

Novel Precipitation Method for Producing Dispersed Crystalline Copper Powders for Electronic Applications

Dan V. Goia, Ionel Halaciuga, and Syllas LaPlante
Clarkson University, Potsdam, NY 13699-5814, USA
Tel.: 1-315-268-4411; Fax: 1-315-268-2139;
e-mail: goiadanv@clarkson.edu

Abstract

The paper describes a simple environmentally friendly method for preparing dispersed crystalline copper particles by reacting aqueous dispersions of CuCl with Fe(II) citrate. By varying the experimental conditions, it was possible to obtain copper particles with sizes from 0.5 to 1.5 μm . In contrast with other powders precipitated in aqueous solutions, the powders obtained by this method display a very good oxidation resistance. This attribute, along with the simplicity of the process and the absence of polymeric dispersants, makes the described method a versatile and economical route for preparing copper powders suitable for electronic applications.

Introduction

Due to their applications in catalysis, medicine, biology, microelectronics, metallurgy, and energy sustainability, metallic particles are the object of intense research. In the electronic industry, copper is in many situations the best choice as it offers an excellent electrical conductivity at a fraction of the cost of noble metals. For this reason, copper particles of various sizes and shapes are used in large quantities to build conductive structures incorporated in multi layer ceramic capacitors¹, printed circuit boards², and many other electronic devices³. Various methods including atomization⁴, pyrolysis⁵, electrolysis⁶, radiolysis⁷, and reduction of copper salts in reverse micelles⁸ and solutions^{9,10} are available for preparing dispersed copper particles. Among these, precipitation in homogeneous solutions is the most versatile¹¹ approach as it offers a broad range of solvents and a large variety of reductants¹², dispersants, and complexing agents^{13,14,15}. Most dispersed copper powders currently used in microelectronics have an average particle size between 0.5 and 3.0 micrometers and are prepared by precipitation techniques involving high molecular weight polymers/dispersants. As a result, they may contain residual organic matter that can adversely affect their processing into electronic devices. Furthermore, many of these protocols use toxic reagents¹⁶ or result in environmentally undesirable byproducts.

This study shows for the first time, that by using Fe(II) citrate complex as reductant it is possible to reduce rapidly and completely CuCl and obtain well dispersed copper particles in

the absence of polymeric dispersants. Consequently, the resulting particles contain organic residues with low decomposition temperature which do not interfere with their subsequent processing and the consolidation of highly conductive copper layers/structures.

Experimental

Copper (I) chloride (CuCl), trisodium citrate dihydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \times 2\cdot\text{H}_2\text{O}$), and iron (II) sulfate heptahydrate ($\text{FeSO}_4 \times 7\cdot\text{H}_2\text{O}$) were purchased from Alfa Aesar and used without further purification.

The copper particles were prepared by rapidly adding a Fe(II) citrate solution into a vigorously mixed dispersion of cuprous chloride. The reducing Fe(II) citrate solution was prepared by mixing solutions of sodium citrate and ferrous sulfate. After mixing the reactants, the stirring was continued for one hour to ensure the complete reduction of CuCl. Next, the resulting copper particles were allowed to settle and the supernatant was removed. The settled particles were washed several times with deionized water, rinsed with alcohol, separated from the solvent by filtration, and dried at 80°C in vacuum for several hours.

The size and morphology of the solids was assessed by field emission scanning electron microscopy (FESEM) using a JEOL – JSM7400F instrument. The crystalline structure of the copper particles was determined by X – ray diffraction (XRD) with a Bruker D8 diffractometer (Cu K_α 1.5406 Å) and their particle size distribution was measured by laser diffraction using a Malvern Mastersizer 2000s instrument. The thermal properties of the powders were investigated by thermogravimetric analysis (TGA) with a Perkin Elmer Pyris 1 instrument and by thermo-mechanical analysis (TMA) using a TA Q400 analyzer. The complete reduction of the copper salt was assessed by testing for the presence of soluble copper ions in the supernatant with a strong reductant (sodium borohydride) and by the XRD analysis of the precipitated solids.

