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RESEARCH PROGRESS ON LEAD-FREE SOLDERS

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Abstract: Along with the implementation of the comprehensive prohibition law of word industry developed countries for containing Pd solders of the production and use on electronic field, the research and development of the lead-free solders have launched vigorously. In this mini-review, we started from the research background of the lead-free solders and then some research progress and status of lead-free solders are concisely summarized. Finally, the problems faced and prospects of the lead-free solders for realizing are analyzed.

1. THE RESEARCH BACKGROUND OF LEAD-FREE SOLDERS

In today's society, the following three problems such as over-population, resource crisis, and environmental pollution are the point of increasing world-wide attention since entering the 21st century. Among them, the environmental pollution is becoming more and more serious. Since China is the biggest one among the developing countries in the world, the task of environmental protection is of extreme significance for it. With the rapid development of electronic technology, the electronic products are updating constantly in our daily life. However, most of the abandoned electronic products are directly discarded or buried which lead to a new kind of pollution, namely, heavy metal pollution. Till recently, solders used in electronics, based on suitability and knowledge-base developed over a period of time, remained to be to lead-based. Successive rapid advances in microelectronic devices make them obsolete within a very short period after their introduction resulting in significant quantities of electronic wastes in landfills. Leaching of toxic lead from such electronic wastes can result in contamination of the human food chain causing serious health hazards. As a consequence, several European and Pacific Rim countries have passed legislation warranting elimination of lead from electronic solders by specific fast approaching deadlines. Then, the standard of lead-free solders for production is proposed that the lead content in the electronic devices should not be more than 0.1% which can reduce the pollution caused by the waste device [1].

Modern society has entered into an information age with the development of science and technology, however, the information level of discretion to measure a country has also became an important symbol of comprehensive national strength. The development of modern electronic industry puts forward increasing high demand. Volume miniaturization, components multi-function, high reliability, and low cost are needed for new electronic products. Due to the technology limitation in miniaturization of the semiconductor chip size, in recent years, related electronic packing technology and materials are considered to be the dominating direction in microelectronic industry technology competition [1]. Microelectronic technology, in which chip manufacturing and electronic packing are the two keys, respectively, is the indispensable base in the electronic information industry and various high-technology applications [2]. However, electronic

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packing is a complex of system engineering involving craft, material, and design, evaluation analytical technology systems.

Electronic packing generally can be divided into three levels, first-level package, second-level package, and third-level package, respectively [3], (see Fig. 1, Scheme of three levels in electronic packaging). First-level package is chip encapsulation, mainly silicon chip in the substrate, second-level package is the connection between electronic devices and printed circuit board, and the third-level package is the connection, seal, and quarantine from the external environment [4]. Micro-connection technology in the electronic package plays an essential role in the whole process.

Soldering is the preferred method of joining components to printed circuit boards in electronics. It is generally a relatively low temperature (<250 °C) process, therefore, avoiding thermal damage to the polymeric materials of the PCBs or the components [5]. Sn-Pb alloys are the primary solders used widely in manufacturing because of their unique combination of material properties and low cost [6]. The electronic industry has been using Pb-bearing solders for interconnection applications for over fifty years, however, the presence of lead in the actual solders is considered to be very dangerous for the environment due to the huge amounts of printed circuit board and electronic devices to be recycled from municipal waste dumps [7,8]. There are several pending national and international legislation proposals forbidding the wide use of Pb in solders such as Sn95Pb and Sn37Pb solder because of the toxicity of lead and its harm to the environment and human health; thus these Sn-Pb solders are not allowed to be used in the electronic products. The European Community, the U.S., and Japan, as well as electronic industry companies launched initiatives to look for lead-free solders having physical, chemical, and technological properties comparable to or better than the Sn-Pb alloys in use [9]. The development of lead-free solders has been a pressing task for material scientists due to the health and environment concerns over the lead content of conventional solders used in electronic industry widely.

The new lead-free solder alloys, which has been used in the electronic industry and attracted extensive attention, need to meet a variety of properties such as good wettability, low soldering temperature, low-cost, environmental friendly, adequate strength, good thermal fatigue resistance and so on which are superior to or even consistent with that of conventional Sn-Pb solders at least.

