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在世界范围内，电子组装正转向无铅焊料，但对于可加工性、可靠性和可利用合金的选择仍存在担心。美国国家电子制造动议（NEMI）于1999年开始无铅组装项目，以解决关于该行业向无铅转变的问题。今天，可直接利用在无铅焊料焊接的加工和可靠性方面所获得的成果。NEMI最初着手工作以来，已推出几种商业性无铅合金。这些合金的成分同NEMI合金几乎完全相同。本文探讨合金系统之间的关系，并展示其相似性。

NEMI's Lead-Free Alloy

Alan Rae and Carol Handwerker

Still applicable to today's commercially available alloys.

Electronics assembly is moving to lead-free solder worldwide, but concerns still exist about processability, reliability and the choice of available alloys. The National Electronics Manufacturing Initiative (NEMI, Herndon, VA) launched the Lead-Free Assembly Project in 1999 to address the many issues surrounding industry transition to lead-free interconnects, and the results obtained on processing and reliability of lead-free solder joints are directly applicable today.

NEMI's work focused on enhancing basic understanding of the material and assuring its reliability to assist industry with timely implementation of lead-free assemblies. Some accomplishments include:

- recommendation of an industry standard lead-free alloy: Sn3.9Ag0.6Cu(±0.2%) for reflow and Sn0.7Cu for wave solder
- definition of modeling and data needs for lead-free solders and compilation of a physical and mechanical properties database, which is available to industry at www.metallurgy.nist.gov/solder/
- extensive reliability testing.

The NEMI Phase 1 work described above was the foundation of the organization's lead-free initiatives. It established a model system in the tin-silver-copper (Sn-Ag-Cu or SAC) phase diagram and extensively characterized the recommended alloys, establishing the processability and reliability of lead-free solder joints.

Several commercial lead-free alloys have been introduced since NEMI first began its work. The compositions of these alloys are virtually identical to the NEMI alloy, considering the joint composition after it is modified by dissolution of copper or silver from boards or surface finishes. This article examines the relationship between alloy systems and demonstrates their similarity.

Implementation Progress

Industrial Solder Alloys

Many industrial solder alloys have been lead free for some time—plumbing alloys and automotive alloys, in particular. They are optimized for their particular application, such as tin with 5% antimony for low solubility of solder in drinking water and a large working range or tin with 3% copper for low cost and workability.

Legislation

To date, the only legislation that actively bans lead in electronic solders is the European Union's Reduction of Hazardous Substances (RoHS) Directive, which will become law throughout Europe on July 1, 2006. Currently, aerospace/military and communications applications are exempt from this directive, which primarily covers consumer electronics, handheld devices and personal computers. Automotive applications are also exempt because they are covered under the End-of-Life Vehicles (ELV) Directive, which allows automotive electronics to use leaded solder. However, automotive may be included under the RoHS umbrella in the near future.

In other regions, indications are that the government of China will pass regulations similar to RoHS.

Potential Lead-Free Alloy Systems

Removing lead from interconnects requires use of either a different metal or a different system. The question asked repeatedly is: Why can't we just make a drop-in substitute for tin-lead alloys with the right properties? This drop-in would be simple, except

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that we want the joints to perform as well as tin-lead joints at the same price and with lower toxicity.

The various metals considered are discussed below. Alternative systems are conductive adhesives and mechanical attachment. Although extensive work has been done to improve isotropic and anisotropic adhesives, they still do not compete on a performance or economic basis for attaching components to rigid boards.

Metals Properties

If we sort the available metals through a screen of melting point, toxicology, cost, availability and chemical resistance, our choices narrow rapidly for a mainstream alloy. Tin, copper and silver are the frontrunners, followed closely by bismuth, antimony, indium, zinc and aluminum. Bismuth and antimony are partially produced as byproducts of lead and have, therefore, come under scrutiny because of future supply concerns as lead is eliminated from electronics. Ironically, lead production is rising as we need more lead-acid batteries, and electronic consumption accounts for less than 1% of lead use.

