LEAD-FREE ELECTRONICS

iNEMI PROJECTS LEAD TO SUCCESSFUL MANUFACTURING

Edited by

Edwin Bradley
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Jasbir Bath
Richard D. Parker
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IEEE PRESS

WILEY-INTERSCIENCE
A JOHN WILEY & SONS, INC., PUBLICATION

LEAD-FREE ELECTRONICS

IEEE Press
445 Hoes Lane
Piscataway, NJ 08854

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BICENTENNIAL 1807 WILEY 2007 BICENTENNIAL

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A JOHN WILEY & SONS, INC., PUBLICATION

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Library of Congress Cataloging-in-Publication Data is available.

ISBN 978-0-471-44887-7

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

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PREFACE

The International Electronics Manufacturing Initiative (iNEMI) is an industry-led consortium whose mission is to assure leadership of the global electronics manufacturing supply chain. With a membership that includes many large electronics manufacturers, suppliers, associations, government agencies, and universities, iNEMI provides an environment in which partners and competitors alike can collectively anticipate future technology and business needs and effectively develop collaborative courses of action to meet those needs.

Deployment of new technologies requires extensive evaluation and characterization of new materials and processes as well as demonstration of reliability. iNEMI members use existing resources to develop and deploy new manufacturing technologies and efficient business practices necessary to maintain a responsive supply chain infrastructure. Combined, these companies have sufficient critical mass to make an impact, whether it is in influencing development of industry standards or creating consensus requirements to reduce risk for users and suppliers.

The movement to lead (Pb)-free electronic assembly represented one of the largest challenges ever to the electronics industry. For well over 50 years, eutectic lead–tin (Pb–Sn) solder has been studied, categorized, and optimized for electronics manufacturing applications. In a few short years, Pb-free solder assembly would have to be put into wide-scale production, disrupting the status quo. Much of the work to rally the electronics industry to prepare for Pb-free assembly is described in this book.

The first chapter describes the search for a Pb-free replacement solder and the reasoning behind the alloy formulation ultimately recommended. Characterization on the recommended solder was carried out and reported in Chapter 2, while Pb-free solder paste requirements and evaluations are described in Chapter 3. The effect of Pb-free assembly on components is reported in Chapter 4. Chapters 5 and 6 report on iNEMI efforts to characterize the reliability of the new materials, and they present a literature review comparing Sn–Pb and Pb-free solder reliability. Chapter 7 describes the present understanding of a specific reliability risk—tin whiskers—that may arise with the move to Pb-free assembly. Chapters 8 and 9 summarize iNEMI projects on assembly and rework with the chosen Pb-free solder. Chapter 10 discusses the work of iNEMI members on the infrastructure required to implement Pb-free assembly in high-volume manufacturing.

Several hundred researchers from more than 100 companies, universities, and government agencies have contributed to the material in this book. The editors would like to thank them for providing the hardware, facilities, and data generation that has made this book possible. We hope the material herein will help the electronics industry to move forward.

RONALD W. GEDNEY

July 2007

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INTRODUCTION

JASBIR BATH and CAROL A. HANDWERKER

In 1999, electronics companies in Japan were driving green consumer products for the 2001–2004 market. Primarily this was achieved by eliminating tin–lead (Sn–Pb) solder in the assembly process. At the same time the European Union was proposing legislation to ban Sn–Pb solder in electronic products by 2008 (which was later moved to 2006). Dr. Iwona Turlik, Motorola, a member of the Board of Directors of the National Electronics Manufacturing Initiative (NEMI), now the International Electronics Manufacturing Initiative (iNEMI), foresaw the dramatic impact this initiative would have on electronics manufacturing. She convinced the iNEMI Board that projects had to be undertaken immediately, because it would take several years to adequately address a new solder technology. The iNEMI Lead-Free Assembly Project was established to begin the work to implement Pb-free soldering into electronics manufacturing. As the project developed, several goals emerged: (1) Choose, if possible, a single Pb-free solder that could be recommended as an industry standard; (2) provide a set of manufacturing processes and tools that would enable a participating company to quickly implement lead-free soldering if it decided to do so; and (3) provide sufficient data to demonstrate manufacturability and reliability of the alloy and processes chosen.

It was recognized that one project would not be able to address all the issues that would need to be solved with the introduction of a lead-free soldering process. Follow-on projects were undertaken to fill in the gaps. Results from several of these projects are also provided in this book.