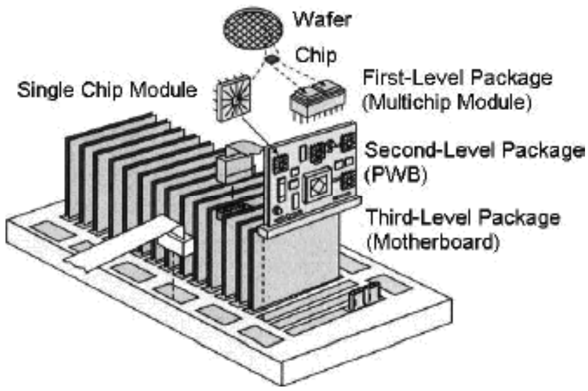

Fig. 1. Scheme of three levels in electronic packaging.

Internationally, the lead-free solder is defined as based of Sn due to its good conductance which is doped with Ag, Cu, Zn, Bi, In to form binary, ternary, or even quaternary eutectic alloys to improve the performances of pure Sn, in addition, the Pb-content is less than 0.1%. Global concern over the environmental impact and health effects of Pb-based solders in consumer electronics has led to the development of lead-free solders alternatives. Lead-free solders were never an industry choice until recent UK legislation has enforced their use since the introduction of Eu RoHS directive. As a consequence, a specific family of alloys has emerged that are likely to become industry standard for surface mount reflow solder joints. The SAC(Tin-Silver-Copper) family of solder alloys are recommended by most of the electronics industries governing bodies own to superior mechanical properties, good wettability, improved creep resistance and long thermal fatigue life, but the Sn-Ag-Cu eutectic composition is still in question [11] such as the liquidus temperature of the Sn-Ag-Cu solders is about 30 °C higher than that of the Sn-37Pb (187 °C) solder which would bring serious oxidation problem to the solder surface and decrease the wettability between the solder and substrate [10]. So the research of new lead-free solders with equivalent mechanical performances and microstructural stability to eutectic tin-lead solder is an urgent task.

2. THE RESEARCH STATUS OF LEAD-FREE SOLDERS

Considerable effort has been made to explore various solders [12-19] and the design of reliable joints with newly developed lead-free solders in order to understand completely their mechanical properties

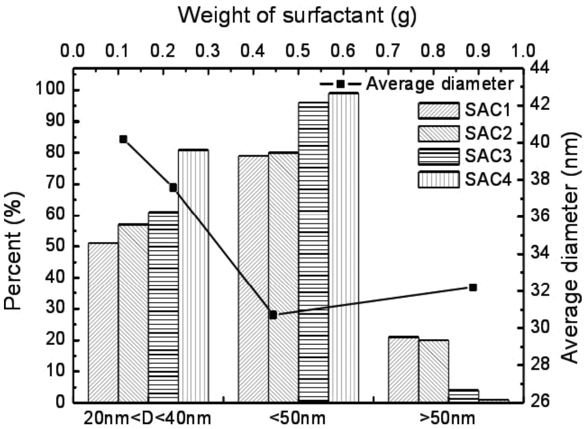

Fig. 2. The relationship of the different particle sizes and average diameter with surfactant (the content of surfactant SAC1, SAC2, SAC3, SAC4 is 0.1110 g, 0.2220 g, 0.4440 g, 0.8880 g).

and deformation mechanism. The role of solder joints in electronic products is not limited by interconnection of the electronic components only, but also they ensure the structural reliability of the electronic package. Nanosoldering is a promising technique for nanoscale joining and interconnect formation for many newly emerging nanofabrication processes and nanobuilding blocks. With the burst of nanotechnology in the last two decades, researcher's ability to explore various nanostructures has improved significantly.

There is an increasing technology interest for low melting point alloy suitable for use in soldering with lead-free materials. Surojit Pande *et al*. [20] adopted a straightforward route to gram level synthesis of pure phase of the Sn-Ag nanoalloy in an eutectic composition (96.5:3.5) in a mixture of ethylene glycol and silicone oil using hydrazine as the reductant and then the direct reduction of Sn(II) acetate and Ag(I) nitrate gave the Sn-Ag nanosolder. Smaller particles with a melting point as low as 128 °C were obtained when the nanoalloy disintegrates by sonication and reforms by heating.

