A STUDY OF THE ELECTRICAL RESISTIVITY OF SINTERED COPPER NANOPARTICLES

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Abstract

Microscale Selective Laser Sintering is a novel Additive Manufacturing process being built to fabricate parts with microscale resolution for applications in the microelectronics industry where small feature sizes are critical. This process works by sintering nanoparticles to give a better control on feature sizes. To get an idea of the mechanical strength of the parts fabricated with this process, it is important to be able to quantify the density in the manufactured parts. However, the parts fabricated with this process are too thin to physically handle enough to measure the density, but it is possible to measure the electrical resistance of these parts. So, in order to get the density of these parts, the relationship between electrical resistance and density has to be known. As such this paper presents an experimental study done on sintered copper nanoparticles to relate density to electrical resistance.

Introduction

With the drive towards creating microprocessors capable of handling rising computational demands at record speed, there is a need for processes able to fabricate high aspect ratio 3D interconnect structures. The 3D manufacturing capabilities inherent in Additive Manufacturing (AM), makes AM technology a potential solution to fill this need in the microelectronics industry. However, current commercially viable metal AM processes have minimum feature sizes on the order of hundreds of micrometers which is too high for the sizes of parts needed in the microelectronics industry [1,2]. Microscale Selective Laser Sintering (μ-SLS) is a solution to this limitation.

μ-SLS is an AM process where energy from a laser is used to fuse particles together into a full part. μ-SLS uses the sintering of nanoparticles to give a better control on the feature sizes of the manufactured parts. Because the resolution of the part is restricted to the size of the particles that make up the part, the particles have to be smaller than the desired resolution. Therefore, to achieve submicron resolution the particles that make up the part have to be nanosized. In addition to the nanoparticles, a Digital Micromirror Device (DMD) array is used to achieve spot sizes of about 1 μm. The combination of the use of a DMD array and carrying out sintering on nanoparticles, makes it possible for the μ-SLS system to create parts with submicron resolution [3-5].

Because the parts fabricated with the μ-SLS system are so small, it is difficult to measure physical properties like the density of the manufactured parts. Measuring the density of the parts fabricated allows for knowledge to be gained of the degree of porosity in the manufactured parts, which gives a measure of the strength of the parts made from the μ-SLS system. Thus, it is important to be able to quantify the degree of densification of the sintered parts. While the sizes of the manufactured parts make it difficult to measure their density, it is however much easier to measure the electrical resistance of the fabricated parts using a four-point probe measurement setup. To be able to get a sense of the physical properties of the parts using the electrical resistance measurements, the connection between the electrical resistance and density has to be determined. This paper presents the approach to determining the relationship between electrical resistance and density for copper nanoparticles. Sintering is performed using the μ-SLS system and the density of the manufactured parts as a function of the sintering parameters is presented, by mapping the measured electrical resistance to the density.

Methodology

The map between resistance and density for copper nanoparticles was derived from performing sintering experiments on copper nanoparticle pellets. These experiments were carried out on CI-005 copper nanoparticle ink supplied by NovaCentrix. 2 mL of the ink was placed in a petri dish to dry. Once dry, the dried ink was formed into pellets in crucibles and placed in a furnace to sinter. The density of the pellets of dried nanoparticles was measured from the mass and the volume of the pellets. The density was measured after sintering in the furnace, and then the relative change in density was calculated using these measured density values. The experimental flow for the measurements performed on the copper nanoparticle pellets is shown in Figure 1.

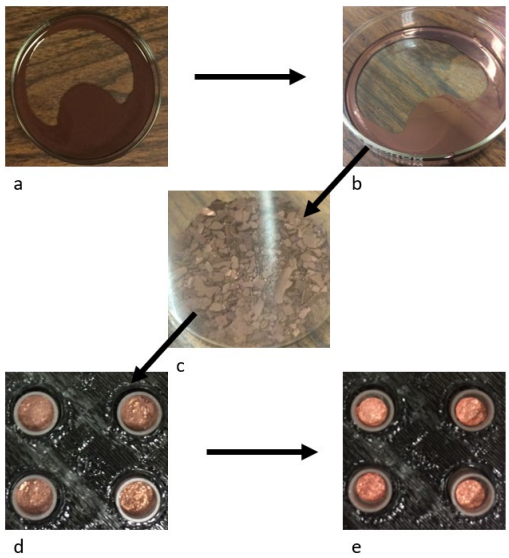

Figure 1. Experimental procedure. a. Copper nanoparticle ink. b. Dried ink. c. Scraped off dried flakes. d. Pellets in crucible before sintering. e. Pellets in crucible after sintering