The over-arching goal of the iNEMI program was to provide the necessary processes and tools (to be as compatible as possible with existing assembly infrastructure) so that each member company could decide on implementation for its own needs and on its own schedule.

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LEAD-FREE ASSEMBLY PROJECT

The primary objective of the iNEMI Lead-Free Assembly Project initiated in 1999 and completed in 2002 was to demonstrate the capability to deliver products with Pb-free interconnects in volume, utilizing, as much as possible, processes similar to Sn–Pb solders and existing assembly tools. To realize this objective, the project team set out to:

- Facilitate a common Pb-free solder alloy composition for electronics assembly.

After a thorough literature survey and consultation with six solder suppliers, there were a small number of solders that might be acceptable replacements for the Sn–Pb eutectic. Picking one of these and concentrating efforts on that alloy allowed a more thorough study to be undertaken and began the effort toward a global industry standard.

- Work with component and PCB suppliers to develop specifications necessary to meet the higher temperature reflow conditions required for the new alloy.

Through the IPC, input from a number of printed wiring board companies was collected on which board materials would be acceptable, as would interconnect finishes. The test boards used in this study were a result of the best inputs available at the time.

- Develop criteria that industry could use to evaluate Pb-free processes.
- Monitor environmental legislation to adjust activities if necessary.
- Share information in a timely manner to promote a successful, common path to Pb-free assembly.

The project participants included OEMs/EMS companies such as Agilent Technologies, Alcatel Canada, Celestica, HP, Delphi, IBM, Intel, Eastman Kodak, Lucent, Motorola, Sanmina-SCI, Solectron, and StorageTek (now SUN); solder suppliers such as Alpha Metals, Heraeus, Indium Corp., Kester Solder, and Johnson Manufacturing, component suppliers such as ChipPac, Intel, Motorola, TI, and FCI; and government; other institutions such as the National Institute of Standards and Technology (NIST), SUNY Binghamton, ITRI (US), and IPC and equipment suppliers such as BTU, Universal Instruments Corporation, DEK, Vitronics-Soltec, Orbotech, Sonoscan, and VJ Technologies.

The Pb-Free Assembly Project was broken down into four specific group efforts as shown:

- Alloy
  - Development of alloy material properties and databases for modeling
  - Interface with academia, professional societies, and government agencies

- Components/PCBs
  - Effect of high-temperature reflow
  - Pb-free terminations
- Process Development
  - Generic processes for the reliability test boards
  - Process characterization benchmarking
- Solder Reliability
  - Transparent test procedure
  - Common data to share with the industry

ALLOY GROUP

1. Responsibilities of the Alloy Group

The primary responsibility of the iNEMI Pb-Free Assembly Alloy Group was to provide the Task Force with critical data and analyses needed for making decisions with respect to solder alloys, manufacturing, and assembly reliability. This responsibility required the Alloy Group to provide assessments of candidate solder systems to allow the group to make an informed choice of industry standard lead-free alloys for reflow and wave soldering.

- Generate key data for decision making if not available in the literature.
- Develop recommended practices and experimental procedures to measure the mechanical, thermal, electrical, and wetting properties of lead-free solders.
- Develop public domain solder databases for properties and literature references for lead-free alloys.
- Promote modeling for solder joint reliability through generation of best possible data and modeling methods.

2. Assessment of Candidate Solder Systems

The first task of this group was to recommend a standard lead-free solder alternative. Industry could benefit significantly by focusing on one alloy for replacing the common Sn–Pb solder:

- Electronic Manufacturing Service (EMS) companies, in particular, would not have to have multiple manufacturing lines to handle a variety of solder alloys.
- By concentrating available resources on one solution, data could be gathered more quickly, speeding up introduction of lead-free soldering to manufacturing.
- Component and/or board lead finishes would only have to be compatible with one new alloy.

By cooperatively developing a single alloy solution, it was recognized that it would be possible to implement a replacement sooner, avoid multiple manufacturing processes, and enhance basic understanding of the material while assuring its reliability.

3. Selection Criteria

The Alloy Group, led by Jasbir Bath and Carol Handwerker, began with a literature review, in order to identify and use as much existing data as possible for the alloy choice. A general call went out to the electronic packaging community for data, published and unpublished, on the properties, manufacturability, and reliability of Pb-free solder alloys. Members of the task group also sought opinions from experts in the field, such as NIST in the United States and Soldertec [formerly the International Tin Research Institute (ITRI)] in the United Kingdom, obtained a patent search, and sought the advice of six North American solder manufacturers. These data were gathered and distributed electronically by NIST and were reviewed and discussed in an open forum at the IPC Works Conference in 1999.