Zou [21] focused on the research aimed to lower the melting temperature of the lead-free solder alloy through decreasing the particle size down to nanometer level using the tin(α)2-ethylhexanote, silver nitrate, copper(α) ethoxide monohydrate as the starting materials, anhydrous ethanol as the solvent, sodium borohydride as the reductant and the 1,10-phenanthroline as the surfactant by chemical reduction method. The Sn3.5Ag and Sn3.5Ag0.5Cu nanoparticles (average size about 30 nm) are obtained by adjusting the drops rate of reductant, the concentration of surfactant and reactant. The results showed that the larger ratio of the weight of surfactant to the precusor leading to smaller particle size and size distribution due to the capping effect caused by the surfactant molecules coordinating with the nanoclusters. Fig. 2 depicts the relationship of the different particle sizes and average diameter with surfactant. When the addition rate of reductant is decreased, the particle sizes and size distribution showed the same result. Also, the melting temperature of lead-free solder showed strong size-dependent tendency and the melting temperature of Sn3.5Ag and Sn3.5Ag0.5Cu nanoparticles with average size of 30 nm was 210 °C and 201 °C, much lower than that of bulk alloy. Theoretical analytical showed that the melting temperature can be as low as that of eutectic Sn-Pb solder alloy when the particle size was decreased to 10 nm.

Gao [22] synthesized nanoscale Sn/Ag, Sn, and In lead-free solders directly onto multisegmented metal nanowires by an electrodeposition method in nanoporous templates. The diameter of nanosolder nanowires ranges from 30 to 200 nm and the length from 1 to 10 μm. The thermal properties of the solders were treated using a temperature-programmable furnace tub under a controlled atmosphere, it was found that nitrogen plays an essential role in the solder reflow process. Base layer, diffusion barrier layer, and wetting layer effect on solder reflow were studied and Nickel/gold surface finishing was found to be effective for the nanowires. Solder joints were formed when the nanosolder were reflowed in a liquid medium, which showed the great potential based self-assembly technology to integrate nanowires into 2D or 3D functional structures or other electronic devices.

Intermetallic compounds (IMCs) are formed when interconnections in integrated circuit (IC) packages

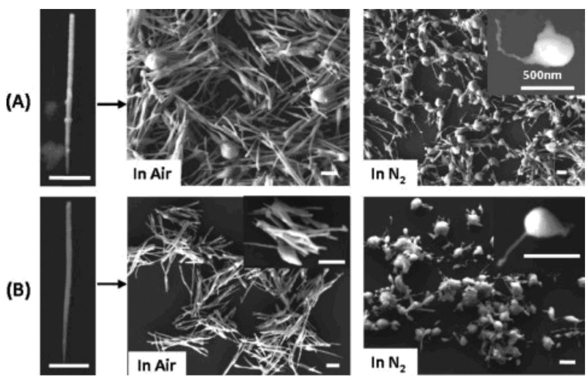

Fig. 3. Reflow of Sn and Sn/Ag nanowires in (A) air and (B) nitrogen. Scale bar:1 μm.

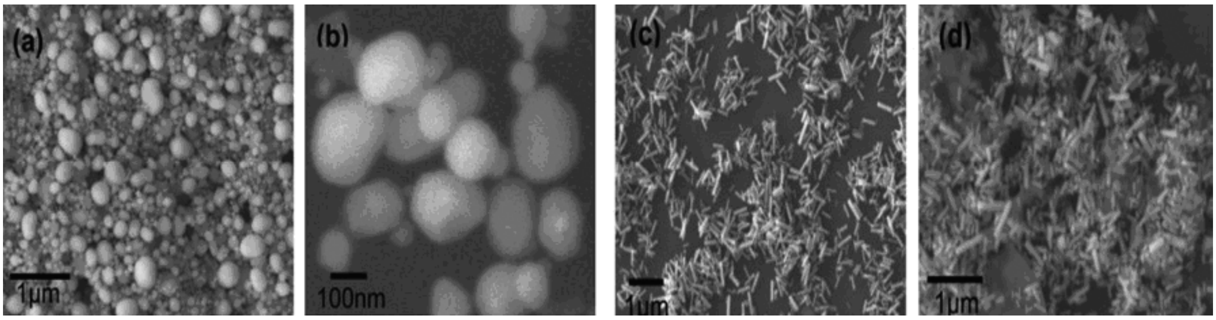

Fig. 4. Tin nanostructures formed at different SDS concentrations of (a) 0.4, (b)1 ,(c)10, (d)15 mM.

