Al solder is similar to that of Pb-5Sn solder (so it can be used immediately in industry) (Kim et al., 2008; Kang et al., 2009). The price of zinc and aluminum is very low (they are even cheaper than lead). However, Zn-Al solder has several drawbacks compared to other solder alloys. It has a galvanic corrosion problem due to the corrosive metal zinc and poor wettability due to the high oxygen affinity of Zn and Al materials. A few papers reported improvement of its properties by the addition of a third material (e.g., Ag, Cu, Ge, Mg) to Zn-Al solder (Shimizu et al., 1999; Aksoz et al., 2011; Cheng et al., 2012; Gancarz et al., 2012).

In the case of Zn-Sn solder alloy, a hypereutectic composition, Zn-(20, 30, 40)Sn, where the eutectic composition is Sn-8.8Zn (Fig. 2B) (Moser et al., 1985), has been studied. This alloy system has the advantages of excellent thermal conductivity and mechanical properties (ductility and high ultimate tensile strength) and oxidation resistance in high-temperature high-humidity conditions (Lee et al., 2005; Santos et al., 2014). However, in addition to the corrosion problem due to zinc, there is a serious problem that the solidified solder joint returns to a solid+liquid mixed phase at the secondary reflow temperature (~250°C), which is higher than the eutectic temperature of 199°C (Fig. 2B). Nevertheless, Suganuma et al. (2009) suggested that this hypereutectic alloy can be used as a high-temperature solder by controlling the liquid fraction at the secondary reflow temperature. They reported that the volume expansion caused by formation of the liquid phase (remelting) in the solder joint is not large enough to distort the bonding structure if the Sn content is <30 wt% (Lee et al., 2005).

Table 1 summarizes the advantages and disadvantages of high-temperature Pb-free solder candidates.

INTERFACIAL REACTION BETWEEN HIGH-TEMPERATURE PB-FREE SOLDER AND SUBSTRATES

When solder is joined to a substrate, an interface intermetallic compound (IMC) is formed by diffusion of the constituent atoms in the solder and substrate. These IMCs grow by solid-liquid phase diffusion and solid-solid phase diffusion. Solid-liquid diffusion occurs by mass transport between the melted solder (liquid) and substrate (solid) during the bonding process, whereas solid-solid diffusion is responsible for IMC growth after the bonding process. IMC growth reportedly has an important effect on the reliability of solder joints.

According to research papers on Zn-based solder, Cu-Zn IMCs ($CuZn_4$ and Cu_5Zn_8) were formed when Zn-based solders were bonded to a Cu substrate (Takaku et al., 2008; Hui et al., 2009; Kim et al., 2009a, 2009b; Haque et al., 2010a, 2010b; Mahmudi & Eslami, 2010; Takahashi et al., 2010; Haque et al., 2012; Wang et al., 2012). Takaku et al. (2009) reported that an Al_3Ni_2 IMC was formed when Zn-Al-Cu solder was joined to a Ni substrate. The linear relationship between d (the IMC thickness) and the square root of t (the time) was confirmed and follows the parabolic law

$$d = k\sqrt{t}$$

where k represents the growth rate coefficient for the consumption rate (experimental values).

Bi-Ag solder alloy does not form any interfacial reaction layer with a Cu substrate and makes solder joints in such a way that the Ag penetrates the grain boundaries of the Cu substrate. Further, $NiBi_3$ and NiBi phases were reportedly formed during connection with a Ni substrate (formation of the interface reaction layer differs depending on the Ag composition of Bi-Ag solders) (Song et al., 2006; Shi et al., 2010; Iseki & Takamori, 2012). In the case of Sn-based solder alloys, Cu_3Sn and Ni_3Sn_4 IMCs were reportedly formed when the solder joined with Cu and Ni substrates (Chen et al., 2006, 2008).

As summarized in Table 2, the number of papers that have studied the interface reaction layer is still small, and the research results consist only of simple phase analysis using scanning electron microscopy (SEM) images and phase diagram data.