Based on the findings of these initial investigations, the industrial members of the alloy selection group defined the following criteria for alloy selection:

1. If possible, stay with ternary alloys (or less). Quaternary alloys can present control difficulties.
2. The new alloy should be near-eutectic (e.g., no large pasty range during cool-down).
3. The new alloy should be as close as possible to eutectic Pb–Sn in melting point and manufacturability (in order to be able to use existing manufacturing tools where possible).
4. The new alloy should be equal to or better than eutectic Pb–Sn in reliability (when used in electronic assemblies).
5. The new alloy should create minimal cost impact over eutectic Pb–Sn (understanding that the solder cost is a very small part of assembly cost).
6. Avoid using a patented alloy if possible, so industry freedom of action is guaranteed.
7. Using the best knowledge available, do not choose an alloy that will have environmental issues in the future.

4. Candidate Alloys

A key report used by the iNEMI selection group in identifying potential alloy replacements came from a three-year study by the National Center for Manufacturing Sciences (NCMS) which evaluated over 79 solder alloys. Based on this study, input from the alloy selection group, and other information including oral and written reports from the EU DTI and IDEALS consortia, a short list of solders was chosen as follows:

1. Sn–58Bi eutectic alloy
2. Sn–Zn–Bi system

3. Sn–Ag–Bi system
4. Sn–Ag–Cu system
5. Sn–3.5Ag eutectic alloy
6. Sn–0.7Cu eutectic alloy

These solders were evaluated by the alloy selection group to determine the relative advantages and disadvantages of each, and details are presented in the Alloy Selection chapter.

In November 1999, the iNEMI Task Force announced its recommendations for lead-free solder. For reflow applications (which represent at least 70% of all board assembly production), iNEMI recommended the use of Sn–3.9Ag–0.6Cu, a predominantly tin-rich alloy with 3.9% silver and 0.6% copper (percentages are by weight). For wave solder production (which requires larger amounts of solder), the group recommended Sn–0.7Cu, a less expensive tin–copper alloy (tin with 0.7% copper), or an alternative standard Sn–3.5Ag (tin with 3.5% silver). The Sn–3.9Ag–0.6Cu ternary alloy could also be used for wave soldering; the other two alloys were recommended because many of the project participants wanted a lower-cost alternative to Sn–3.9Ag–0.6Cu for wave soldering.

Following iNEMI's recommendation of specific lead-free alloys, the Alloy Group, then led by Carol Handwerker, concentrated on developing data needed for modeling alloy thermodynamics, mechanical properties, and solder joint reliability and on assisting the other groups in interpretation of the manufacturing and reliability data being developed.

PROCESS GROUP

The task of the process group was to determine if the chosen Sn–Ag–Cu alloy would be manufacturable on current assembly manufacturing lines. The process development was led by Jasbir Bath at the Solectron facility in Milpitas, CA. To ensure manufacturability, the process was transferred to an assembly facility at Universal Instruments in Binghamton, NY, for the reliability test hardware build.

A tin–lead (Sn–37Pb) no-clean solder paste and a lead-free Sn–3.9Ag–0.6Cu no-clean solder paste were selected for the iNEMI tin–lead and lead-free reliability test board builds based on evaluations on printability, solderability after reflow, and X-ray inspection after reflow. The selected tin–lead and Sn–Ag–Cu pastes were used to successfully assemble components and boards with both tin–lead and lead-free finishes for accelerated thermal cycle (ATC) reliability testing using existing manufacturing tooling. The six types of lead-free and tin–lead components assembled were CSP169, CSP208, PBGA256, CBGA256, TSOP48, and 2512 chip resistor. Differences in the visual appearance between the tin–lead and lead-free solder paste assembled boards were noted. From a reliability perspective, these visual differences were not found to be significant in subsequent ATC testing.

COMPONENT GROUP

The Component group, led by Richard Parker of Delphi, worked on identifying and recommending the best materials for the supplier industry to use, in delivering compatible components and printed wiring boards (PWBs) that met the Pb-free requirements. Recommendations were made for PWBs and terminal finishes for the reliability testing.