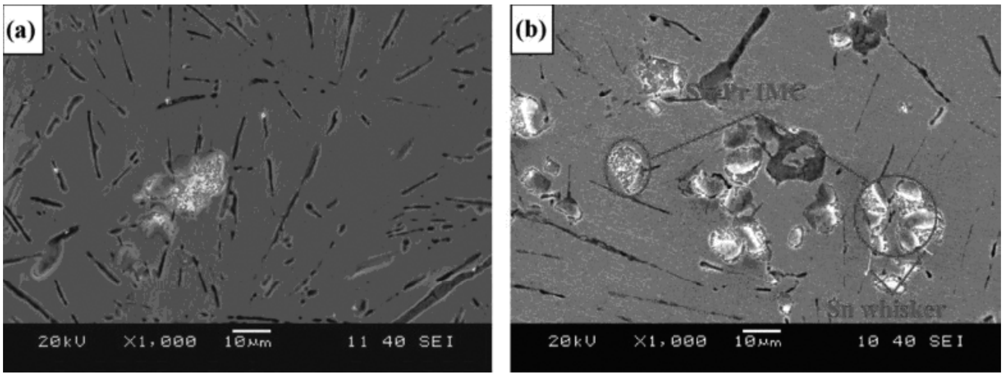

Fig. 5. SEM images of Sn-9Zn-0.5Ga-0.7Pr solders: (a)image of Sn-9Zn-0.5Ga-0.7Pr initial solder, (b) image of Sn-9Zn-0.5Ga-0.7Pr solder after exposure.

are joined with solder. Although IMCs are not present in large amounts, they usually have a dominant influence on the reliability of the interconnection because of their material properties [23]. Xu *et al*. [24] studied systematically the formation and evolution of intermetallic compounds (IMCs) layer between the Sn-3.7Ag-1In-0.9Zn lead-free solder and Ni/Cu substrate at different reflow times. The evolution of the interfacial structures was divided into three stages: a thin Ni_3Sn_4 was formed at the interface at the early reflow stage owing to the presence of the thin plated Ni layer (Ni+Sn $\rightarrow$ Ni_3Sn_4). As the reflow time went on, an intermediate Sn-Ni-Cu ternary compound was observed when the Ni layer was consumed completely, because of the reaction of the Ni_3Sn_4 and diffused Cu (Ni_3Sn_4+Cu $\rightarrow$ Sn-Ni-Cu) ternary compound. Finally, the Sn-Ni-Cu ternary compound changed into Cu_6Sn_5 (Sn-Ni-Cu ternary compound+Cu $\rightarrow$ Cu_6Sn_5), see Fig. 3.

The effect of surfactant concentration on the various shape nanostructures was analyzed using a simple surfactant-assisted method, see Fig. 4. As shown in Figs. 4a and 4b, polydispersed spherical tin nanoparticles are synthesized at low SDS concentrations of 0.5 and 4 mM, however, high-yield, uniform tin nanorods are formed with a further increase of SDS concentration up to 10 mM (see Fig. 4c). When the concentration increases up to 15 mM, the nanorods turn into a less uniform mixture containing nanoparticles and nanorods (see Fig. 4d). The results obtained indicate that these nanotubes are promising candidate for nanoscale soldering [25].

Generally, the reasons of Sn-Zn solders bad wetting is a high interfacial tension between the solder and substrate and the hindering effect of high interfacial tension of solder and accumulation of oxide [26,27]. Wu [28] prepared new solders doped with small amounts of Cu or Ni to improve the performances of Sn-Zn solders. The oxidation resistance of the solders on Cu substrate was evaluated using colorimetric analysis; mechanical properties were also tested. Experimental results showed that the addition of Cu and Ni into Sn-Zn-Al solders improve the wettability, in contrast to basic compositions, it has no significant effect on the oxidation resistance.