Combinations of bismuth, lead and tin produce a 96°C low-melting alloy that can promote fillet lifting and encourage joint failure on thermal cycling. Antimony, although widely used as a 5% alloy in tin as plumbers' solder, has been suspect in Europe on health grounds for many years. Bismuth, produced at 3,000 tons per year, and indium, at 500 tons per year, are not abundant enough to replace the 10,000-plus tons per year of lead used in conventional electronic solders. Zinc and aluminum oxidize rapidly in processing and use. Silver is also a byproduct of lead manufacture and has significant toxicity. It is relatively abundant and is primarily used currently in photography.

Economically, the news is all bad. Copper and zinc are the only metals that remotely approach the low price of lead. However, tin is 10X the price of lead, and copper, silver and indium are 300 to 400X the cost of lead.

The lead-free alloys are all 95%+ tin, which brings up the question: Does enough tin capacity exist to cope? New tin production totals around 70,000 tons per year, whereas 240,000 tons of tin are recycled, with the main use still tin cans. So, tin supply is not an immediate problem.

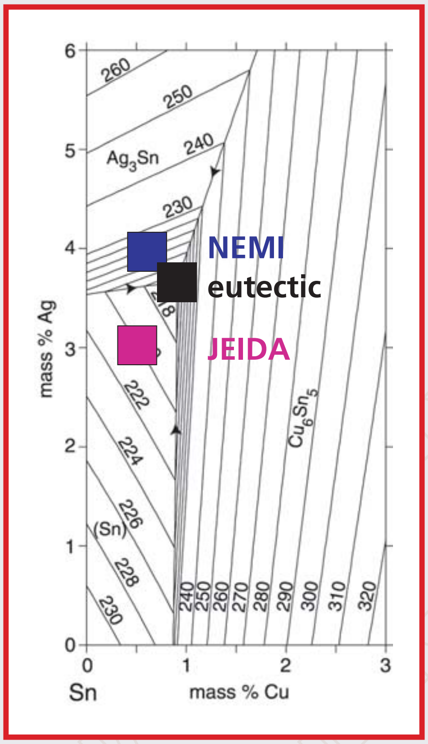

FIGURE 1: Experimental and thermodynamic assessment of tin-silver-copper (Sn-Ag-Cu) solder alloys by NIST.[1] The axes represent the copper and silver additions to tin. The point at 0 % Ag and 0% Cu is pure Sn. The lines on the plot are the lowest temperatures in (°C) where Sn-Ag-Cu alloys of the compositions given by specific points on the graph have no remaining solid.

Process Tolerance, Reliability

If we are to produce a new solder alloy, its melting point should be as close as possible to tin-lead eutectic, have a melting range that is neither too small (promoting tombstoning of small components) nor too large (hindering self-alignment, promoting bridging in wave solder and causing fillet lifting). It should fit with the existing infrastructure and materials and be tolerant of small amounts of contamination from board and components. That means a process temperature less than the limiting temperature of many packaging and board materials (260°C) and a tolerance to copper, silver, gold, nickel and palladium finishes. Additionally, a tolerance to bismuth is needed in products in Japan where tin-bismuth finishes are used. Finally, reliability should be equivalent to or better than tin-lead eutectic.

Tin-Silver-Copper: An Acceptable Compromise

No single alloy meets all of these requirements. Developing a lead-free alloy that melts at 183°C is relatively easy, but, when we add the requirement that the melting range be small, most of these alloys are eliminated. The ones remaining contain indium or zinc, which have their own problems: cost and availability for the former and oxidation during processing and use for the latter. Given that no drop-in replacement exists, alloys of tin, silver and copper have emerged as an acceptable compromise.

The Tin-Silver-Copper Choice

Alloy Melting, Solidification Criteria

The eutectic temperature in the tin-silver-copper system is 217°C, higher than eutectic tin-lead by 34°C. The reasons for choosing tin-silver-copper alloys in spite of their higher melting point can be seen by looking at the phase diagram of the tin-silver-copper system (Figure 1). A phase diagram is a three-dimensional (3-D) graph of the equilibrium melting, solidification and precipitation behavior of alloys as functions of their composition and temperature.