Surface Finishes for IC Lead Frames

A number of component lead finishes appeared to be satisfactory [i.e., nickel–palladium–gold (Ni–Pd–Au), Ni–Pd, tin–bismuth (Sn–Bi)], but the predominant solution being offered by industry was the pure tin (Sn) finish. However, the use of high-percentage Sn alloys or pure Sn coatings have renewed concerns regarding Sn whiskers, which is discussed in more detail in Chapter 7 of this book.

Moisture Sensitivity for Plastic Packages

Molded plastic packaged IC components were believed to be the most sensitive components, as a family, to the increased temperature exposure that would result from the industry transition to lead-free solders. The main area of concern was the moisture sensitivity level (MSL) of these packages. A desire to limit peak reflow temperatures (PRTs) led to several studies to help understand the thermal mass effects on real circuit boards. This resulted in new temperature testing parameters being proposed for the IPC/JEDEC MSL standard specification (J-STD-020).

RELIABILITY GROUP

The Reliability Group, led by John Sohn of Lucent, was charged with evaluating Pb-free solder utilizing appropriate Pb-free component and board finishes against a standard Sn–Pb control. The group devised the experimental matrix, lined up individuals and companies to do the actual testing, and analyzed the results. A thorough experimental matrix was devised covering various components, solder–component combinations (including current Pb-containing components assembled using Pb-free paste), and printed wiring board materials and finishes. The reliability tests chosen were:

- Thermal cycling (0°C to 100°C and −40°C to 125°C)
- Three-point bend testing of assembled BGAs
- Electrochemical migration testing of Sn–Ag–Cu soldered no-clean pastes

NIST provided a thorough failure analysis (metallurgical cross-section and analysis) of all test cells to understand the root cause of thermal cycling and three-point bend test failures. In addition, red-dye-penetrant testing was carried out on ball-grid-array (BGA) parts. Several companies provided statistical analysis of the resulting data, which was essential to developing and determining the project conclusions.

The reliability of the Pb-free solder joints was found to be equivalent or superior to the reliability of the Pb-containing joints made using current material sets and assessed by thermal cycling and three-point bend testing. No electrochemical migration issues were identified for the Sn–3.9Ag–0.6Cu no-clean solder paste reflowed alloy.

FOLLOW-ON PROJECTS/WORK

The electronics assembly industry has accumulated some 50 years of experience in processing Sn–Pb solder. A single project could not begin to address all the issues associated with such a huge undertaking as Pb-free assembly. A number of follow-on iNEMI projects were initiated, many of which are still ongoing.

Tin Whiskers

The formation and growth of tin whiskers pose potentially significant long-term reliability issues for electronic components with pure tin or high tin content Pb-free finishes. Reducing the risk of tin-whisker-related failures involves a combination of choosing an effective mitigation strategy and conducting tin whisker acceptance testing and process control of the tin plating process. This chapter deals with the first two aspects of this threefold approach. Recommended mitigation strategies and tin whisker test development are discussed in detail. The importance of ongoing process monitoring is mentioned, although the topic of tin-plating process control is beyond the scope of this work.

Lead-Free Reflow and Rework

This chapter provides an overview and assessment of the printability of lead-free solder pastes together with reflow, rework, and inspection of lead-free solder in surface mount technology compared with tin–lead. The effect of the wetting, temperature profile, and solder joint peak temperature of the solder joints is discussed in relation to reliability, visual appearance, and associated assembly issues. Studies determining the temperatures that will likely occur on board and components during lead-free reflow and rework are reviewed. An assessment is made on the need for equipment changes (if any) for lead-free reflow and rework soldering and any adjustments required in inspection equipment/criteria for X-ray and AOI inspection. Acoustic microscopy of lead-free soldered parts is also reviewed.

Case Study: Pb-Free Assembly, Rework, and Reliability Analysis of IPC Class 2 Assemblies

A team of iNEMI companies collaborated for three years to develop Pb-free assembly and rework processes for double-sided, 14-layer, printed circuit boards (PCB) in two thicknesses (0.093 in. and 0.135 in.) with electrolytic Ni–Au and immersion Ag board surface finishes. This extended the work carried out by the first iNEMI Pb-free development team (1999–2002) to large, thicker boards. All SMT assembly, PTH wave assembly, and component rework processes were carried out on production equipment. Various test vehicles including the reliability test board were used in a multiple-phase development project to develop Pb-free assembly and rework parameters and temperature profiles prior to a 100-board process technology verification build. Following the double-sided SMT and wave assembly build, half of the printed circuits assemblies were passed through a series of representative component rework protocols. Each build group was then subjected to a series of mechanical and thermal reliability stress tests followed by failure analysis. A special reliability test board was designed utilizing a high-temperature laminate designed for Pb-free soldering. Approximately 30% of the assemblies were Sn–Pb control samples. The rework development process used the NEMI Sn–3.9Ag–0.6Cu solder. The rework of large, thick PCBs with Pb-free solder poses a significant challenge to the industry. The lessons learned and recommendations for future work are discussed.