Most perspective candidates for lead-free solder alloys are based on eutectic Sn-3.5Ag solder with some additional elements aimed to decrease high melting temperature and improve wetting ability. When Ga is added into the Sn-9Zn lead-free solders, the effects of Ga on melting temperature, wetting properties as well as the mechanical properties of soldered joints were investigated, respectively. In general, the optimum additive amount of Ga in Sn-9Zn solder is about 0.5% [29].

The influence of rare earth elements Ce, Er, Y, and Sc on physical, wetting, and mechanical properties of Sn-Ag-Cu alloy with Sn-3.0Ag-0.5Cu based solder as master alloy was analyzed. The test results show that RE elements would affect the properties of the solder in different ways. The properties can be further improved by the addition of trace rare earth Ce into the solder [30].

Sn whisker growth is a serious reliability concern for electronic devices with high-density packing since Sn whisker as a conductive metal wire should lead to many potential risks such as short circuiting, metal vapor arcing, and interference with other components and finally results in the failure of devices [31,32]. It is found that many various lengths of needle-like Sn whisker originate spontaneously from the Sn-Pr intermetallic compounds of the solder at a rate of 3.5 Å/s during the exposure of Sn-9Zn-0.5Ga-0.7Pr bulk solder at ambient conditions for a few hours as shown in Fig. 5. It is proposed that the driving force for whisker formation in the bulk solder is related to the compressive stress owing to the oxidation of Sn-Pr phase and so the free Sn atoms released from the oxidation reaction feed the growth of Sn whisker during the exposure [33].

In addition, the effect of nano-TiO_2 particles on the interfacial microstructures and bonding strength of Sn3.5Ag0.5 Cu composite solder joints in ball grid array package with immersion Sn surface finishes have been investigated by J.C. Leong [34]. Metallography reveals that the addition of nano-TiO_2 particles retarded wicker-Cu_6Sn_5 IMC formed in the Sn3.5Ag0.5Cu composite solder joints. The thickness of the interfacial intermetallic compounds of the solder joint was decreased with the increased addition of nano-TiO_2 particles (0.25-1.0 wt.%), however, further addition up to 1.25 wt.% decreased the beneficial influence which suggests that the presence of small amount of nano-TiO_2 particles is effective for suppressing the growth of the compounds layer. Also, the shear strength of the solder joints was enhanced by larger nano-TiO_2 occurring at 1.0 wt.% of nano-TiO_2 into the solder. Therefore, we think that we don't only confine the metal element to be doped in the lead-free solders, but also try to other appropriate metal oxides to obtain more preferable solders.

3. THE PROSPECTS OF LEAD-FREE SOLDERS

The lead-free welding theory and practice both belong to the soldering technology fields. In the process of transformation from lead-bearing to lead-free solders gradually, the implementation of lead-free solder is still a long-term and hard task. However, at present, the soldering development is in the coexistence state of lead-containing and lead-free leading to a serious lead pollution. Another problem is a higher melting temperature which can do damage to other electronic components. There is a great increasing promise for the development of lead-free solders, but when they are used in practical applications still facing a lot of problems such as high cost, the collage between components and substrate, the performance of reflow furnace tube, the exploitation types of lead-free solders and the joints reliability to the lead-free solders and so on. Therefore, more efforts and research need to be paid to accelerate the process and improve the properties of lead-free solders to satisfy the needs of electronic industry. We strongly believe that lead-free solders must replace the lead-bearing solders with the further research and requirements to the environmental protection in the near future.