After sintering of these copper nanoparticle pellets, the electrical resistance of the sintered pellets was also measured using a four-point probe setup. The four-point probe setup uses four different contact points to measure the resistance in a circuit, thereby eliminating contact resistance from the resistance values measured [6]. In the four-point probe technique, current is flowed into the material through the outer probes, and the potential difference across the middle probes is measured. The resistance is then calculated using Ohm's law as the ratio of voltage difference to current. However, since the degree of sintering is not even throughout the sintered pellets, the electrical resistance could not be measured using a simple four-point probe setup across the surfaces of the sintered pellets. Instead, a new measuring tool had to be designed to take advantage of the four-point probe resistance measurement setup, while also measuring the resistance through the pellets. The requirements for the tool used to measure the resistance are listed below.

i. Allow for the use of the four-point probe for measuring resistance, ensuring that contact resistance does not feed into the resistance values measured
ii. Measure resistance through the pellets. This gives an average of the resistance in the pellet regardless of the degree of sintering at the top or bottom of the pellets
iii. Have repeatable probe locations. That is, the location of the probes on the pellet should change as little as possible with each new experimental run to ensure repeatability between measurements on different samples
iv. Should be able to carry out the resistance measurements regardless of the degree of sintering in the pellet

Going off these requirements, it became clear that all of these requirements could not be met using a single pellet. To measure resistance through a pellet requires probes being placed on both the tops and bottoms of the pellets. Trying to do this on the same pellet would result in difficulties with positioning the pellets in a manner that ensures that the probe locations on the surface of the pellets are always repeatable. So, to satisfy the requirements, a circuit was designed that would allow current to flow through the sintered pellets in a way that probe positioning is repeatable. The CAD drawing for this system is shown in Figure 2.

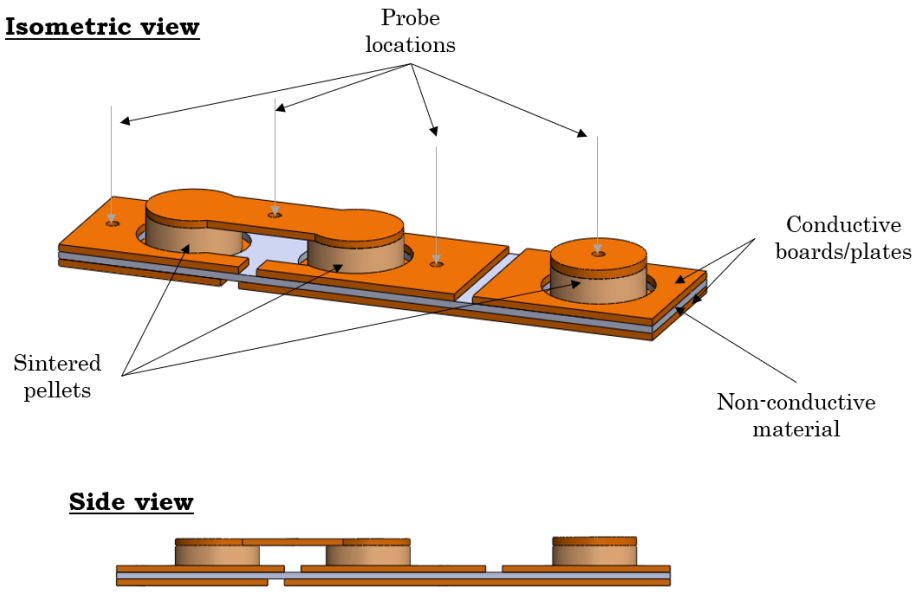

Figure 2. CAD drawing for measuring resistance through sintered pellets

The setup in Figure 2 allows the use of the four-point probe using 3 pellets sintered to the same degree to calculate the contact resistance. Current is passed into the circuit through the leftmost probe (grey arrow) and it flows through the bottom board to the first pellet and then through the first pellet to the top orange conductive material. The second probe allows for the measure of the voltage drop through the second pellet, where the current flows through the pellet to the second bottom board, disconnected from the first through the break in the material. The current flows through the last pellet to the rightmost probe. This satisfies all the requirements as the four-point probe setup is used, resistance is measured through the pellet, the probe locations are repeatable because they are set in the tool, so even when the sintered pellets are changed the probe locations remain the same. The embodiment of this design is shown in Figure 3.