Implementing RoHS and WEEE-Compliant Products

There is much more to the conversion to Pb-free electronics than the resolution of technology gaps. In today's distributed manufacturing environment, cooperation across the value chain is a necessity—from product design through to end-of-life disposition—in order to achieve RoHS compliance. While the focus of this chapter is on the deployment issues associated with a particular set of regulations, the concepts described here would generally apply to any major regulation-driven technology change that is broadly adopted by industry, and thus these observations will remain relevant for future applications.

This work has resulted in a solid first step for the successful introduction of lead-free soldering by the North America electronics industry and has been referred to on numerous occasions globally as a model/benchmark for successful company collaboration and important lead-free development work. Although the basics are complete, the engineering work to improve reliability, cost, and manufacturing yield is ongoing with ever more follow-on projects adding to the platform of knowledge. An engineer's work is never done.

We gratefully acknowledge the efforts of Iwona Turlik and Ron Gedney, the iNEMI program manager for Pb-free projects, in making this project a success: Iwona Turlik for having the vision and drive to initiate the project and Ron Gedney for leading us to completion of the project and this book. We dedicate this book to them.

CHAPTER 1

Alloy Selection

CAROL A. HANDWERKER, URSULA KATTNER, KILWON MOON, JASBIR BATH, EDWIN BRADLEY, and POLINA SNUGOVSKY

1.1. INTRODUCTION

Between 1991 and 2003, national and international research projects in the United States, the European Union, and Japan were formed to examine lead (Pb)-free alternatives to tin–lead eutectic solder and to understand the implications of such a change before it became required by law, by tax, or by market pressure [1–18]. The UK Department of Trade and Industry (DTI) developed a comprehensive report on the major results of these lead-free solder research projects [18]. Parallel to these multi-participant studies were similar investigations by individual companies and research organizations into Pb-free alternatives to Sn–Pb eutectic and near-eutectic solders. All of these studies determined that there was no "drop-in" replacement for Sn–Pb eutectic solder.

In 1999, with the proposed ban on lead in the European Union combined with the substantial Pb-free solder development efforts by Japanese manufacturers, the International Electronics Manufacturing Initiative (iNEMI) formed its Lead-Free Task Force with the goal of helping the North American electronics industry develop the capability to produce lead-free products by 2001. The first task of this group was to recommend a "standardized" lead-free solder alternative [9–11]. In approaching the overall issue of lead-free solders, the iNEMI team members realized that they could make a major contribution to the industry if they could recommend a single solder solution to replace the tin–lead eutectic paste used for high-volume surface-mount component assembly. This is of particular importance to the electronic manufacturing service (EMS) providers, for minimizing their investment in equipment and process optimization required for solders with different assembly behavior, and for components with different moisture sensitivity levels. This became the overriding goal of the project.

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In making an alloy selection, the iNEMI team carried out a thorough literature review and patent review and gathered all available data that 30 member companies, including five solder manufacturers, could bring to the table. The NCMS and IDEALS Project Reports were particularly helpful in narrowing the decision [1–8, 13, 14]. The NCMS work, for example, demonstrated that a solder with a large "pasty" range leads to stresses in through-hole joints during the cool-down phase and, in many cases, to separation of the solder fillet along its interface with the printed wiring board (PWB) copper land (also known as "fillet lifting") or to pad delamination [1, 2]. Solder manufacturers generally recommended selection of an alloy with no more than three elements for ease of solder manufacturing. Analysis of the available data led to the following criteria for selecting a new "standard" solder alloy for board assembly:

1. Melting point should be as close to Sn–Pb eutectic as possible.
2. Alloy must be eutectic or very close to eutectic.
3. There should be no more than three elements (ternary composition).
4. Avoid using existing patents, if possible (for ease of implementation).
5. Potential for reliability should be equal to or better than Sn–Pb eutectic.