The eutectic composition is indicated by the black square in Figure 1. This composition of Sn3.5(±0.2)Ag0.9(±0.2)Cu is the only one in the Sn-Ag-Cu system that has a zero melting range at equilibrium. The numbers in the parentheses in the formula above indicate the laboratory measurement uncertainty in the eutectic composition.

When we consider the typical tolerance ranges of alloy compositions in solder pastes (±0.2), the melting range for the eutectic composition Sn3.5Ag0.9Cu becomes 13°C. Likewise, when the typical tolerance of (±0.2) in alloy composition is included, the NEMI alloy Sn3.9Ag0.6Cu, shown by the blue square in Figure 1, has a melting range of 12°C. The typical Japanese tin-silver-copper alloy Sn3.0 Ag0.5Cu, shown by the purple square, has

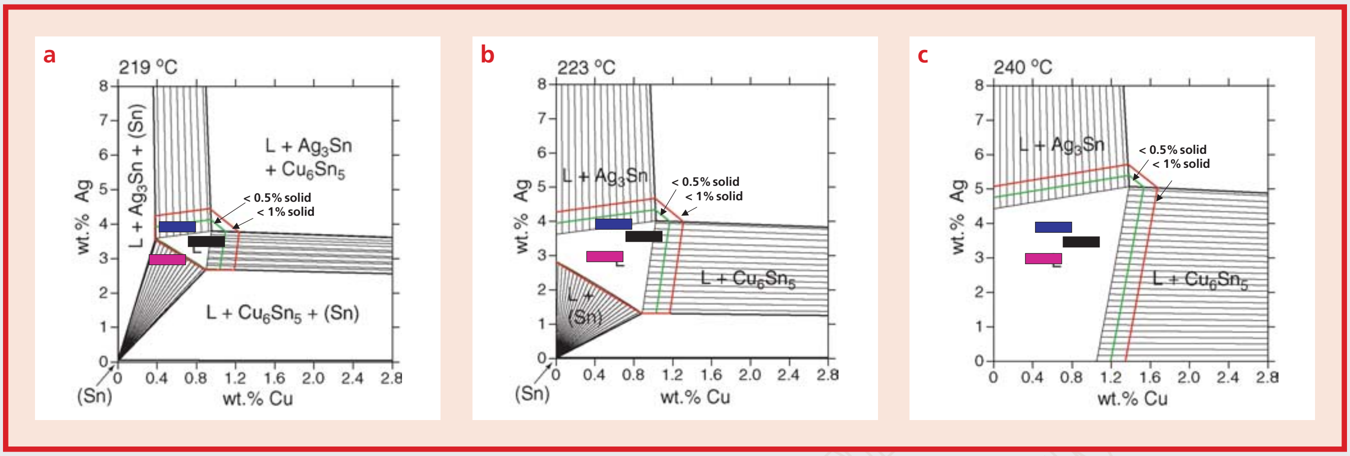

FIGURE 2a-c: The Sn-Ag-Cu phase diagram shown at specific temperatures: (a) 219°C, (b) 223°C and (c) 240°C. (Note that the scales on the two axes have been changed from Figure 1.) The rectangles correspond to the NEMI (blue), eutectic (black) and JEIDA (purple) alloy ranges. The region bounded by the green line contains less than 0.5% solid; the region bounded by the red line corresponds to less than 1% solid.

a melting range of 5°C. In spite of these seeming differences, in practice these alloys all melt in a remarkably similar way, making a wide range of alloy compositions acceptable in terms of their melting behavior.

Figure 2a-c shows how much solid remains as the temperature increases from 219°C to 223°C to 240°C. In Figure 2a the region marked "L" and bounded by the black triangle is the range of compositions that are completely liquid at 219°C. The regions outlined in green and red are compositions with less than 0.5% and 1% solid, respectively, at temperatures higher than 219°C. The values of 0.5% and 1% were chosen since the presence of less than 1% solid is expected to have no effect on the reflow behavior of solder pastes. The remaining solid phase particles at this fraction are significantly smaller than the solder alloy powder particles from which they formed and will have a negligible effect on melting and coalescence of the alloy powders as they melt.