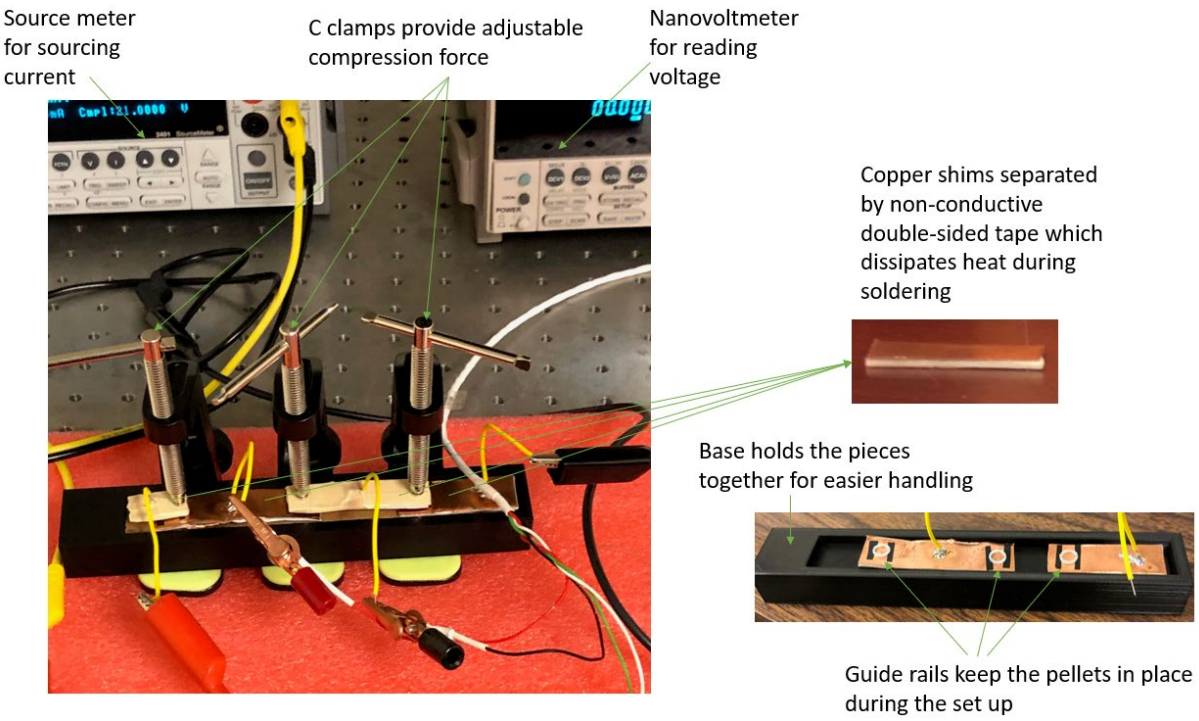

Figure 3. Final apparatus used for measuring the resistance of the sintered copper pellets

The C-clamps were added to ensure enough contact between the pellets and the bottom and top boards, so that there was no additional resistance introduced as a result of incomplete contact between the pellets and the boards. With the use of the adjustable C-clamp, the amount of force needed to ensure contact between the pellets and the boards could vary until the optimum force is found which leads to the minimum resistance measured. Copper shim boards are used as the low impedance material for passing current between the pellets because the copper shims are flexible enough to bend, and conform to variations in the heights of the pellets being measured. The probe locations in the final setup are fixed by soldering wires to the copper shim boards as shown in Figure 3. These wires are then connected to the current source, which provides the current needed for the resistance measurements, and the voltmeter which measures the resulting potential difference. A thick piece of non-conductive tape was added to the coper shims to improve the strength of the solder joints. Adding the tape gave a means of heat dissipation which allowed for better soldering of the wires to the thin copper shims.

Once the measurements of the density and the electrical resistance of the sintered copper pellets were concluded, experiments were performed on the μ-SLS system to measure the electrical resistance of the manufactured parts as a function of the laser sintering parameters. These experiments were performed using the same copper nanoparticle ink used for the pellet measurements discussed above. An image of the μ-SLS system is shown in Figure 4.

