Supercooled Solder Pastes in Low-Temperature Attach Applications

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ABSTRACT

Metastable solder pastes present an alternative solution to low-temperature soldering, allowing the ability to create full metal interconnects at much lower temperatures than traditional solders of the same alloy compositions. Lower temperature interconnects enable next generation electronics where material, geometry, and performance would degrade at higher processing temperatures, such as in additive printed electronics. This paper presents progress-to-date using supercooled solder pastes of core-shell bismuth-tin (BiSn) particles to accomplish solder interconnects below the melting point of the alloy. Reflow of the supercooled BiSn paste is achieved in an inline reflow oven with a peak temperature of 125°C, which is 40°C lower than what is found in a typical reflow profile of the alloy. Cross-sectional images demonstrate sufficient intermetallic compound growth having taken place at 125°C. Comparisons between supercooled BiSn solder pastes and traditional BiSn pastes are discussed and progress towards process development and application guidelinesare presented.

Key words: supercooling, low-temperature soldering, LTS, BiSn, heat sensitive

INTRODUCTION

Miniaturization and heterogeneous integration in electronics continue to push design and process engineers to maintain high assembly yields of next-generation assemblies, but is also pushing them to find ways to lower energy usage[1]. The unending march of progress puts a strain on the solder reflow process in the metal selection, chemicals allowed, energy used, and temperatures tolerated. Soldering is the tried-and-true package-attach process to create interconnects because of its ease of use and reliability. The soldering material itself, specifically solder reflow paste, has been developed over many decades to make high-quality and long-lasting full metal interconnects, though requiring a high processing temperature when using lead-free solders[2].

The lead-free solder alloy in much of the solder reflow paste is made from tin-silver-copper (SAC), the most used composition of which is Sn-3.0Ag-0.5Cu (SAC305). Typically, a reliable interconnect made from SAC305 is formed during a high-temperature reflow, usually at or above 240°C. The traditional SAC305 solder paste method of forming solder interconnects, with its high-temperature process needs, poses a significant barrier to advancements in electronic design and manufacturing innovations.

A simplified depiction of the effect of high heat in these figures is illustrated by the deflection of the package relative to the printed circuit board (PCB) in Figure 1. The multi-layer, thin packages will distort when heated as a result of the coefficient of thermal expansion (CTE) mismatch among the thin layers, which leads to deflections on the edges[3]. This is called dynamic warpage and it is significant during high temperature reflow. A lower melting lead-free alloy alternative to SAC305 is based on the eutectic composition of bismuth and tin. With reflow temperatures in the range of 165-180°C, and in some cases lower, the alloy has been studied and developed for applications in package-attach to control dynamic warpage.

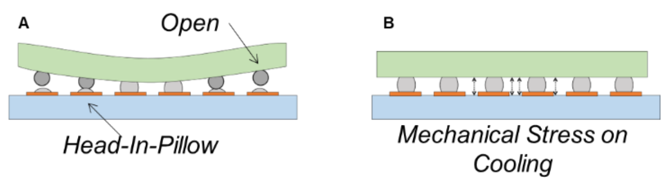


Figure 1. Examples of dynamic warpage and material challenges.

In addition to traditional rigid electronic devices, there is an effort to drastically change the way electronics are made by making flexible and flexible-hybrid electronics using new materials, technologies, and plastic substrates[4]. This will result in higher throughput production, lower costs, and lighter electronics in unique configurations and geometries.

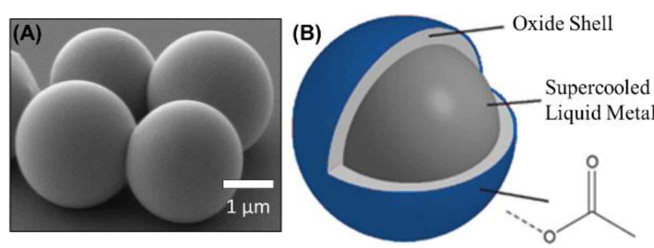


Figure 2. Core-shell microcapsules: (A) scanning electron micrograph of supercooled liquid metal microcapsules; (B) basic schematic of core-shell structure with the layers of the shell labeled.

