As originally published in the IPC proceedings.

NanoCopper Based Solder-free Electronic Assembly Material

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Abstract
The Advanced Technology Center of the Lockheed Martin Corporation has developed a nanotechnology enabled copper-based electrical interconnect material that can be processed around 200 °C. The readily scalable Cu nanoparticles synthesis process uses a low cost solution-phase chemical reduction approach. A pilot plant is fully operational producing one lb per batch of nanomaterial. We have demonstrated assembly of fully functional LED test boards using a copper-nanoparticle paste with a consistency similar to standard solder. Further improvements have led to the assembly of a small camera board with a 48 pad CMOS sensor QFN chip and a 26 pin throughhole connector. In addition, we have a fully functional nanocopper assembly line in place for process development using standard industrial off-the shelf equipment. We are currently working with a commercial assembly house to dial-in the board assembly process. The fused material shows a tensile strength that is already in the range of space qualified solder. Once fully optimized, the nanocopper-based (trademarked CuantumFuse^{TM}) solder-like material is expected to produce joints and interconnects with up to 10 times the electrical and thermal conductivity compared to tin-based solders currently in use and with a bond strength comparable or better than eutectic SnPb. Applications in space and commercial systems are currently under consideration.

Introduction
In response to government legislation and regulation around the world regarding lead content in consumer electronics,[1] electronics producers have quickly converted to lead-free tin/silver/copper (SAC) solder. In 1997, a comprehensive $11 million National Center for Manufacturing Science (NCMS) project was conducted by 11 private and public institutions to determine a suitable replacement for tin/lead solder (SnPb).[2] After studying 70 candiate alloys, it was concluded that alloys near the eutectic SAC composition would be best suited for their applications. Additional studies and consortia (National Electronics Manufacturing Initiative, Center for Advanced Vehicle Electronics, INEMI, HDPUG, IDEALS, Pb-Free Electronics Risk Mitigation) perpetuate near eutectic SAC alloy as the most popular lead-free replacement out of the now over 300 alloys in use. Its reliability has proven acceptable to the consumer electronics industry where short product life cycles and relatively benign operating environments are common. The primary difficulty of the SnAgCu system is its high melting point at 217°C, requiring processing temperature in excess of 250°C to ensure complete melting of the high melting phases Ag_3Sn and Cu_6Sn_5 that could be present (see Figure 1).

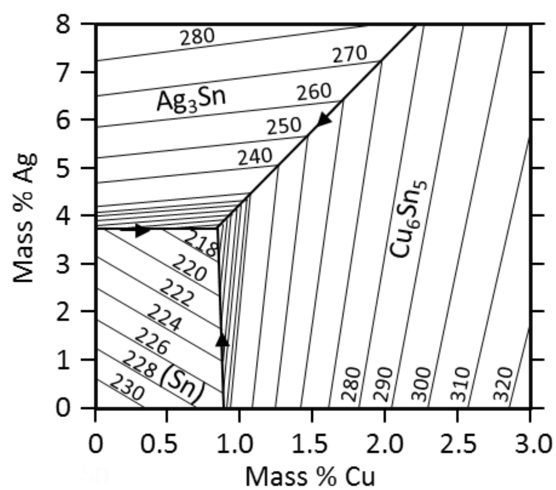

Figure 1 – Phase diagram of the Sn-Ag-Cu system. Graph generated from NIST data.

Such high temperatures can damage the polymeric materials used for components, staking, and boards, unless more expensive components and materials are used and limit the number of rework cycles.[2] Additionally, it brings new and reemerging failure modes in electronics, including tin whisker growth.[3] For defense and space applications, reemergence of this issue with SAC raises concerns regarding increased infant mortality, latent failures, and the need for complete requalification. Establishing new qualification procedures is made more onerous as the behavior of SAC alloys are still not