Results and discussion

When the reducing solution {Fe(II) – citrate complex} was added to the CuCl dispersion at room temperature, the reduction of Cu(I) species started in approximately 30 seconds. The formation of the copper particles was indicated by the emergence of a reddish tint in the green color of the cuprous chloride dispersion. Over the remaining reduction time (1 hour) the green color completely disappeared and the dispersion acquired the typical red-pink color characteristic for dispersions of fine copper particles. The inspection of the isolated solids by field emission electron microscopy revealed well dispersed Cu crystalline particles, approximately 1.5 μm in diameter (Figure 1a). The nucleation of the copper phase was faster when the precipitation was carried out at 60°C, the emergence of the red color being observed after only 2-3 seconds. The faster reduction had a noticeable impact on the formed particles, their average size decreasing to ~0.5 μm (Figure 1b).

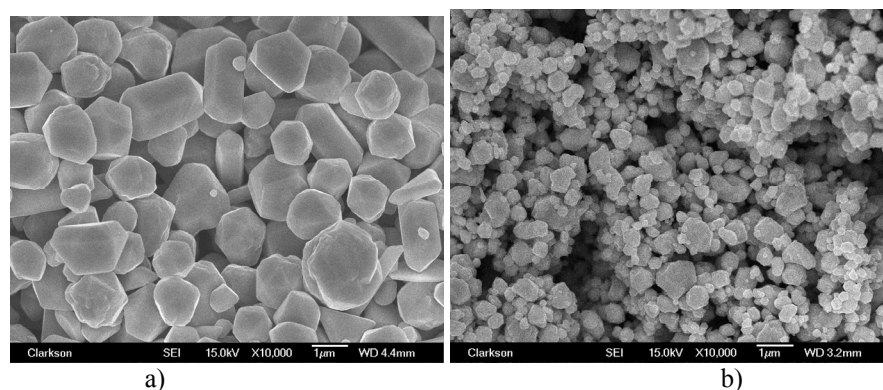


Figure 1. FESEM images of copper particles obtained at: a) room temperature, and b) 60°C.

The particle size analysis (Figure 2) confirmed that the formed copper particles were well dispersed, the average diameter of 2.2 µm being in good agreement with the size observed by electron microscopy.

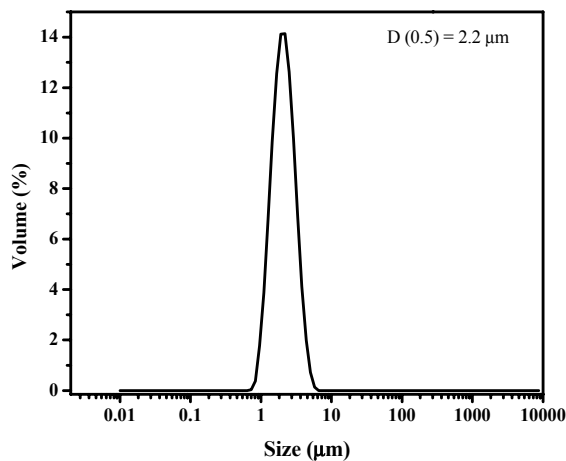


Figure 2. Particle size analysis for copper particles obtained at room temperature.

The slight difference between the measured average size distribution value and the average diameter observed by electron microscopy indicates minimal particle aggregation. For this reason, it is very likely that the powders can be easily dispersed to yield smooth conductive pastes and form well packed ‘green’ deposits of copper particles. A further confirmation of the non-aggregated nature of the particles and their ability to pack well was the high tapped

density (TD) of the dried powders. For the particles obtained at room temperature the TD was 3.6 g/cc while for the smaller particles obtained at 60°C the value was 2.9 g/cc.

The X – ray diffraction pattern for the isolated solids (Figure 3) was at both low and high temperature characteristic of pure metallic copper. This finding and the fact that unreduced copper ions were not present in the removed supernatant indicated that the copper salt was completely converted to copper metal.