Heat is quite often a detriment to many materials, such as affordable plastic substrates like polyethylene terephthalate (PET) that curl or degrade under heat, organic electronic materials that lose function or degrade, or heat-sensitive components like batteries that could degrade or create a safety hazard. These new materials have limits on maximum temperature which makes them incompatible with the +240°C temperature of a standard lead-free soldering reflow process or even the temperatures used for BiSn solders. A need exists for a <135°C peak reflow temperature to preserve the board and component properties. This would require change in alloy design and final joint reliability. Current low-processing temperature conductive adhesives have found a role in electronics assembly but do not have the same reliability quality that a true metallurgical solder joint provides; thus, alternatives are being explored[5-7]. Lowering the processing temperature to create an interconnect while still maintaining the same reliabilities would be of interest to both traditional and emerging types of electronics manufacturing.

BACKGROUND

Soldering technology is thousands of years old, and though the process has been greatly refined in modern times, it is still accomplished by heating the metal alloy above its liquidus, which leads to the issues depicted in Figure 1. A new technology has been created to keep a metal alloy particle in a metastable liquid state as it cools to temperatures well below its melting point, a phenomenon known as supercooling. This supercooled liquid metal particle, or microcapsule, is a new material that can create soldered interconnects at dramatically reduced temperatures.

Supercooling is a phenomenon that all materials experience during solidification[8-11]. As a metal in a molten liquid phase cools through the melting point to a temperature below the normal melting point, the atoms enter into a thermodynamically unfavorable, kinetically-trapped state. Here the metals are thermodynamically driven to be solids, but the path to solidification has not presented itself due to the lack of a nucleation catalyst. The presence or spontaneous formation of a nucleation catalyst triggers the crystallization of the continuous whole material.

The supercooling technology presented in this paper consists of microparticles of liquid metal surrounded by a thin oxide shell, similar in concept to a water balloon (see Figure 2)[12,13]. The particles can be made by emulsifying a molten metal ingot in the presence of shell-forming chemistries, which upon cooling, yields microcapsules in a supercooled liquid state (see Figure 2). In brief, the substance of the technology is the prevention of heterogeneous nucleation via protection from the container and a statistical strategy with small (2-11 µm) particle size.

Since the metal core inside the microcapsules is a supercooled liquid, it can flow after removing the shell below the solidus. The resulting metal solid would then need to go above liquidus to fully melt. It has been demonstrated in product development research that these microparticles can be mechanically activated by using pressure to join wires and repair metal films or by chemically dissolving the shell[14,15]. The following work will focus on using a solder flux to trigger the reflow of a BiSn-based alloy. When the thin oxide shell on the outside is dissolved by a solder flux, the liquid metal within the particle flows out and solidifies, which is analogous to a traditional solder paste that uses acidic fluxes and rosin to remove surface oxides and aid in solder wetting.

MATERIALS AND EXPERIMENTAL

Materials

Eutectic BiSn was alloyed with a small amount of indium to make the alloy used for all experiments. This alloy is referred to as a “BiSn-based” alloy. A proprietary emulsification process was used to produce BiSn-based microcapsules of a type 7 size. Particle size distribution was determined by MicroTrac Bluewave laser diffraction. Differential scanning calorimetry (DSC) of the produced microcapsules was performed using a hermetically sealed aluminum pan and scanning up to 170°C and down to -30°C, twice. All DSC data is plotted with exotherm up. A type 7 powder of Field’s Metal (bismuth/indium/tin 32.5, 51, 16.5 wt.%) was used as an additive to the reflow paste to extend the time in which the BiSn-based supercooled liquid metal microcapsules are flowable once the shell is dissolved. The ratio of Field’s Metal to BiSn-based alloy in the solder paste was 1:19. Note that the terms “particle” and “microcapsule” are often used interchangeably.

Experimental

Reconstitution

In this paper, reconstitution refers to the process in which solid microcapsules are heated to temperatures above their liquidus temperatures, thus restoring their supercooled liquid state. The solid BiSn-based microcapsules were combined with Field’s Metal particles (both suspended in a solvent) in a mass ratio of 19:1 and then reconstituted by baking the mixture in a lab oven set at 160°C. A thermocouple was embedded into the bulk of the mixture to monitor the temperature in order to ensure complete reconstitution.