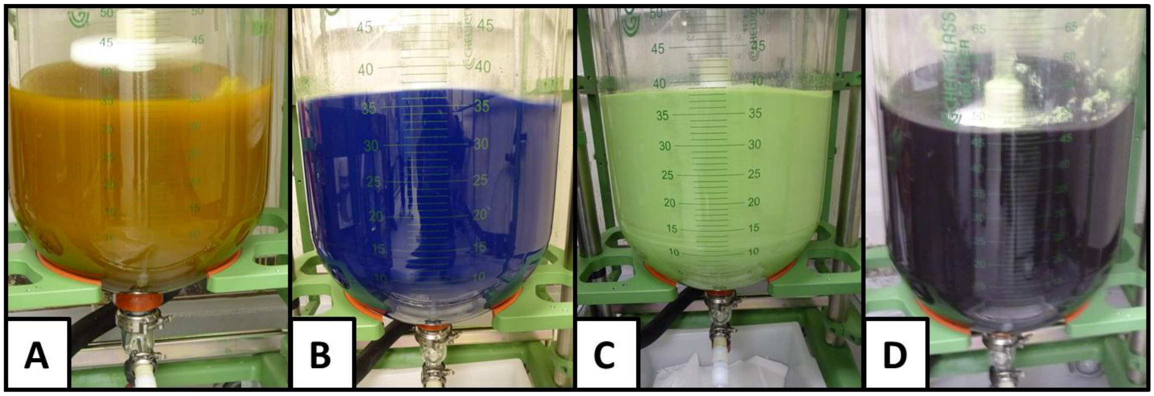

Figure 2 - Reaction progression from a soluble copper salt (A-C) to reduction to copper nanoparticles (D).

fully characterized or understood. Additionally, the most common alloy system exhibits a number of known drawbacks, making it unreliable for long-term use in harsh environments with shock, vibration, heat or thermal cycling.[4-8]

When alternatives to SnPb solder are considered, the first restriction on available materials is tradtionally the melting point. The material must be processable at a temperature that will not compromise the electronic components or the substrate. Hence, low melting metals and alloys are the first candidates, while materials that are more cost effective like copper or aluminum or have excellent electrical and thermal properties such as gold, silver, copper, and aluminum are immediately passed over due to their high melting points. However, in this instance, nanotechnology allows access to more of the periodic table. It is well documented that as a metal particle size shrinks to the nanometer scale, the temperature at which these particles will join together drops significantly below the melting point of the bulk material.[9] It should be possible, then, to develop a pure copper solder by forming sufficiently small copper nanoparticles such that the melting point is reduced from the bulk value of 1084°C to a traditional electronics processing tempearature around 200°C. Developing such a solder paste must address a number of requirements including: 1) sufficiently small nanoparticle size, 2) a reasonable size distribution, 3) reaction scalability, 4) low cost synthesis, 5) oxidation and growth resistance at ambient conditions, and 6) robust particle fusion when subjected to elevated temperature. This paper outlines the development of a novel nanocopper material (CuantumFuse^{TM} – from synthesis to board level integration – as a solder-free electronic assembly material. Copper was chosen because it is already used throughout the electronics industry as a trace, interconnect, and pad material, minimizing compatibility issues. It is cheap (1/4th the cost of tin; 1/100th the cost of silver, and 1/10,000th that of gold), abundant, and has ten times the electrical and thermal conductivity compared to commercial tin-based solder.

Nanocopper Synthesis

Oxide-free copper nanoparticles with diameters in the 5-25 nm range were synthesized via solution chemistry (Figure 2). An inexpensive copper salt precursor is the basis of the reaction. The salt is dispersed in a suitable solvent, and subsequently reduced with sodium borohydride ($NaBH_4$). The resulting copper atoms agglomerate into larger entities and are stabilized by the addition of surfactants to the reaction mixture. Quick cooling, after the reaction is complete, helps to arrest particle growth. The reaction output is then repeatedly washed to isolate the nanocopper particles and to remove side-products. Throughout the synthesis process, temperatures, color changes, solution viscosities, and times are monitored closely. None of the chemicals used in the synthesis are rare or prohibitvely expensive.

