

Lower Temperature Soldering Using Supercooled Liquid Metal

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ABSTRACT

Lead-free solder metal alloys can be formed into supercooled liquid metal microcapsules and used to create solid full metal interconnects at dramatically lower processing temperatures. These alloys can be made with or without bismuth. The technology encapsulates known and established RoHS compliant solder alloys inside a thin oxide/organic shell nanofilm that keeps the metal in a metastable supercooled liquid state at ambient temperatures. The thin oxide/organic shell can be mechanically broken or chemically dissolved to release the liquid metal that then rapidly solidifies all without requiring heat. The novel solder interconnect technology avoids thermal damage to components and materials, or quality issues caused by coefficient of thermal expansion mismatch.

Key words: Supercooling, CTE, flexible, Low Temperature soldering, LTS, SAC305.

INTRODUCTION

With increases demand of flexible electronic materials, which degrade due to high temperature soldering flow, it is of high demand to develop low temperature soldering material and process. Again, the ongoing miniaturization puts a tremendous strain on the tried-and-true solder-assisted die attach and component attach processes developed over many decades. [1] With practical limitations looming for the growth of Moore's law, coupled with the high energy demand that the current trends will require in the next decade, there is interest in new materials and/or processes in chip fabrication and attach. Traditional solder interconnects, with their high temperature process needs, pose a significant barrier to this advance. In consumer and specialty applications, the constant push for higher resolution displays, more complex integrated circuits, and more sophisticated scientific equipment leads to chip packages of larger areas with thousands of underlying solder bumps or balls in ever increasing densities and decreasing pitches. The same strains on interconnect technology in solder ball grid array (BGA) board level assembly are present in the component level die attach since the die attach just has smaller features. Additionally, new materials and technologies such as plastic substrates, organic electronics,

and batteries have real limits on maximum temperature that are incompatible with the temperature of a standard lead-free soldering reflow process. [2,3]

A general reflow process and its impact on large package geometry is shown in Figure 1 and Figure 2. The main heat effect depicted in these figures is the deflection of objects and movement relative to each other. This is called dynamic warpage and it is significant during reflow. The multilayer and thin packages will distort when heated caused by the coefficient of thermal expansion (CTE) mismatch among the thin layers, which leads to deflections on the edges. [3] The dynamic warpage-induced challenge is primarily the physical separation between the bumps on the device edge and the bump beneath them, the movement of components relative to one another during the whole reflow process, as well as the mechanical stress put on many of the solder interconnects while the thin and large area chip is cooled (see Figure 2). Electronics manufacturers have reported that large area packages with larger pitch BGAs in board level assembly using solder paste have issues with solder hot tears. [3] The solder is just not strong enough to bear the stress caused by CTE mismatch induced mechanical stress during the cooling step of reflow. The larger area dies with higher density solder joints are more susceptible to this because their joints are smaller and the magnitude of the deflection of the die is much larger, which compounds the problem. [3,5]

Dynamic warpage work-arounds to using solder materials in these types of assemblies include using a thermo-compression bonding process, using flip chip bonders with formic acid, using low temperature bonding, or using fixtures to keep the chips planar during reflow. These solutions have problems with cost, rework can be limiting, as well as that of low temperature bonding which is done in additional subsequent soldering steps. [1] It is challenging and costly to bond curved chips without a support chip or wafer, custom tools, or specialized solder bump structure. To summarize the problems, dynamic warpage creates opens, hot tears, and residual mechanical stress in the solder joints because of the high heat process.

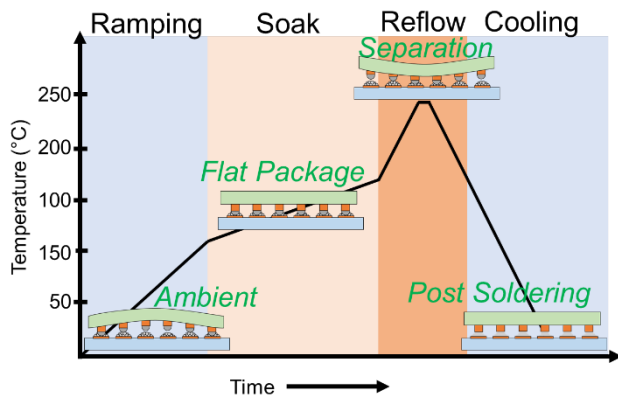


Figure 1: General reflow process and the relative movement of a BGA package (green) and a circuit board (blue) as the assembly is heated in a reflow oven. During the reflow process the initially curved package becomes somewhat planar during heating and can continue to warp with further heating during reflow. Separation can occur on the device edge and can ideally be overcome by limiting the warpage to create a solid solder connection with no failures or opens.