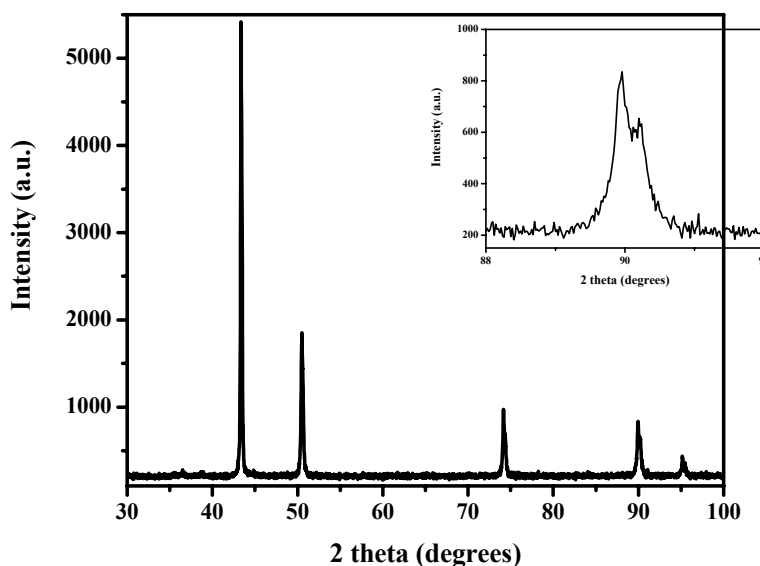


Figure 3. X-ray diffraction pattern for the copper powder precipitated at room temperature

The X – ray analysis revealed that the temperature had a significant effect on the crystallinity of the resulting copper particles. The powders obtained at room temperature were very crystalline as indicated by the very narrow diffraction peaks and by the splitting of the higher reflection peaks ($2\theta = 90^\circ$) caused by the $K_{\alpha 1}$ and $K_{\alpha 2}$ components of the incident radiation (Figure 4, inset). The crystallite size of ~ 42 nm, estimated with the Scherrer equation¹⁷, is higher than the values typically measured for copper powders precipitated in aqueous medium and comparable to those measured for copper powders produced by the polyol process¹⁸. The faster nucleation and reduction at 60 °C resulted in particles with a decreased crystallite size (~ 24 nm).

The dried copper particles displayed a very good oxidation resistance at room temperature, the pink color typical of non-oxidized copper surface persisting even after prolonged exposure to the surrounding environment. This attribute is a significant advantage as it

provides a better shelf life and less demanding packaging and storing conditions. When the copper particles prepared at room temperature were heated in air they gained ~24.5% in weight (Figure 4). This gain is very close to the theoretical weight gain of pure copper and is a further indication that the Cu(I) salt was completely reduced to metallic copper.

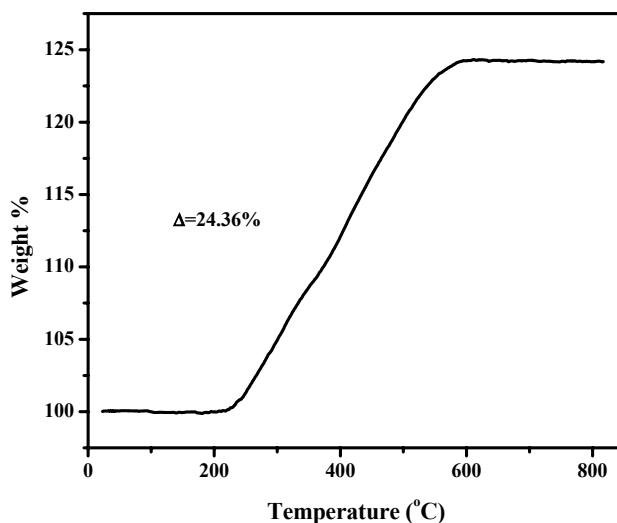


Figure 4. TGA of copper particles shown in Figure 1a

The delayed and slow oxidation of the particles when heated, both desirable attributes in the manufacturing of electronic components, is very likely the result of their highly crystalline nature and reduced internal grain boundaries. The thermogravimetric analysis of the powder in reducing atmosphere was an additional confirmation of the complete reduction of the copper precursor, as only a weight loss of 0.49% was registered at 700 °C in forming gas (a mixture of 95% nitrogen and 5% hydrogen) (Figure 5).