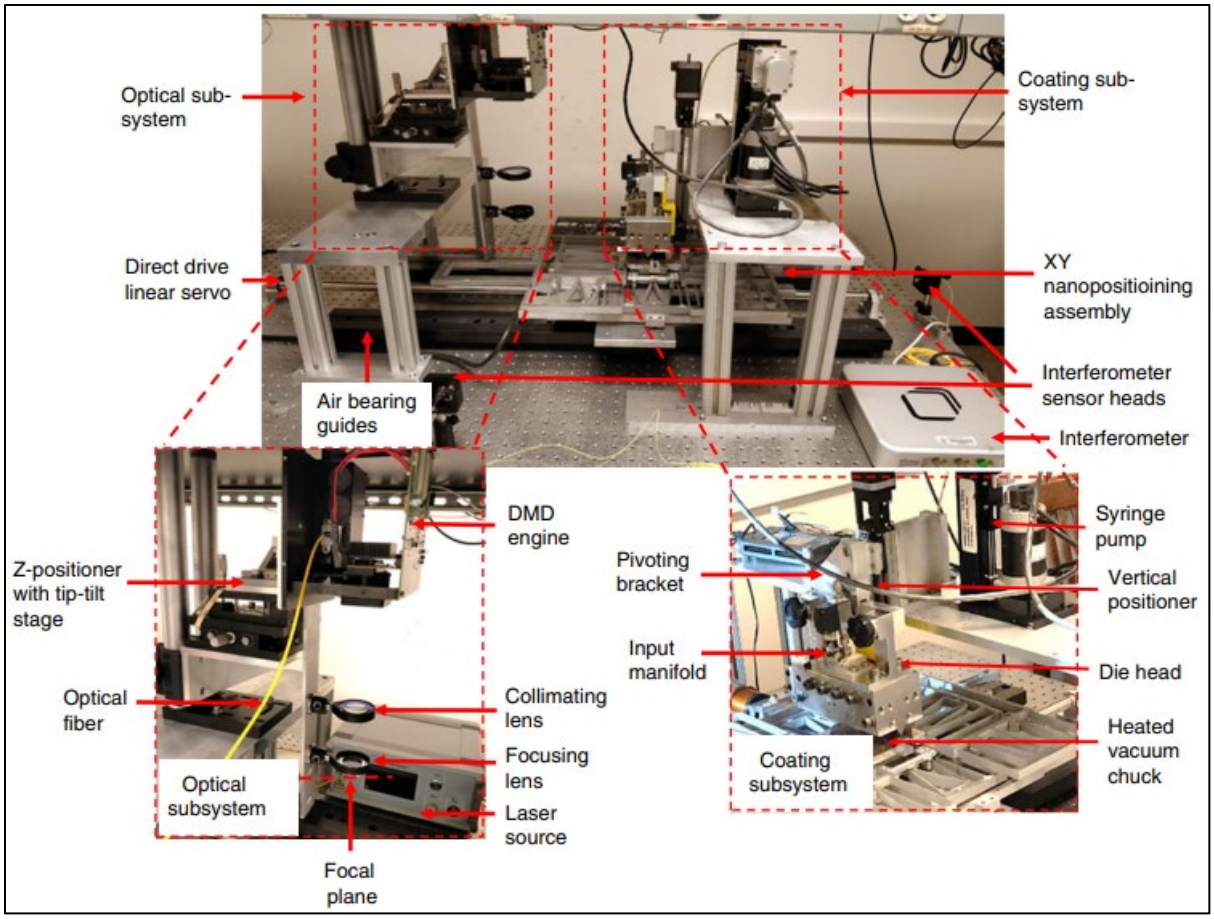

Figure 4. Microscale Selective Laser Sintering System with the subsystems highlighted

The copper nanoparticle ink was deposited onto glass substrates and then rectangles were sintered at varying laser exposure times, using the same laser power for sintering. Examples of sintered rectangles from the μ-SLS system are shown in Figure 5. The electrical resistance of these rectangular samples was then measured using a simple four-point probe setup as shown in Figure 6, and the relationship between electrical resistance and laser exposure time was derived. The results gotten from the pellet experiments as well as the experiments performed on the μ-SLS system are presented and discussed in the Results section.