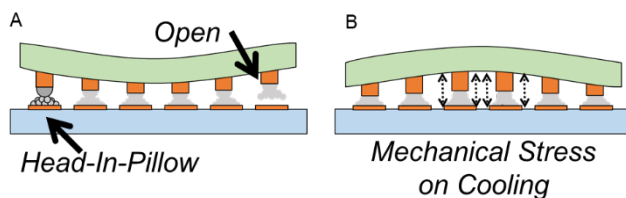


Figure 2: Examples of major deviations from the ideal that lead to poor interconnect yield and reliability issues in large packages. Head-in-Pillow is a failed joint with a distinct boundary between the solder ball on the part and the solder paste. (A) At reflow temperatures. (B) After cooling to ambient temperatures.

In addition to traditional rigid electronics devices, there is an effort to make flexible and flexible hybrid electronics using new materials, technologies, and plastics. [5] Heat is quite often a detriment to affordable plastics targeted as substrates causing them to curl or degrade, to organic electronic materials that lose function or degrade, and to heat-sensitive components like batteries that could degrade or create a safety hazard. Current low processing temperature conductive adhesives have found a role in electronics assembly here but do not have the same quality of reliability that a true metallurgical solder joint provides as thus alternatives are being explored. [6-8] Lowering the processing temperature of creating an interconnect while still maintaining the same reliabilities would be of interest to both traditional and this new type of electronics manufacturing.

BACKGROUND

Soldering technology is thousands of years old, and though the process has been refined in modern times it is still accomplished by heating the metal alloy until it is melted before applying the metal hot, which leads to issues depicted in Figure 2. A new technology has been to keep a metal alloy particle in a metastable

liquid state as it cools to temperatures well below its melting point, known as supercooling. This supercooled liquid metal particle or microcapsule is a new material that can make soldered interconnects at dramatically reduced temperatures.

Supercooling is a phenomenon that all materials experience at a phase transition [9-12]. As a metal in a molten liquid phase cools through the melting point and to a temperature below the normal melting point, the atoms enter into a trapped state which is thermodynamically and kinetically unfavorable. Here the metals are thermodynamically driven to be solids but the path to solidification has not presented itself. The material is now in a supercooled liquid state. The pathway to solidification in a supercooled liquid metals is through a solidification nucleation catalyst. The presence of or spontaneous formation of a nucleation catalyst triggers the crystallization of the continuous whole material.

There are two major physical pathways for crystallization. One is heterogenous nucleation. Heterogenous nucleation only requires a small impurity in the material or a container surface to trigger crystallization by lowering the activation energy needed for the phase transition. The low activation energy makes it the most common pathway. The second pathway is through homogenous nucleation and requires the spontaneous and stable formation of an arrangement of atoms into a nucleation catalyst. It has the highest activation energy needed and therefore is a rarer process.

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. [15-16] The particles can be made by emulsifying a molten metal ingot in the presence of shell-forming chemistries, which upon cooling leave microcapsules in a supercooled liquid state (see Figure 3). The shell protects the metal from the outside container and prevents heterogenous nucleation via the container and other surfaces. The microcapsules formed via the emulsion process are single digit micrometers in diameter. As the particle size gets smaller and smaller during the emulsion process, the percent of pieces of metal that have impurities that act as nucleation catalysts decreases. So, the substance of the technology is the prevention of heterogenous nucleation via protection from the container and via a statistical strategy with particle size.

Since the metal core inside the microcapsules is a liquid, it can flow after chemical activation of the shell. The action that is subject of this paper is chemical activation. When the thin oxide shell on the outside is dissolved by a solder flux and the liquid metal within the particle flows out and solidifies. This is analogous to a traditional solder paste that uses acidic fluxes and rosin to remove surface oxides and aid in solder wetting. It has also 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. [17-18] In this paper, we have shown that soldering can be done at much lower temperature (~165 °C) than the traditional high temperature (~240 °C) soldering using our super-cooled SAC305 microcapsules particles. This low temperature soldering technique will solve a lot of problems in modern electronic industries in many ways.

