RC22423 (W0205-011) May 2, 2002
Materials Science

IBM Research Report

An Overview of Lead (Pb)-Free Solders and Soldering Technologies in Microelectronics

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UKC2002, July8-11, Seoul, Korea,
Symposium on Electronic Materials (Packaging Materials Session)

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Abstract

Recently, the research and development activities for replacing lead (Pb)-containing solders with lead-free solders have been intensified in microelectronic industry due to competitive market pressures and environmental issues. As a result, a few promising candidate solder alloys have been identified, namely, tin-based alloys. In this paper, the recent progress in lead-free solders and soldering technologies for microelectronic applications is reviewed in terms of solder alloys, soldering processes, mechanical/electrical properties, interfacial reactions, reliability of solder joints, and other related issues.

INTRODUCTION

An acceptable Pb-free solder solution must satisfy both process requirements and reliability objectives (1, 2). Ideally, it should be suitable for mass production applications of both surface mount and pin-in-hole soldering. Furthermore, the process technologies currently in use for Pb-Sn eutectic or other Pb-containing solders must be adaptable to the new solder without major changes in manufacturing processes or significant capital investments. The wettability of the new solder should be better or equivalent to that of the Pb-Sn solder, and yield a better or equivalent defect rate in the assembly line. The selected Pb-free solder should be usable with water-soluble or no-clean fluxes. The melting temperature of the new solder is desired to be lower than those of the current solders in order to reduce the magnitude of thermal stresses experienced during soldering. The new solder must also be able to produce solder joints with acceptable joint strength while simultaneously withstanding thermal fatigue over the projected operating life of the soldered assembly, and meet other reliability requirements, such as adequate corrosion, oxidation or electromigration resistance. Lastly, the material cost of the new solder should not be so high as to overwhelm the assembly cost. With the above guidelines in mind, a number of Pb-free solders have been recently revisited or newly developed (3-14). Consequently, several promising Pb-free solder alloys have been identified for microelectronic applications as listed in Table 1. This list include the solder alloys such as Sn-3.5%Ag, Sn-3.5%Ag-0.7%Cu, Sn-3.5%Ag-4.8%Bi and Sn-0.7%Cu (wt %). All the promising, Pb-free solder candidates are high Sn-based alloys with their melting temperatures between 205°C and 230°C.

LEAD-FREE SOLDER CANDIDATES

In Table 1, in addition to Pb-free solder alloys, two Pb-containing solders (63Sn-37Pb and 97Pb-3Sn) are listed for comparison. The eutectic 63Sn-37Pb with a melting point of 183°C is the most widely used solder in surface mount technology (SMT), plated-through hole (PTH) soldering, ball grid array (BGA) joints, and others, while 97Pb-3Sn with a high melting point, 316°C is mainly used in the solder joints of flip chip or C4 (controlled collapse chip connections). Because of the large difference in the two melting points, a good solder hierarchy has been established when 97Pb-3Sn solder is used for chip interconnection and eutectic Sn-Pb is employed for the next-level solder connection such as card assembly. However, with the proposed Pb-free solders as listed in Table 1, since the maximum possible difference in their melting temperatures is less than 30°C, it can not achieve such a solder hierarchy established with the Pb-containing solders. The near-ternary-eutectic Sn-Ag-Cu alloy has been recommended as a leading candidate for the applications of SMT, PTH, BGA solder joints and others (15), while the binary eutectic alloys of Sn-Ag and Sn-Cu have been demonstrated for flip chip applications (5). Although the Bi-containing, ternary Sn-Ag-Bi solder has a low melting point and good wettability, the observation of fillet lifting in PTH joints (separation of liquid solder from a solder land in the final solidification process) has led to exclude this alloy from the leading candidate (5). The eutectic Sn-Cu solder is not recommended for SMT due to its high melting point. However, owing to its low material cost over the Ag-containing solders, it is recommended for a wave soldering process as well as for a Pb-free surface finish layer on PCB and components (11). Recently, this Sn-Cu solder has also been considered for flip chip applications (16).

Table 1. Pb-Free Candidate Solders

Composition (wt %)	Melting temp (C)	Applications	Concerns
63Sn-37Pb	183	PTH, SMT, BGA	Pb - environ
Sn-3.5Ag	221	SMT, Flip Chip	Cu dissolution, intermetallics
Sn-3.5Ag-4.8Bi	208-215	SMT	fillet lift in PTH, low mp phase
Sn-3.5Ag-0.7Cu	217	SMT, PTH, BGA	OSP wetting, voiding on finish, intermetallics
Sn-0.7Cu	227	PTH, (wave solder), Flip Chip	poor wetting, Cu dissolution, intermetallics
97Pb-3Sn	316	Flip Chip, C4	Pb - environ

PROPERTIES OF LEAD-FREE SOLDERS AND SOLDER JOINTS

Table 2 summarizes selected bulk properties of Pb-free solders such as ultimate tensile strength (UTS), total elongation to fracture, microhardness (HV), and electrical resistivity. The mechanical properties of Pb-free solders are favorably compared to those of 63Sn-37Pb, except Sn-9Zn. Since its melting point is very close to that of 63Sn-37Pb, Sn-Zn binary or ternary solders have been considered as a drop-in replacement for the eutectic Sn-Pb. However, its mechanical properties are not favorably compared to the eutectic Sn-Pb, and its propensity for oxidation during soldering would lead to poor wetting and thereby to form soldering defects.