NEED FOR TRANSMISSION ELECTRON MICROSCOPY ANALYSIS

In previously published papers, the interface reaction layer between the solder and the substrate has generally been investigated by a combination of microstructural analysis using SEM, chemical composition analysis using energy dispersive X-ray spectroscopy (EDS), and phase analysis using X-ray diffraction (XRD) in conjunction with phase diagrams (Chen et al., 2006; Song et al., 2006; Chen et al., 2008; Takaku et al., 2008; Hui et al., 2009; Kim et al., 2009a, 2009b; Haque et al., 2010a, 2010b; Mahmudi & Eslami, 2010; Shi et al., 2010; Takahashi et al., 2010; Haque et al., 2012; Iseki & Takamori, 2012; Wang et al., 2012). However, SEM and EDS analysis cannot yield accurate results because of technical limitations such as low spatial resolution (large electron beam-specimen interaction volume) and ambiguous peaks and noise signals. XRD analysis is also not a suitable method for analyzing the phase of the interfacial reaction layer because of the difficulty of selecting the analysis region and fine grain detection limit settings.

Table 2. Numbers of papers per analytical method

Type	No. of papers published since 2000	No. of papers reporting IMC analysis using SEM	No. of papers reporting IMC analysis using TEM
Sn-Sb	5	2	0
Bi-Ag	5	4	0
Zn-Al	12	6	1
Zn-Sn	8	4	0

IMC, intermetallic compound; SEM, scanning electron microscopy; TEM, transmission electron microscopy.

Therefore, transmission electron microscopy (TEM) analysis has become important for accurate characterization of interfacial reaction layers. By employing various TEM imaging, diffraction, and spectroscopic techniques, it is possible to obtain reliable analysis results with high spatial resolution. One can obtain crystallographic information using versatile electron diffraction techniques, including selected area electron diffraction, nanobeam electron diffraction, and convergent beam electron diffraction techniques, and chemical composition data from EDS and electron energy loss spectroscopy analysis of a specimen several tens of nanometers thick.

We have studied the interfacial reaction layers between Sn-3.5Ag intermediate-temperature Pb-free solder and electroless nickel immersion gold plating (Ni-15at%P) on a Cu substrate