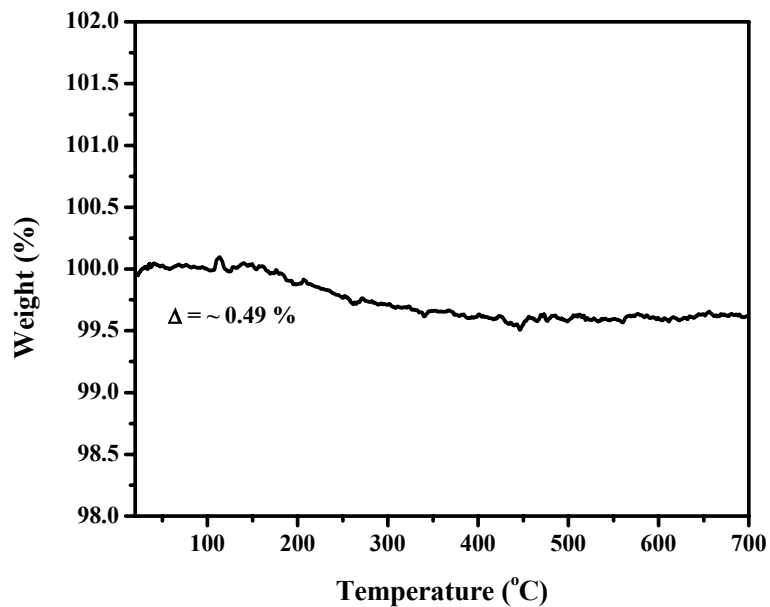


Figure 5. Thermogravimetric analysis of the copper particles precipitated at room temperature.

Since no polymeric dispersants were used in the precipitation process, the nonmetallic residue likely consists of copper oxide and adsorbed citrate molecules. As both compounds decompose at low temperature, it is unlikely that they leave any residue after the binder burn-out or interfere with the sintering of the particles during the fabrication of electronic components.

The thermo-mechanical analysis of the copper particles prepared at room temperature displayed an improved behavior over existing commercial powders, as the data does not show the typical expansion at high temperatures (Figure 6).

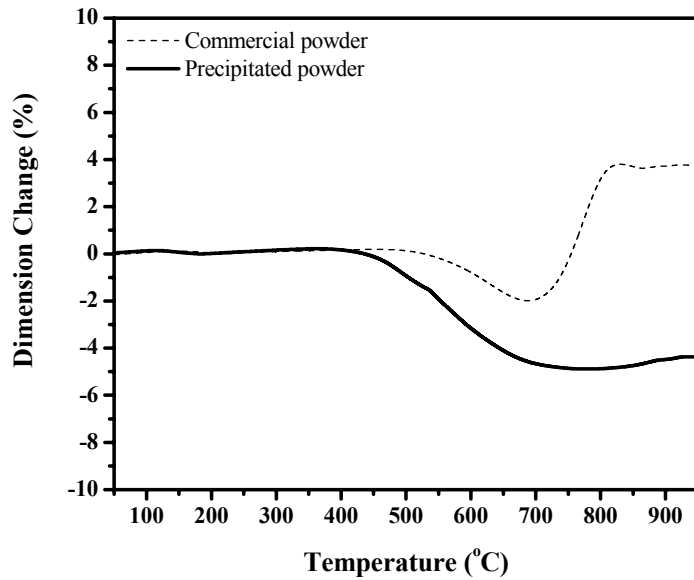


Figure 6. Thermomechanical analysis of a commercial copper powder (- -), and the copper powder prepared at room temperature (-).

The lack of the thermal expansion at high temperature is a desirable attribute in electronic applications as it can prevent the mechanical stresses that cause delaminations and often catastrophic failure in multilayer structures (MLCC's, LTCC's). In contrast, most commercial powders usually need to be subjected to post-precipitation treatments to eliminate such problems.

Conclusions

This study presents a rapid and convenient precipitation protocol for producing copper powders suitable for applications in electronic industry. The system described is attractive as it offers the ability to tailor the size of the resulting copper particles and provides powders with high crystallinity and good oxidation resistance. The simplicity of the process, the high concentration of metal, the lack of polymeric dispersants, and the thermal behavior of the precipitated powders make this process an advantageous route to produce cost effectively and in an environmentally responsible manner dispersed copper particles on large scale.

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