Mixing

The microcapsules and additive particles were mixed into the flux (Indium 5.7LT-1) using a plastic spatula in a plastic weigh boat by gently folding the microcapsules into the flux, followed by a low-shear manual mixing.

The microcapsules and the flux were mixed just before stencil printing. The flux was based upon a flux used in a BiSn type 4 solder paste.

Test Vehicle

The test vehicles were 0805 chip resistor test PCBs with an immersion Ag (*ImAg*) surface finish.

Printing

A paste containing microcapsules was printed manually with a 4-mil stencil on the PCB test vehicle.

The printed microcapsules were examined using Keyence VHX-S750E digital light microscope. The dimensions of the printed patterns were determined using a depth composition technique.

Reflow
The population of the circuit board was performed manually. The populated boards were reflowed in a BTU100N oven in a N_2 atmosphere with a peak reflow temperature of 125°C.

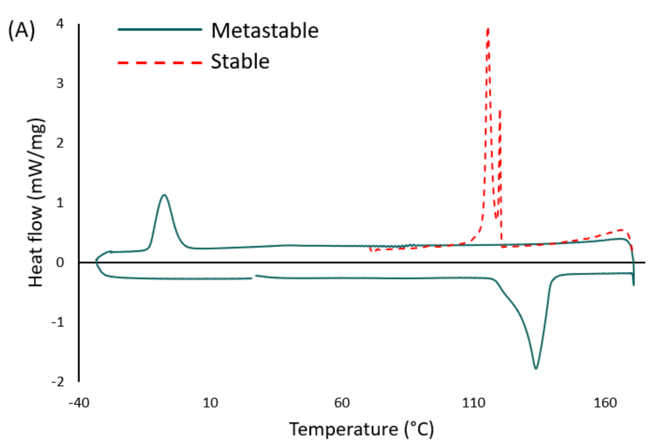
After electrical testing, the assemblies were embedded in a cold-mount epoxy resin. The embedding epoxy was cured overnight at room temperature. The solder joint quality was studied by cross-sectioning, polishing, and SEM-EDS method. SEM analysis was done on a Thermo-Fisher Axia-Chemi scanning electron microscope.

RESULTS AND DISCUSSION

BiSn Supercooling

The supercooling amount is the difference between the metal's normal melting point and the temperature at which the metal freezes (see Figure 3). The emulsion-based technology used to make the microcapsules utilizes a carrier fluid, a shell-creating chemical, and a shearing system to section the metal into droplets and then coat the droplets in the shell. The shell created, which is part-oxide and part-organic, utilizes this metal oxide with an organic coating bound to it. The shell protects the core metal and deepens and stabilizes the supercooled liquid state. The production process used for this paper involves heating a BiSn ingot in a heat-stable carrier fluid above the 135°C melting point of the alloy in the presence of a shell-forming compound, and then applying a high shear force to produce fine droplets of metal with an oxide/organic shell. The conditions were empirically determined to create a type 7 (2-11 µm diameter) powder with the supercooling from 135°C to -8°C (see Figure 3).

A metric used to compare supercooling across metals with different melting points is a factor called "percent supercooling". It is defined as the difference in the melting point and the new freezing point divided by the normal melting point in Kelvin. A percent supercooling has previously been achieved in a low-temperature BiSn-based alloy of 36%. For the BiSn-based microcapsules in this paper, the degree of supercooling was 35%.