MATERIALS AND EXPERIMENTAL

Materials

An alloy of tin/silver/copper (SAC305) of a 96.4:3.08:0.5 was used for all experiments. SAC305 microcapsules of a type 8 size were produced using a proprietary method. Cleaned particles were collected from the filter paper using ethyl acetate and stored in a 20 ml glass vial. Differential Scanning Calorimetry DSC of the dried particle were done using aluminum pan. Scanning Electron Microscopy (SEM) of the particles were done after taking a drop of suspension on a piece of silicon wafer and then drying it. Note: the term particle and microcapsule are often used interchangeably.

Flux A was a commercially available ROL0 tacky gel flux from FCT solder (NL932HFF). Flux B was a flux formulated at SAFI-Tech based upon an organic solvent, organic acid, and amine-containing compound.

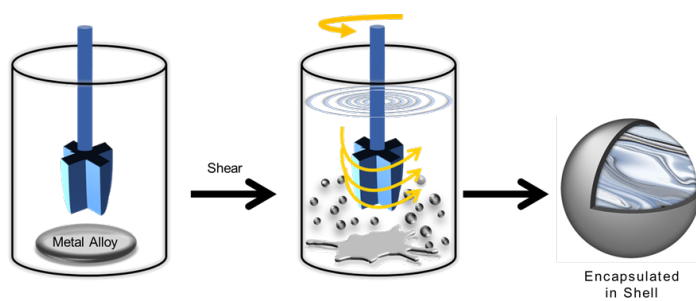


Figure 3: Emulsion process to make microcapsules. A molten metal alloy in the presence of a carrier fluid and shell creating chemicals is sheared while hot into pieces. Upon cooling a core-shell supercooled liquid metal microcapsules is formed.

A base printing formulation was created by mixing ethylene glycol, water, hydroxyethylcellulose, and polyvinylpyrrolidone polymer while gently heating. The clear solution was analyzed via parallel plate rheology. The viscous paste formulation was then mixed with SAC305 microcapsules at an 88 wt.% using a rotary mixer until well blended.

Experimental

SAC305 microcapsules were printed on the printed circuit board (PCB) using manual stencil printing method. The PCB had an immersion Ag (ImmAg) surface finish. Immersion silver was selected for the BGA test assemblies because the microcapsules wet the silver more effectively than ENIG in an air environment. The authors sourced the dummy BGA components from Topline made of silicon with dimensions. The corresponding contact was a simple FR4 circuit board.

The stencil holes were aligned with the copper pads on the FR4 board using optical alignment method and then the solder paste was applied using a fine squeegee. The BGA chip were aligned with the corresponding pad using a BGA alignment two-way camera system and soldered at 165 °C. The solder joint quality was studied by cross sectioning, polishing and SEM-Energy Dispersive X-ray Spectroscopy (EDS) method.

RESULTS AND DISCUSSION

SAC305 Supercooling

Supercooling is the difference between the melting point of the metal and the temperature that which the metal freezes. The emulsion-based technology used to make the microcapsules utilizes a carrier fluid, oxidizing agent, a shell creating chemical, and a shearing system. Each alloy has a different melting point and often different surface chemistries. Tin silver copper is mostly comprised of tin and tin has the highest propensity to oxidize and make up the oxide on the surface. This shell made of tin oxide and organic layer on the outer surface.

The production process involves heating a SAC305 ingot in a high temperature stable carrier fluid above the 220 °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 primary variables that control the process are temperature, carrier fluid boiling point and pH, organic shell binding group/structure, and post-processing conditions. The conditions were empirically determined to create a Type 8 (~5 µm diameter) powder with the supercooling from 220 °C to 75 °C (see Figure 4). The 75 °C solidification temperature was achieved during the cooling cycle of DSC. This solidification temperature is far below than the melting temperature 220 °C. That is why this phenomenon is called supercooling and it is observed in our SAC305 microcapsules. A metric used to compare supercooling across metals with different melting points is a factor called degree of supercooling. It is defined as the difference in the melting point (220 °C here) and the new freezing point (75 °C here) divided by the normal melting point in Kelvin. A degree of supercooling has previously been achieved a low temperature alloy of eutectic BiSn of 36%. [19] For the SAC305 microcapsules in this paper the degree of supercooling was 29%. The phase yield on the supercooled liquid amount below 100 °C was quantitative with nearly 100% of the microcapsules being liquid above 100 °C.