Scale-up

A critical issue for nanomaterials manufacturing is scalability. The controlled fabrication of metal particles in the size range of interest has only been demonstrated previously with gold and silver after a decade of research. In solution-phase nanoparticle synthesis, there are two competing processes: nucleation and growth. Particle nucleation dominates the reaction in the beginning but then levels off over time, and particle growth takes over as the dominant process. However, nucleation does continue, providing a constant flux of very small particles. This leads to an increasing size distribution that is volume dependent. At a small scale, e.g. a few hundred milliliters, the two processes can be controlled quite well, allowing for a suitably narrow size distribution. However, with increasing volumes, e.g. thousands of gallons, controlling nucleation and growth can be more difficult, yielding a very broad size distribution.

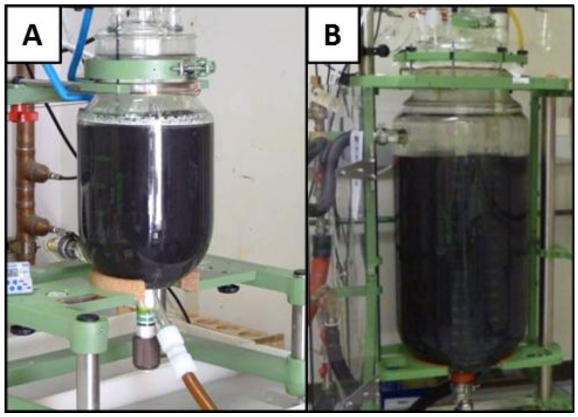

Figure 3 - Nanocopper reaction at the 5 L scale (A) and 80 L scale (B).

This situation was overcome by designing a process that, for the first time, completely separates nucleation and growth without any nucleation additives. The concept works so well that all scale-up steps attempted to date have worked on the first try. This gives a strong indication that this process is fully scalable with little modification.
In order to demonstrate scalability, our facilities were upgraded with 5 L and 100 L chemical reactor systems (Figure 3). The 100 L reactor is now used routinely at the 80 L batch size to produce over 500 g of high quality material.

Nanocopper Characterization

As-synthesized nanocopper exhibits a number of bulk characteristics including color, luster, and consistency that can be used as an initial indicator of material quality. A high quality material is typically dense, exhibits a copper color with metallic luster, and has a paste-like consistency. A more fluffy, powder-like, dull, and brown-to-black appearance warns of an inferior product.

NanoCopper has also been characterized by a variety of microscopy and analytical techniques including scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and high-resolution transmission electron microscopy (HRTEM). The primary form of quality control consists of SEM and EDS. These techniques prove to be quick and low-cost while providing data that can be easily interpreted. For each reaction, a sample of the as-synthesized material and a fused sample (heated to 210°C with a 9 min ramp and a 4 minute soak under constant N_2 flow) are subjected to SEM imaging and EDS analysis from which initial particle size, material purity and the fusion characteristics (necking, growth, porosity) can all be determined (Figure 4). High quality nanocopper material fuses into a continuous network with grains clearly exhibiting crystalline facets. Porosity can also be determined using a combination of ion-beam milling and SEM image analysis. Porosity of the fused material is an important metric in that it has a marked effect on the electrical, thermal, and mechanical properties of the final material.

