NanoCopper Based Solder-free Electronic Assembly Material

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ABSTRACT

The Advanced Technology Center of the Lockheed Martin Space Systems Company has developed a nanocopper-based electrical interconnect material that can be processed at 200 °C in the same fashion as normal solder. This is made possible by taking advantage of the rapidly increasing melting point reduction as the particle size decreases to the sub-50 nm-scale. The readily scalable synthesis of the nanomaterial uses a low-cost, solution-phase chemical reduction approach. XRD, SEM and HRTEM confirmed the formation of stable Cu nanoparticles less than 10 nm in size and the effectiveness of the surfactant mixture to prevent oxidation. We have demonstrated assembly of fully functional LED test boards using this Cu nanoparticle material with a consistency similar to standard solder. Further improvements have led to the assembly of a small camera board with a 48 pad QFN CMOS sensor chip. The fused material shows reasonable tensile strength approaching that of eutectic tin/lead solder.

Keywords: nanocopper, lead-free solder, solder-free electronics

1 INTRODUCTION

In response to government legislation and regulation around the world regarding lead content in consumer products[1], consumer electronics producers have quickly converted to lead-free tin/silver/copper (SAC) solder. The near eutectic SAC alloy has emerged 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 which deals mostly with short product life cycles and relatively benign operating environments. However, it brings new and reemerging failure modes in electronics, including tin whisker growth. 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 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 [2-6].

A fundamentally new approach has to be taken to solve the lead-free solder challenge. Rather than finding another multi-component alloy, a solution has been developed based on the well-known melting point depression of materials in nanoparticle form. Given this nanoscale phenomenon, it should be possible to produce a solder paste based on pure copper allowing a processing temperature 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. 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.

This paper outlines the development of nanocopper – from synthesis to board level integration – as a solder-free electronic assembly material.

2 NANOCOPPER SYNTHESIS

Oxide-free copper nanoparticles with diameters in the 5-25 nm range were synthesized via solution chemistry. 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 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.

2.1 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 tightly controlled, 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.

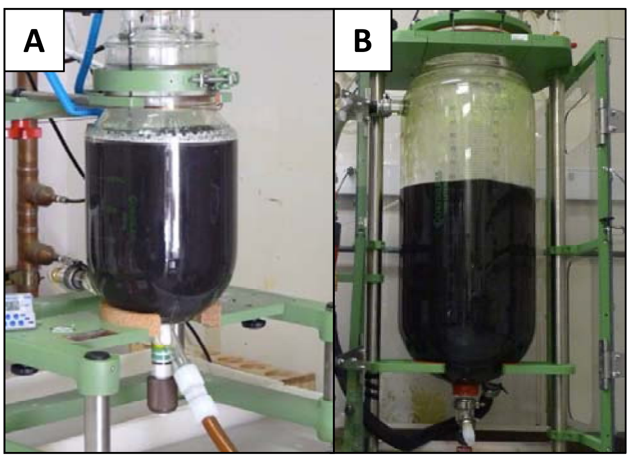

Figure 1. Nanocopper reaction at the 5 L scale (A) and 60 L scale (B).

This situation was overcome by designing a process that, for the first time, completely separates nucleation and growth without any nucleation additives. Rather than growing particles from a solution, we first create the nucleation sites in the desired size range throughout the entire reaction volume and then induce reduction and particle formation. 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. The 5 L reactor is now used routinely at the 4.5 L batch size to produce 26-27 g of high quality material (pure copper theoretical yield is 24.5 g). To date, the 100 L reactor setup has been used multiple times to carry out reactions up to the 60 L scale producing up to 360 g of material in one batch.

2.2 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 powder and a fused sample (heated to 210 °C for 4 min on Al substrate) were 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. 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.

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.

3 NANOCOPPER PROPERTIES AND APPLICATIONS

3.1 Mechanical 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 release of surfactants, suspension, dispersion, and flow properties. 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 substrate and making a qualitative measure of material strength and hardness. Promising formulations were further investigated through SEM and fusion of LEDs onto surfboards to test electrical conductivity.

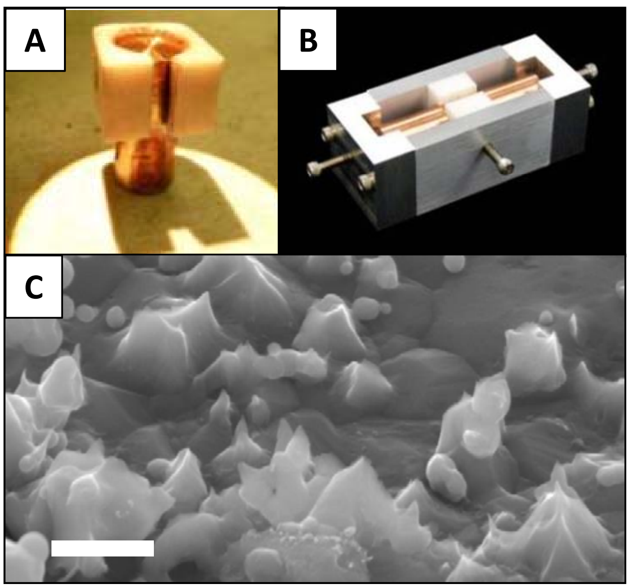

Figure 2. A) A single copper bar used for tensile testing is nested within a teflon collar. B) A tensile specimen loaded in a fixture ready for fusion. C) SEM image of a fracture surface after tensile testing. The scale bar represents 500 nm.

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 fixture with a Teflon collar was used to align the copper bars and apply moderate pressure during the heating cycle (Figure 2A 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 an Instron machine, and the fracture surfaces 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. 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.

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. Fusion of nanocopper material to the bulk copper rod was also seen in many samples (Figure 2C). 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.

3.2 Electronic Board Fabrication

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 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 and to minimize void generation during fusion. 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).

Various application procedures have been developed in the lab and piloted on the R&D Production line in Sunnyvale, CA for both surface mount technology (SMT) and plated through hole (PTH) parts. A typical fabrication procedure involves automated patterning of the nanocopper onto board pads using 4 to 6 mil thick stencil. Next, SMT parts are automatically placed using a Universal 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, a number of paste application methods and paste formulations were developed for this step alone. PTH parts are placed manually using syringe dispense. A completely assembled board was then ramped through a heating cycle with a maximum temperature of approximately 200 °C. Drying procedures were developed to minimize cracking of the nanocopper and ensured integrity of the joints. After fusion, assembled components were protected with a standard Arathane 5750 conformal coating cured at a maximum temperature of 100 °C.

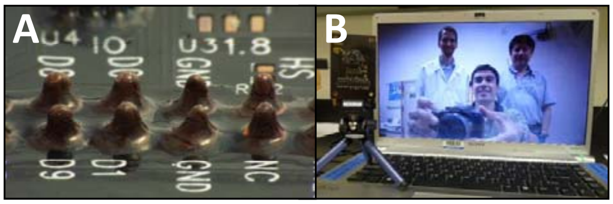

Figure 4. A) Photograph of a section of the 26-pin through-hole connector bonded with nanocopper. B) Demonstration of fully functional camera board using only nanocopper.

Each camera board was subjected to a suite of electrical tests at the component level, such as Takaya 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 4B.

4 CONCLUSIONS

In summary, 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 an electronic assembly material. The electrical conductivity of nanocopper is already high enough to compete with materials 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 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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