Printing

The most common method of placing solder particles on a circuit board is stencil printing. It is a fast and well-known deposition method. Most stencils are made of stainless-steel. The stencil printable microcapsule formulation was developed without the addition of normal acidic flux ingredients. The Type 8 sized SAC305 microcapsules were successfully mixed with poly (ethylene glycol-ran-propylene glycol) Mn ~2,500 (PG) by hand or rotary mixer into a paste with a viscosity of ~1,687,000 cP and thixotropic index of 0.51 (see Figure 5). The PG was analyzed via rheometry before and after the mixing of solder microcapsules. Rheometry was a parallel plate rheology. The viscous paste formulation was then mixed with SAC305-based microcapsules at a 90 wt.% using a rotary mixer until well blended. The high viscosity helped make it easier for the paste to stay in place after printing and the high thixotropic index made it easier to print the paste through the 180 µm apertures by shear thinning. After printing, the microcapsules were evaluated by DSC (see Figure 6). The particles retain a deep supercooling with a peak solidification of 90.5 °C. It was difficult to determine the liquid purity because of the interference of the

paste solvents that appeared in the DSC, though it is clear that the microcapsules are nearly entirely in the supercooled liquid state at the reflow temperature of 165 °C. The particle loading was 88 wt.%; a typical metal loading for solder pastes, which is in the range of a typical solder paste.

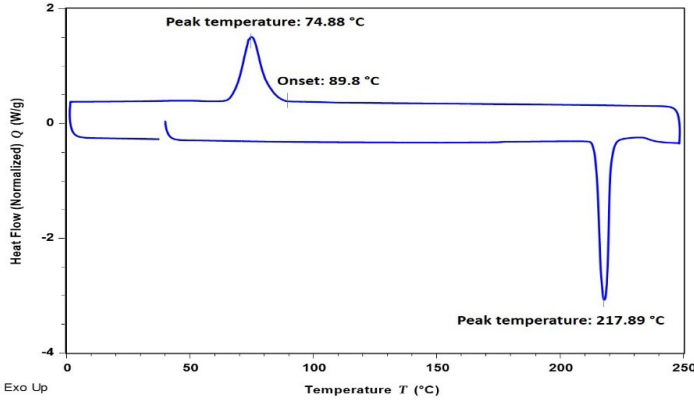


Figure 4: DSC of SAC305 microcapsules made using the powder coating process. Exothermic peaks are up.

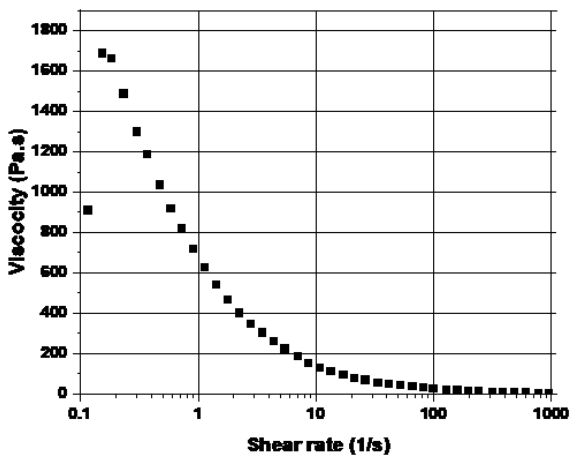


Figure 5: Rheology of SAC305 paste prepared from supercooled particles

The test vehicle of this technical paper was a BGA dummy chip with 368 I/Os, 360 μm pitch, and about a 180 μm feature size. The steel stencil used had an aperture of same pitch but aperture diameter of 180 μm. The created paste was manually printed onto a circuit board under ambient conditions.

After printing, the printed paste was collected and ran into DSC. The DSC curves shows undercooling peak shifted from 90.5 °C up to 107.9 °C, which means nearly half of the product was solid above 100 °C. This means that core of all the particles would still be liquid at the reflow temperature of 165 °C even after mixing and printing. It is expected that mechanical deformation of the particles being pushed through a small aperture caused the organic coating to be deformed or displaced and the metal to be more exposed to oxygen and created a more oxidized/thicker shell. [17,18] In future work a more robust and stable shell will need to be created to prevent this small degradation of the supercooling caused by printing.