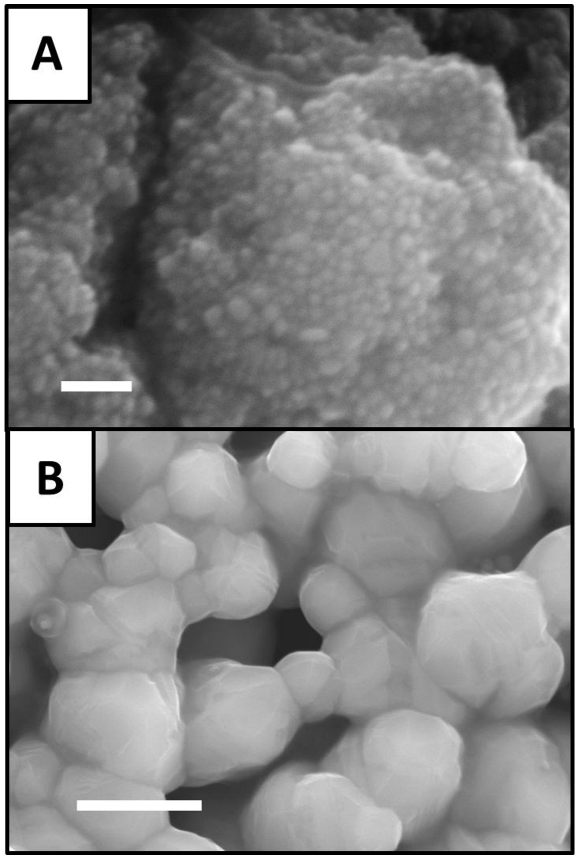

Figure 4 - SEM micrographs of copper nanoparticles isolated from the synthesis (A) and material after fusing at 210°C for 4 minutes (B). The scale bars represent 100 nm and 500 nm for panels A and B respectively.

HRTEM imaging revealed fringe patterns from which crystal structures and phases could be determined. Additionally, images were analyzed to confirm particle sizes and the arrangement of surfactant layers. Fused particles were examined to understand grain and grain boundary development.

Nanocopper Mechanical and Thermal Properties

Before attempting to build electronic boards, a significant effort was undertaken to establish conditions that yielded high nanocopper bond strength. Specifically, the goal was to be comparable to eutectic Sn63Pb37 solder and other high temperature tin-lead solders qualified for use in space. Raw nanocopper material from synthesis was formulated into pastes with additives designed to improve suspension, dispersion, flow properties and fusion. The process for testing formulations was iterative and provided quantitative data on the tensile strength for each formulation. A non-standard tensile test had to be developed since the material does not lend itself to casting bulk dog-bone specimens of consistent quality as ASTM test procedures require.

Formulations were made by washing nanocopper powder several times with various chemicals, such as solvents, surfactants, and thickeners using a variety of methods, such as manual stirring, sonication, and homogenization. The viability of these formulations was quickly screened by performing a quick fusion test on Al substrates and making a qualitative measure of material strength and hardness. Promising formulations were further investigated through SEM and assembly of small LED boards to test electrical performance.

To quantify the tenslie strength of a formulation, a unique tensile test specimen was developed. Tensile specimens consisted of two copper bars that were fused together with nanocopper. A metal fixture with a Teflon collar was used to align the copper bars and apply moderate pressure during the heating cycle (Figure 5A and B). The copper bars were weighed before and after fusion to determine the amount of nanocopper in each joint. Tensile tests were then completed using a tensile test machine, and the fracture surfaces (Figure 5C) were analyzed by SEM and EDS.

Many formulations were considered, created, tested, and down-selected. In total, 41 different sets of tensile tests were performed on nearly 350 tensile specimens. The maximum load held by a nanocopper joint was 1,155 lb or 7,683 psi for a 0.4375 inch diameter bar. Several sets achieved consistent bond strength above 4,400 psi which is the minimum tensile strength of the lowest strength SnPb-based solder alloys currently used for flight hardware assembly. To compare the results of this non-standard test to other materials, a number of baseline test specimens were generated using SnPb solders in place of nanocopper. These samples showed a tensile strength of 11,000 psi.