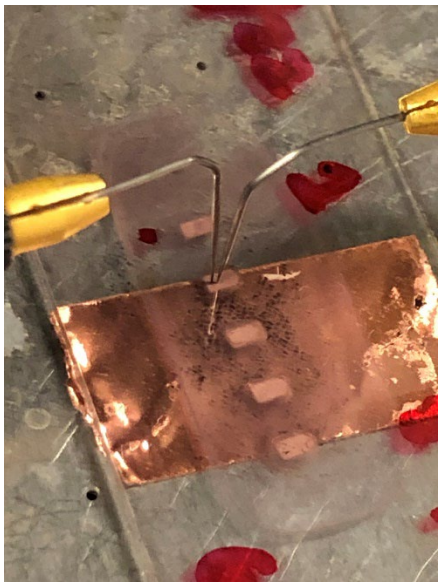

Figure 5. Rectangles sintered by the μ-SLS system

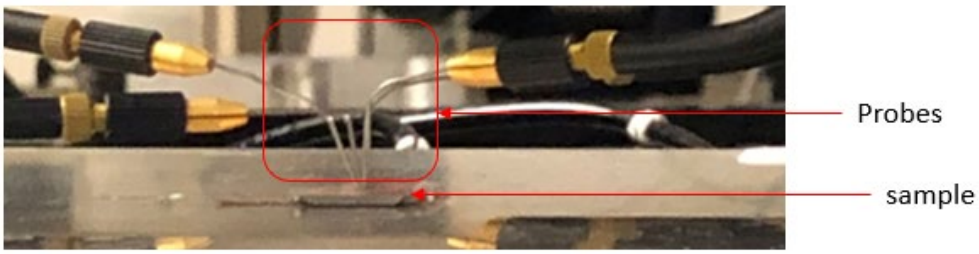

Figure 6. Four-point probe setup for measuring the electrical resistance of the samples made with the μ-SLS system

Results

The experiments were performed on the sintered pellets as described in the Methodology section. For each of the pellets, a range of currents was sourced into the circuit and the potential difference at each current measurement was observed. The resistance for the measurement was then taken as the slope of the current-voltage curve. The results of the experimental runs are collated in the plot in Figure 7. The electrical resistivity is calculated using equation 1.

$$\rho = \frac{RA}{h} \qquad \text{Equation 1}$$

Where R in this equation is the derived resistance from the voltage-current curve, A is the cross-sectional area and h is the height of the pellet. This gives the uncorrected resistivity which is the quantity shown in Figure 7. For each densification point, three measurements are taken, and the value reported in the curve in Figure 7 is the average of these three resistivity values and the

error bars are gotten from the standard deviation of these measurements. The error bars in the densification change are gotten from propagating the error of each measurement taken to calculate the change in density. In general, the curve in Figure 6.22 shows the expected trend of decreasing resistance with increasing degrees of densification of the pellet. The rate of decrease is steeper at lower rates of densification and becomes less steep as the degree of densification increases.

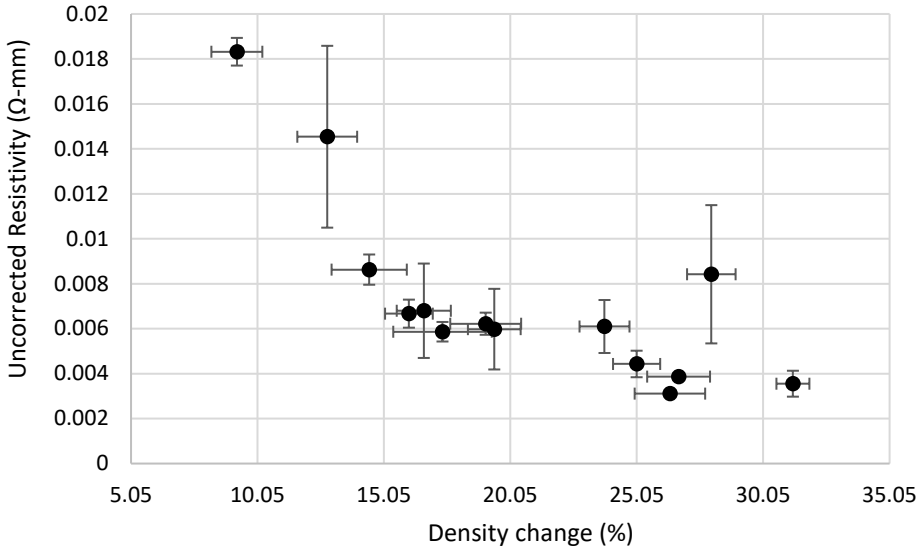

Figure 7. Uncorrected resistivity as a function of densification

The results in Figure 7 do not take into account the geometric corrections which have to be applied with four-point probe tests when the thickness of the sample is much smaller than the spacing between the probe locations. These corrections are a result of the boundaries in the relatively thin pellets which limit the possible current pathways [7, 8]. Haldor Topsoe [7] found that for a sample with finite thickness, the correction factor is a function of the quotient of the thickness and spacing between the probe locations given in Figure 8.