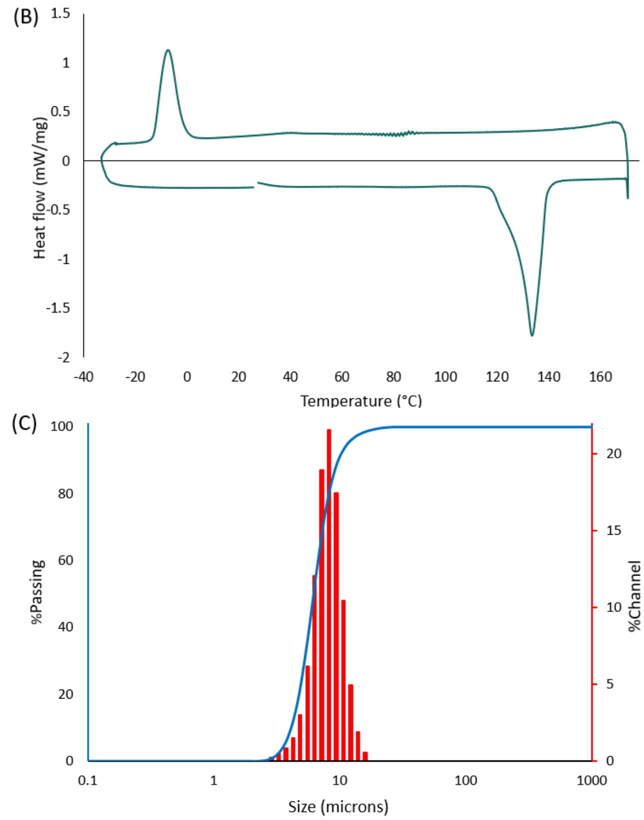


Figure 3. Analysis of BiSn-based microcapsules: (A) representation of DSC of typical solidification of metal ingot in dashed red line and deep supercooling before solidification in greenish-blue solid line; (B) the heat and then cooling DSC analysis of only the supercooled particles of BiSn-based microcapsules that supercool to -8°C; (C) particle size distribution of as produced microcapsules of type 7 size.

The supercooling effect deepened and stabilized by the multicomponent shell is a reversible effect. Bringing the microcapsules below the new freezing point of the alloy crystallizes the alloy within the shell. That crystalized microcapsule can now be heated above the liquidus temperature within the shell (see Figure 3). As long as the shell is intact, the liquid core can be brought down to ambient temperatures and render a collection of supercooled liquid metal microcapsules, a process this paper refers to as reconstitution. The phase yield on the supercooled liquid amount at 20°C was nearly quantitative with ~98.1% of the microcapsules being liquid at room temperature after reconstitution (See Figure 4). It is worth noting that following the reconstitution process, the solidification peak shifted upwards by several degrees. This is linked to a potential degradation of the shell as it was exposed to high heat during reconstitution. The increased diffusivity at elevated temperatures would induce excessive oxide growth, providing unwanted heterogeneous nucleation sites, thus decreasing the degree of undercooling. For our application, since the solidification does not occur until the temperature is well below room temperature even after reconstitution, the degree of degradation of the undercooling during the reconstitution process is of little impact to the yield of the supercooled liquid, as it is abundantly evident in Figure 4B. It is microcapsules from this process that are used for the reflow of solder paste.

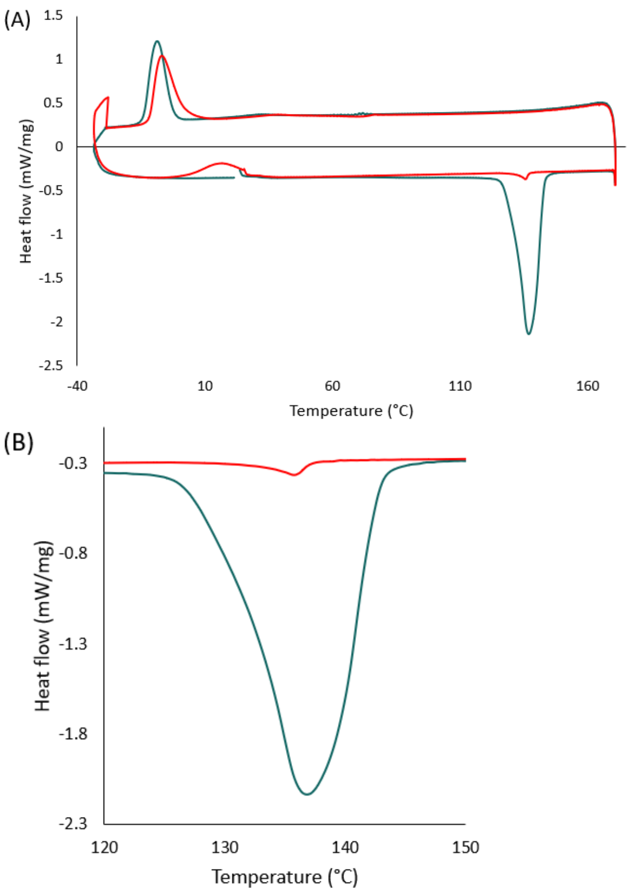


Figure 4. (A) DSC plot showing the heat-cool-heat cycle of solid BiSn microcapsules (greenish-blue) and reconstituted microcapsules (red); (B) DSC plot zoomed on the melting peak for the solid and reconstituted BiSn microcapsules. The area under the greenish-blue curve where all the microcapsules have been frozen was used as the 100% solid and the area under the red curve was used to determine the percent of solid particles left in the powder after reconstitution.