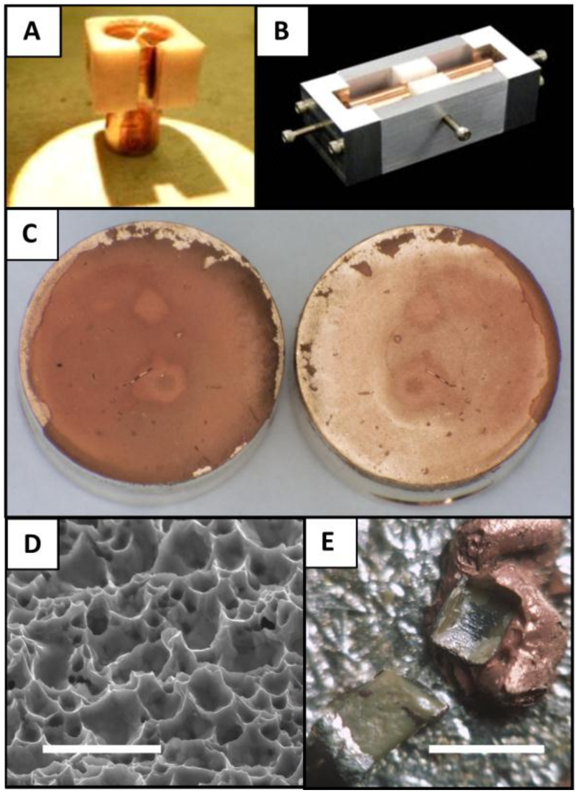

Figure 5 - A) A single copper bar used for tensile testing is nested within a teflon collar. B) A tensile specimen loaded in a fixture ready for fusion. C) Photograph of a fracture surface following tensile testing. D) SEM image of a fracture surface after tensile testing. The scale bar represents 5 µm. E) A surface mount resistor bonded to a Sn surface with nanocopper. The resistor failed in the ceramic rather than the nanocopper when stressed. The scale bar represents 1 mm.

SEM imaging of the fracture surface of tested tensile specimens indicated that the above tensile strengths were achieved with less than 10% cohesive ductile failure. Extrapolation of this data suggests that just 20% cohesive ductile failure should produce joints with strengths equal to that of eutectic SnPb solder. The SEM images showed cup-cone features typical of ductile metal failure, which indicates nanoparticle fusion and formation of strong metallic bonds (Figure 5D). Fusion of nanocopper material to the bulk copper rod was also seen in many samples. This was an important finding as it showed that nanocopper exhibits sufficient activity to react with and bond to a thermodynamically stable bulk copper surface.

Thermal conductivity was tested according to ASTM D5470 yielding a value of 140 W/mK, 35% that of bulk copper, but three times that of SnPb (35-50 W/m*K depending on composition).

Electronic Board Manufacture and Other Applications

A commercial camera board was chosen as the first demonstration build because the assembly required bonding of the most important electronic component types. Each board consisted of 4 surface mount resistors, 14 surface mount capacitors, 3 five-pin surface mount voltage regulators, 4 through hole jumper connections, 1 twenty-six pin through hole connector, and 1 forty-eight contact pad QFN surface mount sensor chip. Additionally, successful camera board manufacture could be easily demonstrated via still and live image capture.

The camera board was procured as a kit from Digi-Key Corporation. The kit included software that provided a smooth interface between the camera and any Windows computer with a USB port. The specific hardware and software used were:

Manufacturer: Aptina Imaging Corporation
Camera board model: MT9V126
Software name: DevWare

Software Version: 4.1.9.27784

Nanocopper pastes were formulated using methods developed during tensile experiments and included additional steps to improve viscosity, minimize void generation during fusion and facilitate bonding to oxidized tin finishes. These formulations were screened for utility by fusing individual surface mount components to a small deposit of nanocopper on a pure tin surface. Some formulations proved so effective that the components broke within their ceramic bodies when subjected to stress (Figure 5E). Formulations have been developed for both manual assembly and automated assembly with stencil and pick-and-place equipment. Syringe application can dispense through needles up to G30 (150 µm inner diameter).