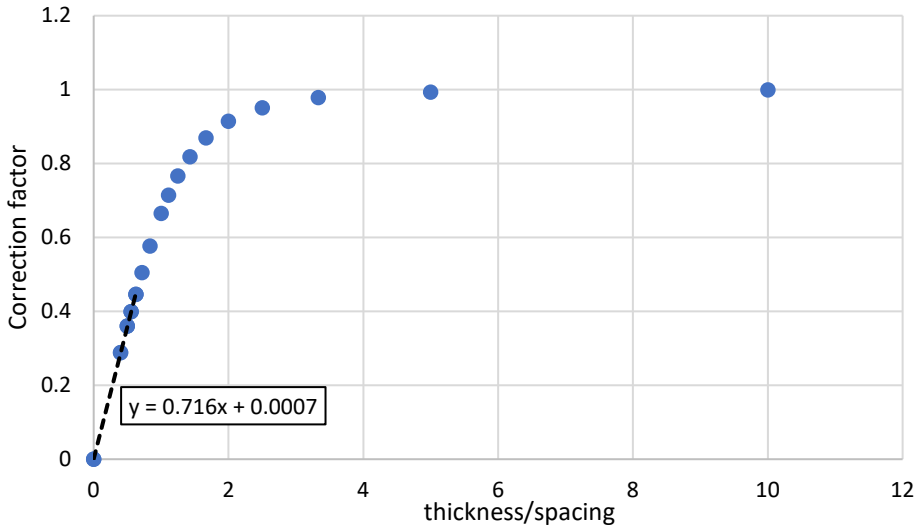

Figure 8. Correction factor as a function thickness and spacing [7]

The copper pellets used in this measurement have maximum heights of 2 mm and the average spacing between the probe locations is 44 mm, so the thickness/spacing is about 0.045 which falls in the area of the curve in Figure 8, where the correction factor applied to the resistivity measurement is much less than 1, and as such is very significant. The equation of the line in the pertinent region was used to calculate the value of the correction factor for the measurements. The corrected resistivity is thus the uncorrected resistivity multiplied by the correction factor. Applying these correction factors to the resistivity measurements yields the corrected resistivity curve in Figure 9.

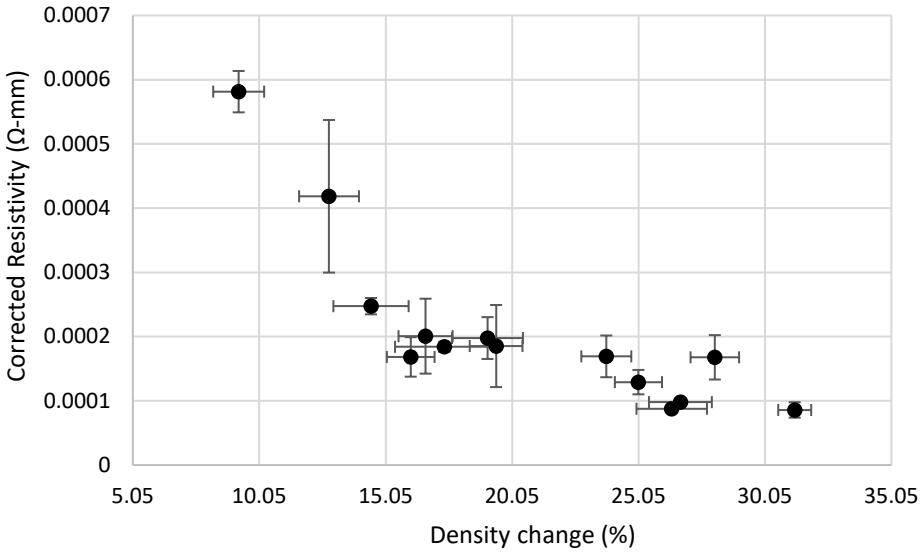

Figure 9. Corrected resistivity as a function of densification

The resistivity in Figure 9 asymptotes towards 8.58x10-5 Ω-mm. The resistivity of bulk copper is 1.72x10-5 Ω-mm, which means the steady state resistivity recorded from the sintered pellets is roughly 5 times the value of bulk copper. A sintered ink resistivity of 9x10-5 Ω-mm was quoted from the ink manufacturer, however this value is dependent on the fabrication process. To determine how close to fully sintered the pellets are, it is important to know what the final resistivity of the copper ink is for the furnace sintering fabrication process used for making these copper pellets. The minimum resistivity achievable with the ink was determined by spin coating a really thin layer of the copper nanoparticle ink onto a glass substrate and then heating the substrate with the ink up in the furnace for 5 hours, flowing hydrogen and argon, as done with the pellets. After doing this, the resistance was measured using the four-point probe setup for flat substrates as shown in Figure 6. The resistivity measurements gave a minimum resistivity of 6.81x10-5 Ω-mm, 3.96 times the resistivity of bulk copper, for the ink sintered using the furnace sintering fabrication process. Figure 10 gives the relationship between density change and the ratio of the measured resistivity to the fully sintered resistivity.