Printing

The type 7 supercooled liquid metal microcapsules were mixed into the flux manually. A small amount (4 wt.%) of Field's Metal particles were added to the BiSn-based microcapsules. The Fields Metal is the ternary eutectic of Bi-In-Sn and has a melting point of 60°C. This small amount of Field's Metal added to the paste will melt well before the activation of the flux and be a thermodynamically stable liquid at the experimental 125°C peak reflow temperature. Its stable liquid nature will assist in wetting and solder particle coalescence. The microcapsules and powder were wet with a solvent before mixing with the flux. The solvent acted as a lubricant to the core-shell liquid microcapsules to prevent their fracturing during mixing. The flux was a modified version of a commercially used flux. This commercial flux was designed for use with BiSn powders above the liquidus of BiSn. The type 7-sized BiSn-based microcapsules were successfully mixed by hand into a paste as seen in DSC. The pastes were stencil-printed by hand using slow and even pressure with steel squeegees and steel stencils. After stencil printing, the printed microcapsules were evaluated by light microscopy (see Figure 5). The particle loading was 85 wt.%.

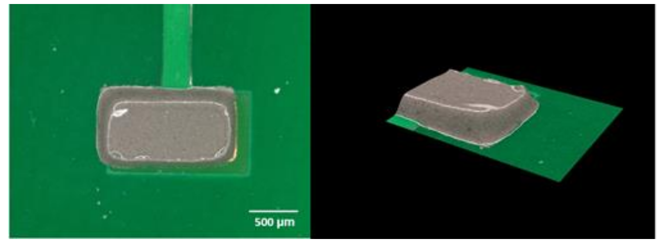


Figure 5. Light microscope images of stencil printed deposits of supercooled liquid metal microcapsules before reflow

Reflow

The printed board was populated with 0805 resistors by hand. Type 7 powders are of a finer size than the widely-used type 4 and type 5 powders. The finer powder has a higher surface area-to-volume ratio than typical pastes. To manage the higher oxygen content, this type 7 paste was reflowed in a N_2 environment (<50 ppm O_2). The reflow profile was designed for the board to reach the peak reflow temperature of 125°C quickly and then sustain the board at that temperature until the end of the process. The profile used is shown in Figure 6.

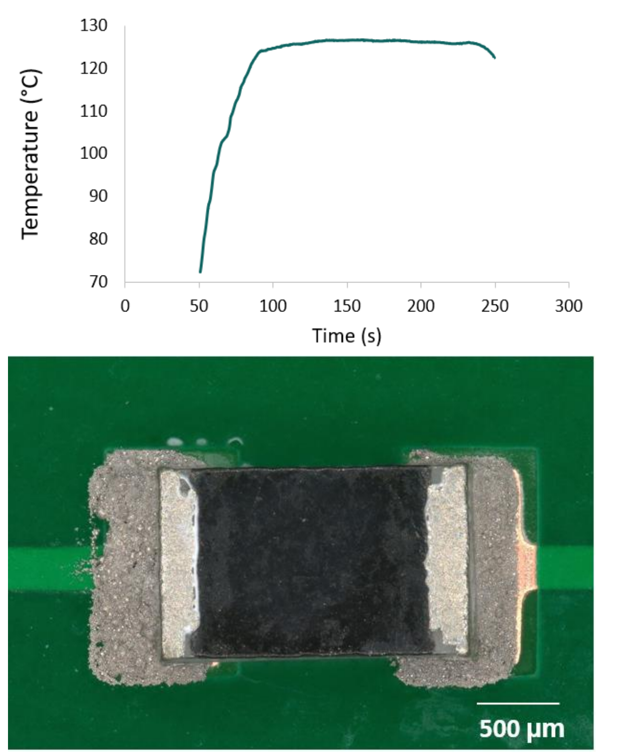


Figure 6. Typical reflow profile with rapid ramp up to the target peak temperature of 125°C and image of soldered 0805 resistor.