Application of these criteria led directly to the iNEMI choice of the Sn–Ag–Cu system, and the specific alloy Sn–3.9Ag–0.6Cu ($\pm 0.2\%$) in the Sn–Ag–Cu (SAC) family of alloys as the most promising solution.

In this chapter, the key results and analyses leading to the choice of SAC alloys by iNEMI are discussed in detail. These include data on phase transformations in solders (including melting behavior, solidification pathways, and interface reactions with substrate and lead materials), on wetting behavior, and on mechanical properties (including thermomechanical fatigue). The materials science issues are illustrated using data from a wide range of sources, including the NCMS Lead-Free Solder Projects (US) [1–4, 13, 14], the IDEALS Lead-Free Solder Project (UK) [3, 6–9], the iNEMI Pb-Free Assembly Project (US) [10–12], various Japanese consortia [15–17], the National Institute of Standards and Technology (NIST) [19–23], and the open literature. Based on the choice of a single SAC alloy, the iNEMI Lead-Free Project could begin to address lead-free assembly, including manufacturing yield, process windows for complex boards, component survivability, and assembly reliability, as described in other chapters in this book.

In the last five years since the iNEMI alloy selection was performed, a worldwide consensus has developed that the general-purpose lead-free alloy should be from the Sn–Ag–Cu family. In Europe, Soldertec, the lead-free solder research arm of Tin Technology, selected the range of compositions Sn–(3.4–4.1)Ag–(0.5–0.9)Cu [9, 18], while the IDEALS consortium recommended Sn–3.8Ag–0.7Cu [5–8]. (Note that all compositions are expressed as Sn–vX–yZ, where the X and Z are alloying elements in Sn, with the composition being v mass fraction $\cdot$ 100 of element X, y mass fraction $\cdot$ 100 of element Z, and remainder being Sn; mass fraction $\cdot$ 100 is also abbreviated as wt%.) While numerous lead-free alloys, including

Sn–Ag–Bi–Cu, Sn–8Zn–3Bi, and Sn–58Bi, were investigated by large Japanese OEMs, the Japanese industry has moved over time toward Sn–Ag–Cu alloys. JEITA (Japan Electronics and Information Technology Industries Association) has recommended the Sn–3.0Ag–0.5Cu alloy, partly due also to concerns over patent issues [15–17]. However, widespread cross-licensing of nearly all the tin–silver–copper family of solder alloys by the solder manufacturers means that alloy selection within the SAC system should be driven primarily by overall performance in product applications and other issues, such as cost, rather than by patent issues. Furthermore, the differences among this range of SAC alloys in terms of manufacturing and reliability are generally believed to be small, based on available melting and reliability data. Additional results and analyses on SAC alloys that have emerged since the iNEMI selection of Sn–3.9Ag–0.6Cu as the standard alloy are also discussed and the differences between SAC alloys are examined.

1.2. LEAD-FREE ALLOYS CONSIDERED BY iNEMI IN 1999 AS REPLACEMENTS FOR TIN–LEAD EUTECTIC SOLDER

Based on input from the alloy selection group, the following short list of Pb-free solders considered as replacements for Sn–Pb eutectic was developed:

1. Sn–58Bi eutectic alloy
2. Sn–Zn–Bi system
3. Sn–Ag–Bi system
4. Sn–Ag–Cu system
5. Sn–3.5Ag eutectic alloy
6. Sn–0.7Cu eutectic alloy

Note that all the Pb-free solders considered were tin-rich solders, with the exception of Sn–58Bi eutectic. These solders were compared by the iNEMI alloy selection group to determine the relative advantages and disadvantages of each. A summary of the group's evaluation is presented below. (For additional discussion of the properties of lead-free alloys, see Refs. 1–9.)

1.2.1. Sn–58Bi Eutectic Alloy

The Sn–58Bi eutectic alloy has a melting temperature of 138°C (eutectic temperature) and has been shown to be resistant to fillet lifting and to outperform eutectic Pb–Sn in the NCMS thermal cycling tests for a range of components [1–4]. Its significantly lower melting temperature than eutectic Sn–Pb will preclude its use in applications where the upper use temperature is close to 138°C. For example, the majority of automotive assemblers are looking toward a higher melting point alloy than eutectic Sn–Pb for under-the-hood applications at 150–175°C. During the transition to lead-free solders, there will be components containing lead from the tin–lead surface finishes for some period of time. The Sn–58Bi eutectic solder will react with the Pb to form some fraction of the Sn–Bi–Pb ternary eutectic phases with a eutectic temperature of 96°C. The possibility of a very large "pasty" range and potentially poor solder joints is considered a manufacturing process issue and potential reliability exposure. A detailed analysis of the melting behavior of Sn–Bi–Pb alloys was performed by NIST as part of this project, as described below [19].