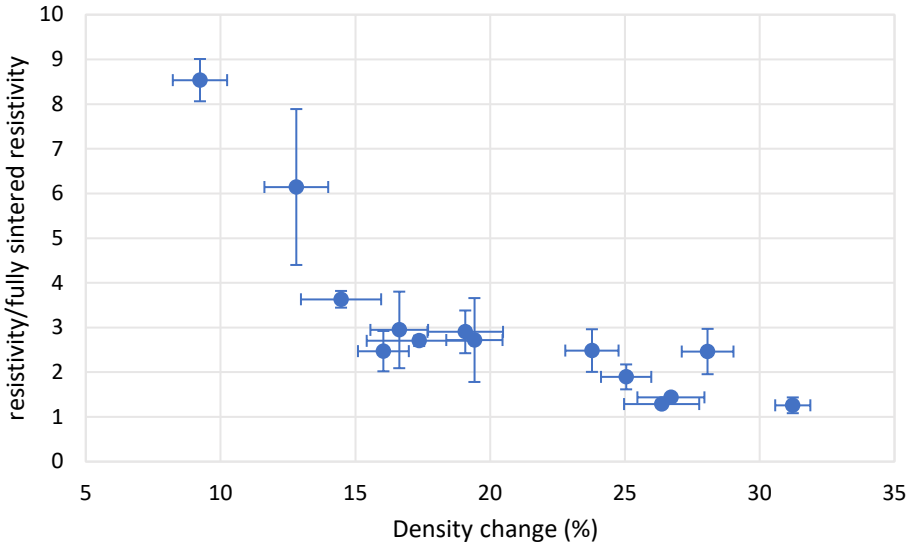

Figure 10. Ratio of resistivity to fully sintered resistivity as a function of densification

Once the relationship between the density and electrical resistance was measured, the experiments were performed on the μ-SLS system and the resistance as a function of the laser exposure time was gotten. The laser exposure time is denoted in units of laser Burst Counts (BC). The results from performing these experiments are shown in Figure 11.

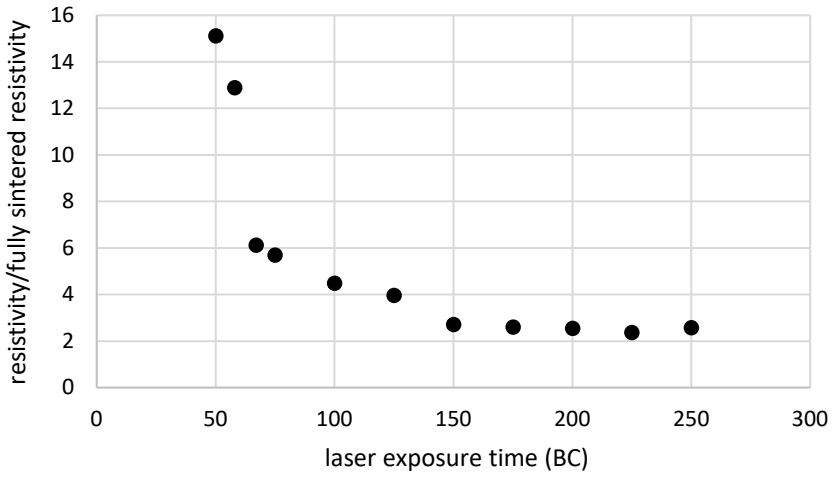

Figure 11. Resistivity as a function of laser exposure time

To map these values back to the densification associated with each laser exposure time, the data in Figure 10 was fit to an exponential curve, giving density change as a function of the resistivity. Once this relationship was gotten, the resistivity values from the μ-SLS system were mapped back to rates of densification. The curve fit gotten from the pellet data is shown in Figure 12. This curve fit is gotten from fitting the data from the pellet experiments to the exponential curve in Equation 2.

$$density\ change\ (\%) = 0.35e^{-0.43x} + 0.09 \qquad \text{Equation 2}$$

Where x in the equation is the resistivity ratio against the fully sintered resistivity. The curve of densification as a function of the laser exposure time, gotten from the curve fit in Figure 12, is shown in Figure 13.