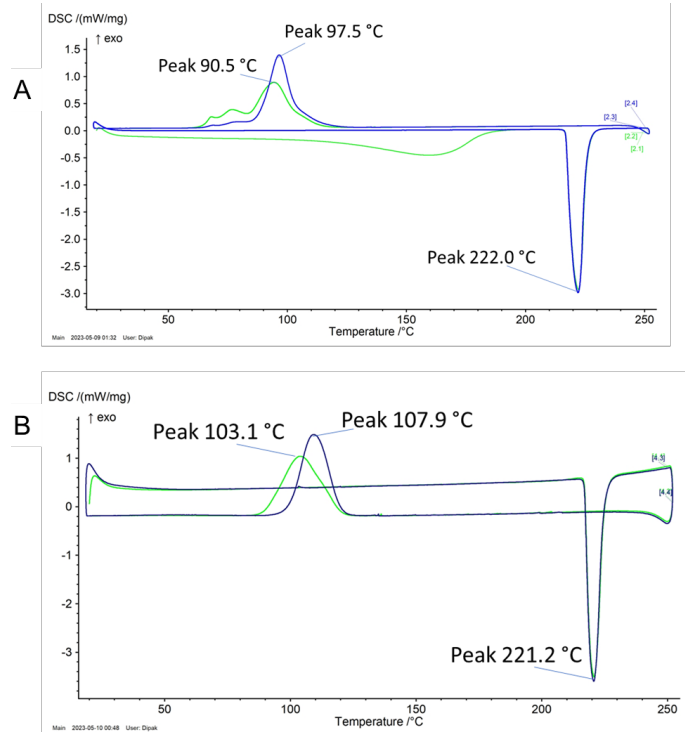


Figure 6: DSC of SAC305 particles (A) after mixing into a paste, (B) after printing through a 180 μm aperture and drying.

Process

The SAC305 microcapsules achieved a deep supercooling to 75 °C but not all the way down to below 20 °C. This temperature creates a limitation of the application processing conditions. In order to demonstrate the potential of using SAC305 at such low temperatures, such as at 165 °C, the microcapsules would have to be handled and printed with solid core, which were then “reconstituted” into a liquid state by heating to above the melting point of the metal. Consequently, this meant that the acidic solder flux would be applied to the solder microcapsules after printing and reconstitution at the target reflow temperature.

The microcapsules were printed on the printed circuit board as an unreactive paste as there was no flux added to paste. This enabled the heating of the particles to 250 °C in order to melt the alloy inside the shell, then followed by cooling them and holding them in a supercooled liquid state above 100 °C without triggering corrosive activity from active flux ingredients. Experiments were performed to understand the effect of a commercially available flux, Flux A, on the shell composition as determined by DSC. During the cooling of the molten metal alloy within the microcapsule the onset of solidification was at 95 °C and increased the amount of metal solidification with decreasing temperature. Most of the metal deeply supercooled to about 75 °C. After exposure to the flux for 1 hour at room temperature the onset was ~110 °C and peak of 96 °C. After exposure to flux for 4 hours at room temperature the onset was ~100 °C and a peak of 95 °C. After exposure to flux for 29 hours at room temperature the onset was ~110 °C with a peak of 96 °C. It appears that the flux does have an immediate change on

the supercooling depth of the microcapsules but does not do much additional changes over 29 hours. The resulting microcapsules could still be used to solder at 165 °C.

The activity of this flux at 165 °C can be seen in Figure 7. The supercooled liquid microcapsules of SAC305 were exposed to Flux A at 165 °C after reconstituting the solder core into a liquid core at 240 °C. Figure 7 shows images of supercooled liquid metal microcapsules before and after exposure to flux at this temperature.

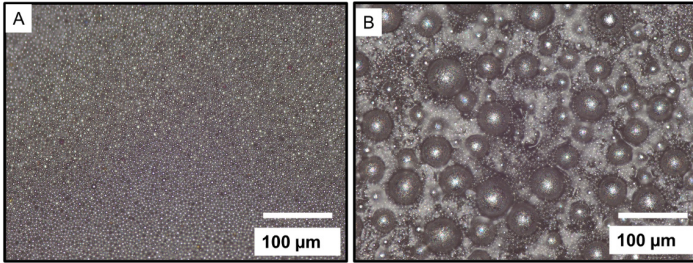


Figure 7: Microscope images of supercooled liquid metal microcapsules covered in a flux at 165 °C. (A) Immediately followed flux deposition and before the shell dissolves on the microcapsules that are so small that they cannot be clearly distinguished. (B) Ten seconds after flux deposition where particles coalesce into particles up to 80 μm.

There were some limitations to the commercially available Flux A. This rosin-based flux was not designed to work at such low temperatures and so had a significant amount of flux residue and unevaporated solvent that hindered the coalescence and made the activity uneven across the deposited particles. To address this issue a solution flux was formulated tailored to the temperature and tin oxide-based microcapsule shell. The initial approach was to select individual chemicals designed to act on the shell and be quite active at the target temperature. Various solvents, carboxylic acids, phosphonic acids, inorganic acids, amines, salts, and conditions were tested. The resulting flux was a solution flux using an organic solvent, organic acid, and an amine and is referred to as Flux B.