An analysis by NCMS determined that there are also issues of cost and continued availability of Bi and other alloying elements for use in such high concentrations. There are approximately 60 million kilograms of tin–lead solder used in electronics per year. Up to 50 million kilograms are used in wave soldering with up to 10 million kilograms in solder paste applications per year. Considering current production and spare capacity, sufficient bismuth to supply the whole electronics solder market would only support a solder containing up to 6 wt% Bi. When additional sources of Bi are considered, the NCMS Lead-Free Project estimated that the Bi composition of a solder completely replacing eutectic Sn–Pb could be as high as 20 wt% Bi, still lower than Sn–58Bi. The eutectic alloy Sn–58Bi may end up being used for some consumer products with low use temperatures and for temperature-sensitive components and substrates [24]. The consumption and availability issue, and its low-melting eutectic formation with lead (Pb) will limit its widespread adoption, particularly until Pb is eliminated from board and component surface finishes.

1.2.2. Sn–Zn–Bi System

A promising alloy in this system (Sn–8Zn–3Bi) has a melting range of 189–199°C, thus having a slightly higher melting temperature than Sn–37Pb (183°C). [The term "melting range" means that the alloy begins to melt at 189°C (solidus temperature) and finishes melting at 199°C (liquidus temperature). The term "melting range" is synonymous with "pasty range."] This temperature range has an obvious advantage over other high-Sn alloys with liquidus temperatures as high as 227°C. However, zinc-containing alloys oxidize easily, showing severe drossing in wave solder pots, are prone to corrosion and have a paste shelf life that is measured in terms of days or weeks compared to months for eutectic Sn–Pb. The bismuth is added to improve the wettability, reduce the liquidus temperature, and reduce corrosion compared with binary Sn–Zn alloys. The presence of bismuth may also result in the formation of low-melting-point eutectic in contact with Sn–Pb-coated components and boards, affecting the reliability of the assembly as in the case of Sn–58Bi. Due to the manufacturing control difficulties, all six of the solder suppliers consulted recommended strongly against adoption of a zinc alloy, as the standard alloy. Given these drawbacks, the suitability of Sn–Zn–Bi as a general replacement for eutectic Sn–Pb is limited.

1.2.3. Sn–Ag–Bi System

The melting range of this alloy family is 210°C to 217°C with bismuth compositions ranging from 3 to 5 wt% and Ag compositions ranging from 2 to 4 wt% [22, 23].

The alloy Sn–3.4Ag–4.8Bi has been shown to outperform eutectic Pb–Sn in thermal cycling tests for all components examined by NCMS [1–4] and by Sandia National Laboratories, which carried out 0–100°C thermal cycling experiments for up to 10,000 cycles on chip capacitors, SOIC gull-wings, and PLCC-J-lead solder joints [25].

In spite of its excellent performance in SMT applications, there are several issues with this alloy. One issue is again the possibility of the formation of the low-melting-point Sn–Pb–Bi eutectic when combined with Sn–Pb-coated components [19]. With low Bi additions, reliability may not be an issue for consumer products: Panasonic has manufactured a consumer product with this type of alloy paste and Pb-containing component finishes and did not detect the presence of lower-melting eutectic in their testing [26]. Alloys of Sn–Ag–Bi have been found to have a severe problem with fillet lifting in through-hole joints with the tendency toward fillet lifting increasing with Bi concentration to a maximum in the range of 5–10% Bi [1–4]. When these alloys are used with tin–lead-coated components and boards, the tendency toward fillet lifting may be increased. All of the other issues noted above for Bi-containing solders also apply to these alloys.

1.2.4. Sn–Ag–Cu System

Alloys in this family with melting ranges near 217–227°C have the most promise as the main replacement for tin–lead solder. The alloys Sn–3.5Ag, Sn–2.6Ag–0.8Cu–0.5Sb, and other high-Sn alloys containing Ag and Cu with small additions of other elements were shown to perform as well as eutectic Pb–Sn for BQFP, PLCC, and 1206 capacitors in thermal cycling tests by NCMS [1–4].