As you can see from this plot, both the NEMI and the eutectic alloys have less than 1% solid remaining at 219°C. Beyond these two alloys, a wide range of alloys meets this criterion of having less than 1% solid remaining at 219°C. At 223°C, the range of compositions broadens further, with all three alloys having less than 0.5% solid remaining. At 240°C, the range of compositions with 0%, less than 0.5% and less than 1% solid remaining are extremely broad. For practical reflow purposes, the number of alloys with a melting range of 6°C is large, as indicated in Figure 2b, and includes all three alloys indicated. Effective liquidus temperatures measured will, therefore, be 217°C for a wide range of compositions.

In terms of solidification as the assemblies are cooled, all of these alloys also show similar behavior. As the joint cools, an intermetallic forms in the solder joint, both at the interfaces with the board and component and in the solder itself. The amount of intermetallic will be determined by the starting composition of the alloy and how much copper and other metals from the board and component leads has dissolved into the molten solder. Tin-silver-copper solder alloys actually cool in the molten state to about 190°C because solid tin has difficulty forming. At about 190°C, all of the alloys quickly solidify to 100% solid.

Based on these analyses, the tin-silver-copper system is quite forgiving in terms of its insensitivity of melting and solidification behavior to composition over a wide composition range.

Practical Processing: Reflow and Wave

Based on these analyses, the tin-silver-copper system is quite forgiving in terms of its insensitivity of melting and solidification behavior to composition over a wide composition range. Therefore, a minimal effect of solder composition on assembly processing should occur for compositions within this range.

The same holds true for wave soldering. The temperatures for wave soldering are much higher than for reflow soldering and are determined by many factors, including the activity of the flux and the board design. The solder alloy composition will affect how much copper and other metals will dissolve in the bath, so one might conclude that the base solder should contain high amounts of copper. A tradeoff in copper concentration actually occurs: Low initial copper concentrations encourage fast dissolution from the boards and the components, while high initial copper concentrations encourage intermetallic formation in colder sections of the bath. This tradeoff has led us to suggest a copper concentration limit in the alloy of 0.5% to 0.6%.

Reliability Demonstrated

The remaining issue is the effect of composition on reliability. The NEMI Phase I reliability testing showed conclusively that the reliability of solder joints made with the NEMI alloy was equal to or better than tin-lead eutectic for a wide range of components. Additional testing on the NEMI alloy by the High Density Packaging User Group (HDPUG) showed the same results.

Motorola has been manufacturing cell phones with the NEMI alloy since 2001 and has reported no issues with solder reliability. Similarly, Japanese manufacturers have been using the Sn3.0Ag0.5Cu alloy and have not reported any issues with solder joint reliability. Based on their melting and solidification behavior, reliability test results and the commercial product reliability, the range of acceptable solder alloy compositions in the Sn-Ag-Cu system is, therefore, wide.

Conclusion

Although the composition of some of the alloys being commercialized varies slightly from the NEMI composition, the NEMI alloy is representative of the acceptable range of lead-free solders. Tin-silver-copper formulations with silver content between 3.0% and 4.1% and copper between 0.5% and 1.0% are virtually indistinguishable in terms of melting point and process features. The NEMI alloy provides a model system for industry that is well characterized, and several NEMI members currently are using the alloy in production. The focus on a single lead-free alloy has helped to accelerate industry convergence on standard solder formulations, manufacturing processes and, ultimately, the timely and cost-effective conversion to lead-free assembly. ■

Reference

1. K-W Moon, et al., *Journal of Electronic Materials* 29 (2000), pp 1122-1136.

Background information and results from NEMI's lead-free initiatives are available on the NEMI Website at www.nemi.org. Ongoing activities include work related to tin whiskers, lead-free assembly and rework and issues related to RoHS transition. Results from the original Lead-Free Assembly Project will be published as a book by IEEE Press/John Wiley & Sons this year. Additional data from NIST on lead-free alloys, including physical and thermodynamic databases, can be found on the NIST Website at www.metallurgy.nist.gov/solder.

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