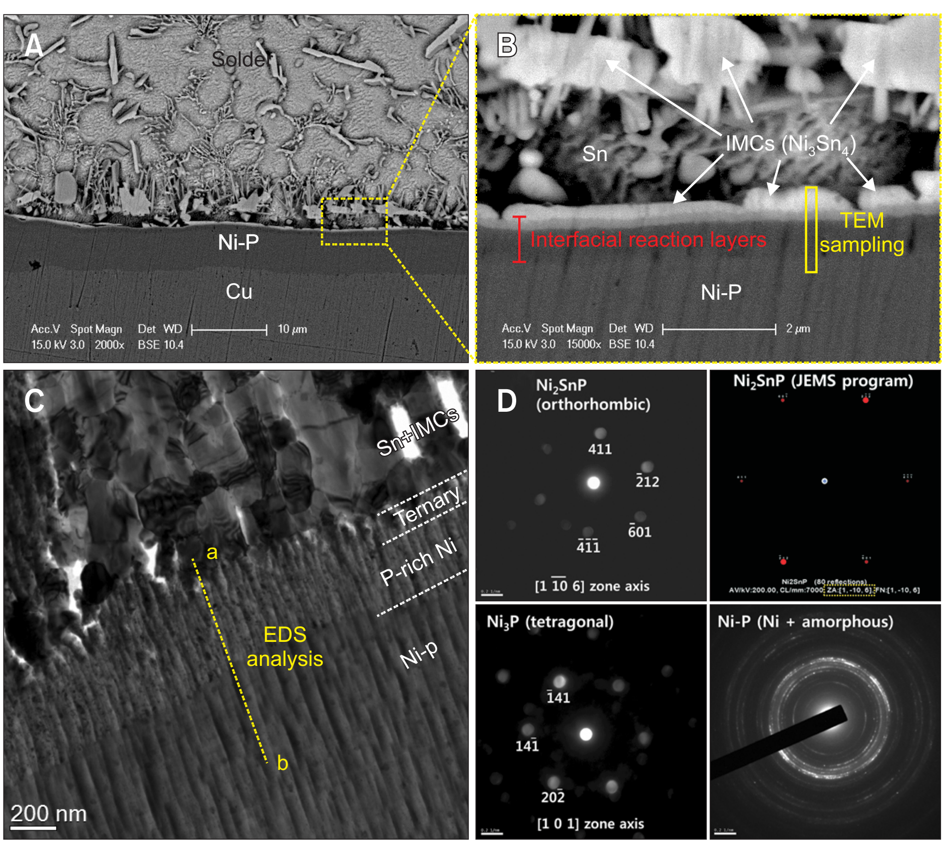

Fig. 3. Electron microscopy images of interfacial reaction layer between Sn-3.5Ag solder and Cu electroless nickel immersion gold plating on Cu substrate. (A, B) Scanning electron microscopy images with low and high magnification. (C, D) TEM image and diffraction pattern of each layer. IMC, intermetallic compound; TEM, transmission electron microscopy; EDS, energy dispersive X-ray spectroscopy.

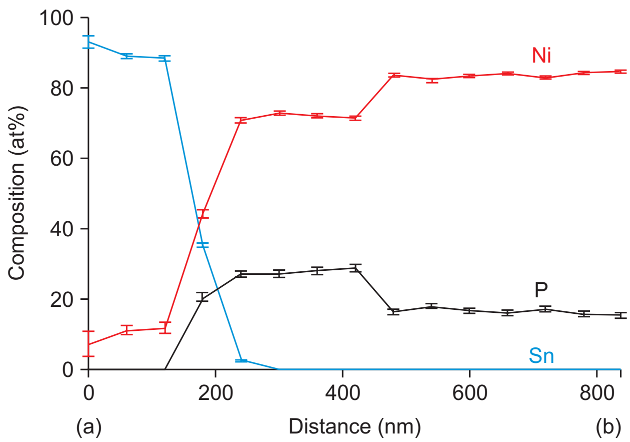

Fig. 4. Scanning transmission electron microscopy (STEM)-energy dispersive X-ray spectroscopy (EDS) analysis showing compositional variation of three elements (Ni, P, Sn) at the intermetallic compound/Ni-P plating layer interface. STEM-EDS was conducted along the yellow dotted line (from 'a' to 'b') in Fig. 3C.

using both SEM and TEM. Fig. 3A and B are SEM images of the reaction area after reflowing at 280°C. Only needle-shaped IMCs were observed at the interface at low magnification. Two thin layers having a different contrast were observed at the joining area in the high-magnification image; however, accurate phase analysis was impossible because of the above-mentioned problems. Fig. 3C and D are analysis results obtained from a TEM sample prepared by ultramicrotomy at the indicated area in Fig. 3B. Although Fig. 3C could not provide a perfect sample image because of knife marks created by mechanical stress during sectioning, each layer of the joining interface can be clearly observed (Fig. 3C), and intermediate layers were confirmed to have deposits of different phases (Ni_2SnP, $Ni_{12}P_5$, and Ni-P) using diffraction pattern analysis (Fig. 3D). The Ni2SnP ternary phase was verified by running the JEMS software (Stadelmann, 1987), a simulation program for diffraction patterns and high-resolution images, along the identical zone axis. In the Ni-P plating layer, two ring patterns (broad amorphous ring pattern and sharp Ni polycrystalline ring pattern) were observed simultaneously. The results of phase identification can be cross-checked and confirmed by performing scanning TEM (STEM)-EDS analysis (Fig. 4). Because the spatial resolution of STEM-EDS is superior to that of SEM-EDS analysis, it was possible to obtain a more accurate composition value that matched well the stoichiometry of each phase.

CONCLUSIONS

In this paper, we reviewed the results of recently reported research on high-temperature Pb-free solder alloys and research trends for characterization of the interfacial reaction layer. Research on these alloys should be conducted continuously to mitigate the drawbacks and improve the properties of these high-temperature solder alloys for eventual use in the field. The number of research papers on the interfacial reaction layer is also increasing gradually. A thin interface reaction layer is generally known to be good for enhancing the bonding property of solder joints because IMCs are brittle and exhibit poor electrical characteristics.

To improve the product reliability of high-temperature Pb-free solder alloys, thorough research is necessary not only to enhance the alloy properties but also to characterize the interfacial reaction layer formed during and after the bonding process. Accordingly, the contribution of TEM analysis to the development of high-temperature Pb-free solders is expected to become more important, and it will provide insight into interfacial reactions at the solder joint.

CONFLICT OF INTEREST

No potential conflict of interest relevant to this article was reported.

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