Since the electrical conductivity of Sn is much better than Pb, the electrical conductivity of Sn-base, Pb-free solders is expected to be generally better than 63Sn-37Pb. By using model joints representing a typical solder joint geometry used in SMT, the electrical properties of several Pb-free solder joints were investigated as a function of surface finishes, reflow time and intermetallic thickness (17). The electrical resistance of Pb-free solder joints was found to increase

Table 2. Bulk Properties of Pb-Free Solders

Properties	Sn-37Pb	Sn-3.5Ag	Sn-5Sb	Sn-0.7Cu	Sn-9Zn
Melting point (°C)	183	221	238	227	199
UTS (MPa)	31-46 [1]	55 [2]	23-42 [3]	31 [4]	60-65 [5]
Elongation (%)	35-176 [1]	35 [2]	90-350 [3]	12 [4]	38 [5]
Hardness (HV)	12.9 [6]	17.9 [7]	17.2 [7]	14.4 [8]	23 [9]
Elec resistivity (mW-cm)	17.0 [7]	7.7 [7]	17.1 [7]	10-15 [10]	10-15 [10]

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initially as a function of reflow time or intermetallic thickness and then to decrease for an extended reflow or aging. This result confirms the electrical resistance of Pb-free solder joints being superior or equivalent to Pb-containing solder joints.

Table 3 compares shear strength of several Pb-free solder joints measured by employing different joint geometry and test methods. It is noted for a same solder alloy, the shear strength of solder joints varies significantly depending on joint geometry (joint gap, solder volume), reflow conditions (reflow temperature, time, cooling rate) and test methods (strain rate, stress state). Therefore, when the mechanical properties of solder joints are compared, a proper attention should be paid to understand the variations or discrepancies among the reported values.

Table 3. Shear Strength of Pb-Free Solder Joints (to Cu substrate)

Solder Alloy (wt %)	Shear Strength (MPa)	Shear Strength (MPa)	Shear Strength (MPa)	Presemt Study (MPa)
63Sn-37Pb	32.7	29	9.2	50
Sn-3.65Ag	37.2	28 (Sn-3.5Ag)	11.4	38 (Sn-3.5Ag)
Sn-0.7Cu	27.0		9.2	
Sn-3.8Ag-0.7Cu	35.1	47 (3.6Ag-1Cu)	12.5	39
Sn-3.5Ag-3Bi				49.6
Strain rate (mm/min)	0.10	0.10	15	0.25
Solder joint Gap (mm)	175	76	100 ?	20
Test method	Ring & plug	4 point bend	Flip chip in shear	Shear test
Reference	J..Foley, et al, p.1258JEM, 2000	B.Cook, et al, p.1214,JEM, 2001	D. Frear, et al p.28, June JOM, 2001	S. Kang, et al, TMS2002

RELIABILITY ISSUES OF LEAD-FREE SOLDER JOINTS

Despite the progress in research and development efforts and the proliferation in published technical findings on Pb-free solders, our knowledge and understanding of these new materials are still at an infancy stage compared to Pb-containing solders. Especially, unresolved issues on the reliability of Pb-free solder joints persist such as; can we make and properly test reliable Pb-free solder joints? What are the implications of higher reflow temperatures required for the new solders? Are the new surface finishes needed? Have interfacial reactions between Sn-rich solders and new surface finishes been adequately characterized? What are the influences of microstructural evolution during thermomechanical processes? What are the failure mechanisms related to thermal fatigue, creep deformation, corrosion, oxidation or electromigration of solder joints? To address all these challenging issues, TMS has been very active over the last several years in organizing a series of symposia on Pb-free solders and soldering technologies.

At the 2002 TMS Annual Meeting, Zribi et al.(18) discussed the formation of intermetallic compounds in the Pb-free solder joints in comparison with in Pb-containing solder joints. Changes in the metallurgies of solder joints to Sn-rich alloys, which require a higher reflow temperature, have caused not only acceleration of the reaction kinetics, but also complication of the mechanisms of interfacial reactions. This has a serious implication on the reliability of new Pb-free solder joints. Song et al (19) discussed the creep deformation of Pb-free solder joints. By analyzing their steady-state creep rates, they found the creep behavior of Sn-rich solder joints is dominated by the deformation of the Sn matrix and an anomalous temperature dependence of stress exponent was noted at temperatures around 100°C, complicating a prediction of the creep behavior of Pb-free solder joints. Gan et al. (20) discussed the electromigration phenomenon in eutectic Sn-Pb and Sn-Ag-Cu alloys for flip chip applications. Electromigration, defined as atomic diffusion driven by high electric current flow, can be a serious reliability problem in a small solder bump where the current density increases continuously as the miniaturization trend of VLSI circuits advances. The experimental techniques developed to study the electromigration were introduced to measure the electromigration failure rates of Sn-Pb and Sn-Ag-Cu bumps. It was reported Sn-Ag-Cu bumps more resistant to the electromigration failure than Sn-Pb.

Another intriguing reliability concern with Sn-rich solders reported by Kariya et al. (21) is the observation of tin pest (the product of the allotropic transformation of white tin into grey tin at temperatures below 286°K) in a Sn-0.5%Cu alloy after aging at 255°K for 1.5 years. Since the allotropic change causes a large volume increase of 26% and the accompanying cracking within the tin matrix, tin pest can be a serious reliability concern in Sn-rich solder joints to be used for low temperature applications.

In summary, the status of Pb-free soldering technologies has briefly been reviewed in terms of solder candidates, properties of bulk solders and joints, and reliability issues of Pb-free solder joints. There is much to be learned especially about various reliability concerns of Pb-free solder joints before we can confidently implement Pb-free solder technology.

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