The Sn–3.8Ag–0.7Cu alloy was recommended by the EU IDEALS consortium as the best lead-free alloy for reflow as a result of reliability testing from −20°C to 125°C for up to 3000 cycles and power cycling from 25°C to 110°C for 5000 cycles [5–8]. In these tests, the reliability of Sn–3.8Ag–0.7Cu was equivalent to or better than eutectic Sn–Pb and Sn–Pb–Ag. The lowest eutectic in the system when lead contamination is present is close to the Sn–Pb eutectic. The 7°C higher temperature compared to Sn–Ag–Bi alloys may be a small price to pay to ensure good reliability of through-hole joints. These alloys have an approximately 4°C lower melting temperature than the Sn–3.5Ag eutectic alloy (221°C) with a potential improvement in solderability and reliability.

At the time of the alloy selection, there were three readily available commercial Sn–Ag–Cu solders with “melting” temperatures near 217°C. These are Sn–3.5Ag–0.7Cu, which is available in Japan, and Sn–3.8Ag–0.7Cu and Sn–4Ag–0.5Cu, which are available in North America and Europe. All these have similar wetting characteristics, mechanical properties, and melting behavior. The NEMI lead-free group decided on the Sn–3.9Ag–0.6Cu as the alloy to recommend to the industry, a composition midway between Sn–3.8Ag–0.7Cu and Sn–4Ag–0.5Cu. The ANSI J-STD-006 specifies that an alloying element less than 5 wt% can vary in composition by ±0.2 wt% so the Sn–3.9Ag–0.6Cu alloy would cover both these compositions and ±0.2 wt% is the usual tolerance that a solder manufacturer gives when manufacturing a particular solder alloy.

NIST [21] used a variety of Sn–Ag–Cu alloy compositions to compare to data from Marquette University [27] and Northwestern University [28] to determine that the ternary eutectic had a melting temperature of 216°C to 217°C with a composition of approximately Sn–3.6Ag–0.9Cu. Alloys with compositions within the range Sn–(3.5–4)Ag–(0.5–1)Cu are close enough to the eutectic to have a liquidus temperature between 217°C and 220°C with similar microstructures and mechanical properties, as described below. The literature indicates that the solderability of Sn–Ag–Cu alloys is adequate. The melting behavior of Sn–Ag–Cu alloys is described in greater detail below.

The patented alloy Sn–2.6Ag–0.8Cu–0.5Sb (CASTIN^{TM}) is in the same Sn–Ag–Cu family with similar melting temperature range, solderability, and reliability as the alloys discussed above [1]. Additions of $<1\%$ antimony do not degrade solderability and only slightly change the melting point. Antimony is considered to be toxic by some companies, but at this low concentration it is not clear whether it would be a major problem.

iNEMI's patent review found many patents in the Sn–Ag–Cu system (Table 1.1) but with considerable overlap. The alloy Sn–4Ag–0.5Cu was reported in a German thesis and a corresponding paper [29] 50 years ago as the ternary peritectic/eutectic, and some solder companies were producing this alloy without any licensing. In the United States, both Sn–3.8Ag–0.7Cu and Sn–4Ag–0.5Cu formulations are available from the main solder manufacturers. Since the selection of the Sn–3.9Ag–0.6Cu alloy, another alloy Sn–3.0Ag–0.5Cu alloy has been used widely in Japan. It appears to have similar characteristics to the other commercially available Pb–free Sn–Ag–Cu alloys.

1.2.5. Sn–3.5Ag Eutectic Alloy

Sn–3.5Ag has been used in the industry for many years in module assembly. Ford (Visteon Automotive Systems) has reported that they have used Sn–3.5Ag solder successfully in production for wave soldering since 1989 [30, 31]. There are no patent issues regarding its use, and it is already available from most of the solder manufacturers in bar, wire, and paste form. The reliability of the alloy is similar to Sn–37Pb [1–4, 30, 31], and the primary difference between the Sn–3.5Ag and Sn–Ag–Cu alloys is the addition of the copper, which lowers the melting temperature by 4°C [16].

1.2.6. Sn–0.7Cu Eutectic Alloy

The eutectic alloy Sn–0.7Cu with a melting temperature of 227°C was another alloy evaluated for reflow and wave soldering. Its melting temperature, which is 10°C higher than the eutectic temperature of Sn–Ag–Cu, makes it undesirable for reflow applications. In wave soldering applications, the temperatures that the boards and components reach are much lower than in reflow soldering. There is a