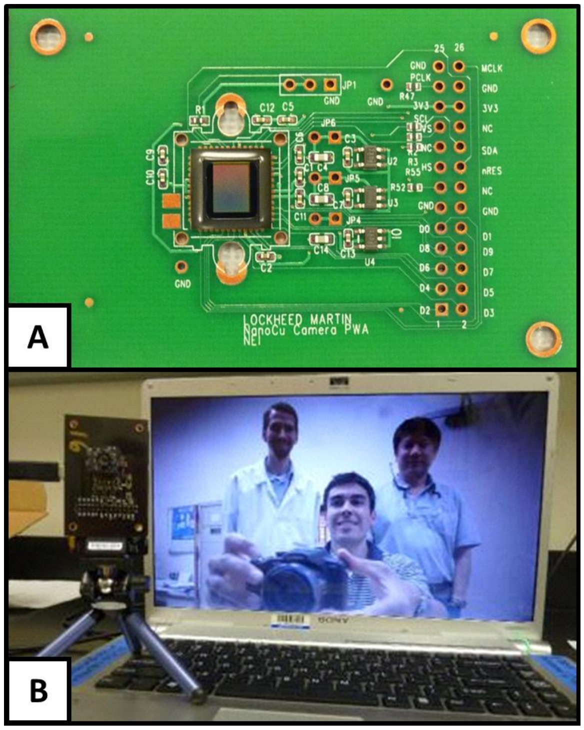

Figure 6 - A) Photograph of a camera board populated with all surface mount components. B) Demonstration of fully functional camera board using only nanocopper.

Various application procedures have been developed in the lab and piloted on a dedicated R&D production line for both surface mount technology (SMT) and plated through hole (PTH) parts. In a typical fabrication procedure, nanocopper was applied in an automated fashion to the boards using a 4 to 6 mil thick stencil. Next, SMT parts were automatically placed using a production pick-and-place machine. Care was taken to minimize short circuits and to ensure wetting of the nanocopper to the pads. The sensor chip was the most complex component, and a number of paste application methods and paste formulations were developed for this step alone. Once all of the SMT components were in place (Figure 6A), PTH parts were added manually using a syringe to apply the nanocopper. A completely assembled board was then ramped through a heating cycle with a maximum temperature of approximately 200°C under constant flow of an inert gas. Drying procedures were developed to minimize cracking of the nanocopper and ensure integrity of the joints. After fusion, assembled components were protected with a standard urethane conformal coating cured at a maximum temperature of 100°C.

Each camera board was subjected to a suite of electrical tests at the component level, such as a production flying probe, and culminated in a final board-level evaluation by interfacing the board with the corresponding software. Fully functioning boards were able to display real-time images as shown in Figure 6B.

Beyond solder replacement, we have explored a number of other applications using nanocopper. Shown in Figure 7 are two flexible electronic devices about 10” long with embedded LEDs. The traces were formed by stencil printing nanocopper and the cured traces sealed-in using a standard $89 laminator. The entire device functions under repeated flexing. Because the required fusion temperature is only 200°C, it is possible to interface with common plastic substrates used for flexible electronics such as polyethylene terephthalate and polyimide.

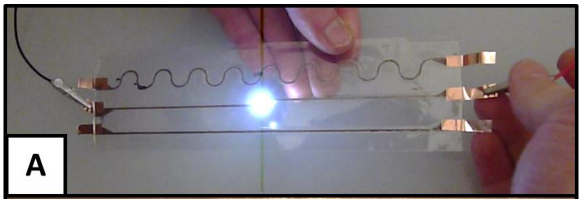

Figure 7 – Photograph of flexible LED circuits with stencil printed nanocopper traces.

Conclusions

In summary, we have developed an all-copper electronic assembly material that can be processed at 200°C. Through improvements in nanocopper synthesis, paste formulation, and processing techniques, a fully functional camera board was successfully assembled using only nanocopper paste. Coupled with the proven scalability of our unique nanocopper synthesis process, this demonstration illustrates the utility and potential of nanocopper as a replacement for SnPb and Pb-free solders. The electrical conductivity of nanocopper is already 2-3 times higher than standard solder currently in use. Also, the tensile strength is approaching that of the best solders available. Nanocopper is still in the early development stages, yet improvements in strength, thermal conductivity, and electrical conductivity have been rapid. There is plenty of room for further improvement as the full materials properties potential of nanocopper have yet to be realized. We are aggressively pursuing further improvements in all areas of perfomance. The fact that this material already performs simlar to or better than existing materials shows the exciting potential of nanocopper to be a robust alternative to the current library of lead-free solders.

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