During reflow, the viscosity of the paste decreases, flux components melt, and flux activity increases. At 125°C, these effects are less pronounced than at 165°C, which slows the soldering process. The addition of the Field's Metal particles was made because of this slower soldering process. The final solder joint made is shown in Figure 7.

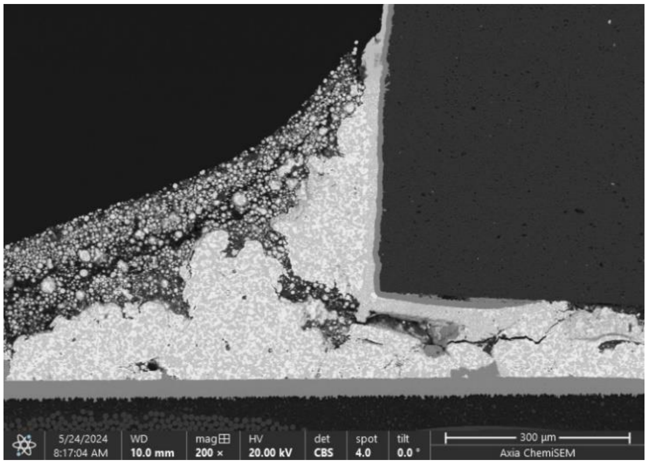


Figure 7. Cross-section of the solder joint formed at 125°C from supercooled liquid metal BiSn-based microcapsules.

Analysis

The reflowed solder joints were embedded in cold mounting epoxy resin and cured overnight to ensure that the heat released during the curing of the resin would not get too hot. If used, a 2-hour cure epoxy resin can release enough heat to raise the temperature of the soldered assembly to above the melting point of eutectic BiSn. The cut and polished solder joints are shown in Figure 7.

When compared to a traditional BiSn solder joint that is reflowed at 165°C and above, one major difference is that the outer surface of the solder mass in Figure 7 consists mainly of individual BiSn-based particles, resembling the graping phenomenon. We posit that these non-coalescent solder particles were not fully reconstituted at the start of the reflow. During reflow, as the reconstituted and supercooled liquid particles coalesce into a single mass, the solid particles were pushed out to the outer surfaces. The solder at the interface can be seen being separated into two somewhat-homogenous masses, one attached to the component and one attached to the board. A visible gap can be seen separating the two, consisting of presumably the fraction of microcapsules that were solid at the start of the reflow. Intermetallic compounds (IMCs) can be seen forming at the solder/board and solder/component interfaces from the Energy-dispersive X-ray spectroscopy (EDS) map shown in Figure 8.

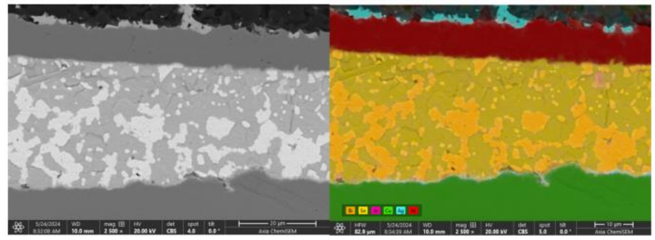


Figure 8. EDS mapping of the cross-section of the solder joint.

CONCLUSIONS AND FUTURE WORK

This work represents progress towards a drop-in replacement BiSn-based solder paste that can be used at an LTS temperature of 125°C, which is 40°C lower than the industry -standard 165°C peak processing temperature of the BiSn alloy. The supercooled liquid microcapsule technology avoids thermal damage to components and materials, or quality issues caused by CTE mismatch. This work has shown progress on the original proof of concept for using supercooled liquid metal microcapsules in production equipment with a commercial flux. This solder joint has the three hallmarks of a solder joint by demonstrating wetting, continuous structure, and IMC formation. This is the first demonstration of all three using the BiSn alloy in a supercooled liquid state.

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