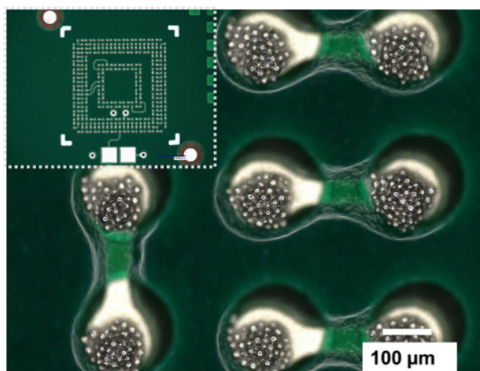


Figure 8: Printed patterns on PCB with low mag inset.

The SAC305 microcapsules containing paste were printed in the BGA test pattern onto the PCB (see Figure 8) and then heated to 250 °C to relieve the metal, then the board was transferred to a

165 °C heated alignment system. The test BGA was dipped in Flux B, aligned above the printed pattern, and lowered to make contact with the printed particles. The flux and the solder met at 165 °C and soldering occurred. An image of the cross-section of the solder joint is presented in Figure 9. The soldered BGA to the ImmAg on copper had less than 20% voiding and greater than 80% of the contact pad was covered in the examined solder joints. This is the first time ever that a SAC305 paste has been used to create an attach at such a low temperature. The solder interconnects are continuous, limited in voiding, and have a fillet (see Figure 9).

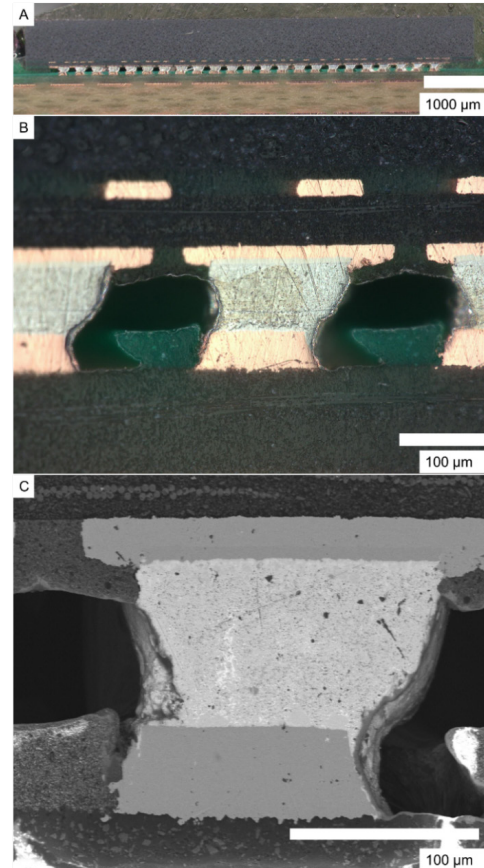


Figure 9: Images of cross section of assembled BGA. (A) Low magnification light microscopy of entire line of assembled joints (B) Higher magnification light microscopy showing the ball soldered to the bottom contact pad. (C) Higher magnification SEM micrograph with backscattered detector

CONCLUSIONS AND FUTURE WORK

This work has accomplished proof of concept for using supercooled liquid metal microcapsules of the lead-free high tensile strength SAC305 at a reduced temperature reflow. A method was developed to make deeply supercooled SAC305 microcapsules with a flowable liquid window of the metal from the melting point of 220 °C down to 90 °C. Printing processes were developed for precisely and accurately depositing high density arrangements of microcapsules. Lastly, reflow of SAC305 was demonstrated at 165 °C that is 80 °C lower than the industry standard 245 °C peak processing temperature of the SAC305 alloy. This low temperature soldering process using the high melting -SAC305 alloy has never

been reported before and very important for maintaining planarity during the soldering process in order to address opens at the device edge and mechanical stress after soldering. This soldering was accomplished on a test BGA. Deepening the supercooling of SAC305 is ongoing and more detailed mechanical testing is part of the future of this product development.

ACKNOWLEDGEMENTS

The authors acknowledge the contributions of Mr. Michael Holmes to the development of the stencil printable formulation, Dr. Shihuai Zhou for his contributions to the initial flux development, and Prof. Martin Thou for his continuing contributions to SAC305 product development. This material is based upon work supported by the U.S. Department of Energy, Office of Science SBIR program under Award Number DE-SC0020704.

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BIOGRAPHIES

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