REFERENCES

[1] F. Guo *et al., Lead-Free Soldering Technology and Application* (Science Press, 2006).
[2] P. Sun, *Interfacial Reaction and Reliability Study on the Lead-free Solder Joints in the Electronic Packageing* (Shanghai: Shanghai University. School of mechanical and electrical engineering and automation, 2007).
[3] M.B. Tian, *Electronic Packaging Engineering* (Tsinghua Univerity Press, 2003).
[4] M. Abtew and G. Selvaduray // *Materials Science and Engineering* **27(5-6)** (2000) 95.
[5] W. J. Plumbrige // *J Mater Sci:Mater Electron.* **18** (2007) 307.
[6] K. Suganuma // *Current Opinion in Solid State and Materials Science* **5(1)** (2001) 55.
[7] Katsuaki Sugamuma // *Current Opinion in Solid State and Materals Science* **5(1)** (2001) 55.
[8] J. Liu and F.W. Zhang // *Journal of Rare Metal.* **24(4)** (2005) 6.
[9] B. Brunetti, D. Gozzi, M. Iervolino, A. Latini and V. Piacente // *J.Chem.Eng.Data* **52** (2007) 1394.
[10] Yee-Wen Yen and Yu-Cheng Chiang // *Journal of Alloys and Compounds* **509** (2011) 4595.
[11] M. Moshrefi-Torbati and J.Swingler // *J Mater Sci: Mater Electron* **22** (2011) 400.
[12] C.E. Ho, Y.L. Lin and C.R. Kao // *Chem. Mater.* **14** (2002) 949.

[13] M.O. Alam and Y.C. Chan // *Chem. Mater.* **17** (2005) 927.

[14] Wei-Kai Liou, Yee-Wen Yen and Kuen-da Chen // *Journal of Alloys and Compounds* **479** (2009) 225.

[15] Min He and N. Sylvester // *Journal of Electronic Materials* **37** (2008) 300.

[16] Alena Pietriková, Jozef Bednarcík and Juraj Durišin // *Journal of Alloys and Compound* **509** (2011) 1550.

[17] Chih-Kuang Lin and De-You Chu // *Journal of Materials Science: Materials Electronics* **16** (2005) 355.

[18] Zhengxiang Xiao, Songbai Xue and Yuhua Hu // *Journal Material Science: Mater Electron* **22** (2011) 659.

[19] W.J. Plumbrige // *J Mater: Mater Electron* **18** (2007) 307.

[20] Surojit Pande and Achintya Kumar Sarkar // *Langmuir* **24** (2008) 8991.

[21] C.D. Zou, *Fundamental research on the melting temperature depression of the Sn-based lead-free solder alloy via size effect of nanoparticles* (Shanghai, Shanghai University, Steel Alloy Profession, 2010).

[22] Fan Gao and Subhadeep Mukherjee // *J.Phys.Chem.* **113** (2009) 9546.

[23] Iting Tsai and Enboa Wu // *Journal of Electronic Materials* **35** (2006) 1059.

[24] R.L. Xu, Y.C. Liu, Y.J. Han, C. Wei, X. Wang and L.M. Yu // *J Mater Sci: Mater Electron.* **20** (2009) 675.

[25] Qingzhou Cui and Karunaharan Rajathurai // *J. Phys. Chem. C* **114** (2010) 21938.

[26] F. Xue, J. Zhou and P.P. Li // *Southeast University Journal: Nature Science Edition* **37(4)** (2007) 634.

[27] E. Lee, K.S. Kim and M. Inoue // *Journal of Alloys and Compounds* **454(1/2)** (2008) 310.

[28] X.Q. Wu, F. Xue and J. Zhou // *Southeast University Journal* **39(3)** (2009) 623.

[29] W.X. Chen, S.B. Xue and Z.J. Han // *Journal of Welding* **29(4)** (2008) 37.

[30] B. Lu, H. Li and J.H. Wang // *Rare Metal and Hard Alloy.* **35(1)** (2007) 27.

[31] K.S. Kim, J.M. Yang and J.P. Appl // *Surf.Sci.* **256** (2010) 7166.

[32] U. Sahaym, S.L. Miller and M.G. Norton // *Mater.Lett.* **64** (2010) 1547.

[33] Huan Ye, Songbai Xue, Liang Zhang, Zhengxiang Xiao, Yuhua Hu, Zhongmin Lai and Hong Zhu // *Journal of Alloys and Compounds* **509** (2011) L52.

[34] J.C. Leong and L.C. Tsao // *J Mater Sci: Mater Electron* **17** (2011).