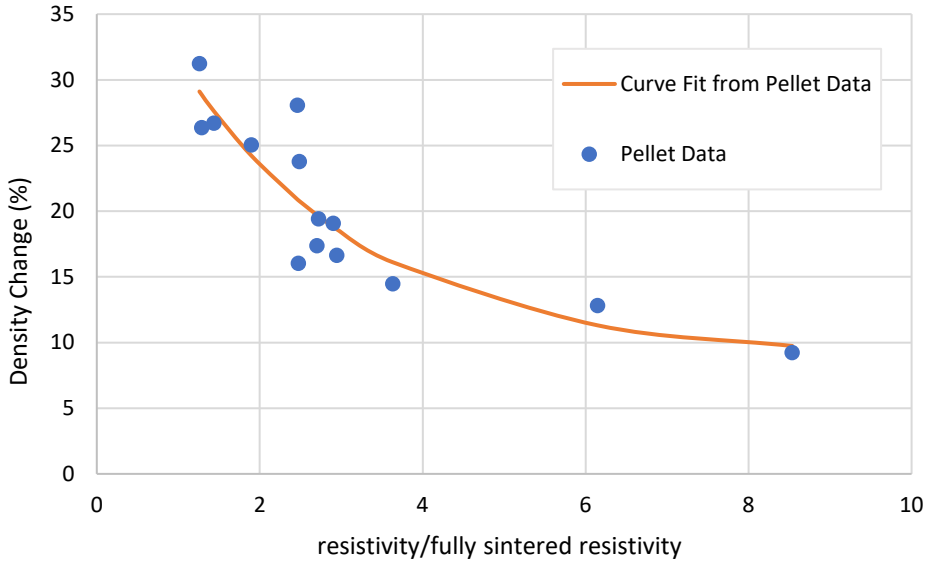

Figure 12. Curve fit of the pellet data for mapping the electrical resistivity measurements from the μ-SLS system to densification rates

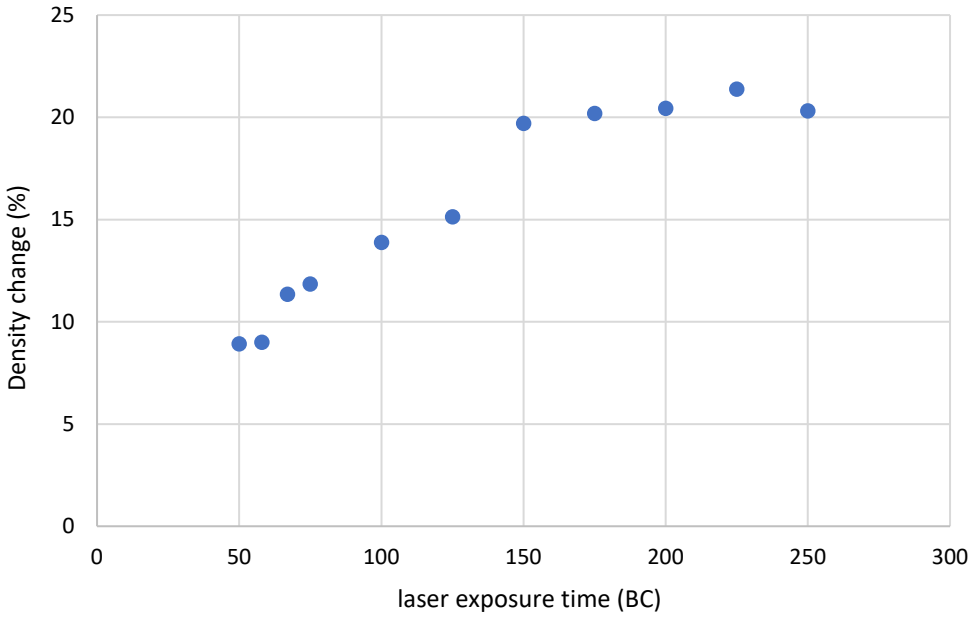

Figure 13. Densification as a function of laser exposure time

To determine how well the densification curve from the laser matches the expected densification trend from the experiments, the densification information in Figure 13, was plotted against previously derived densification information, for the copper nanoparticle pellets sintered

at 450 °C in the furnace [9]. This comparison is shown in Figure 14. In Figure 14 the burst counts are scaled by a factor of a 100, to account for the differences in time scales for sintering in a furnace, which sinters in minutes, versus sintering on the laser, which sinters in seconds. Figure 14 shows a very good agreement between the rate of densification measured in the furnace and that gotten from sintering with the laser in the μ-SLS system. The average error recorded between both data sets is 7.6%.

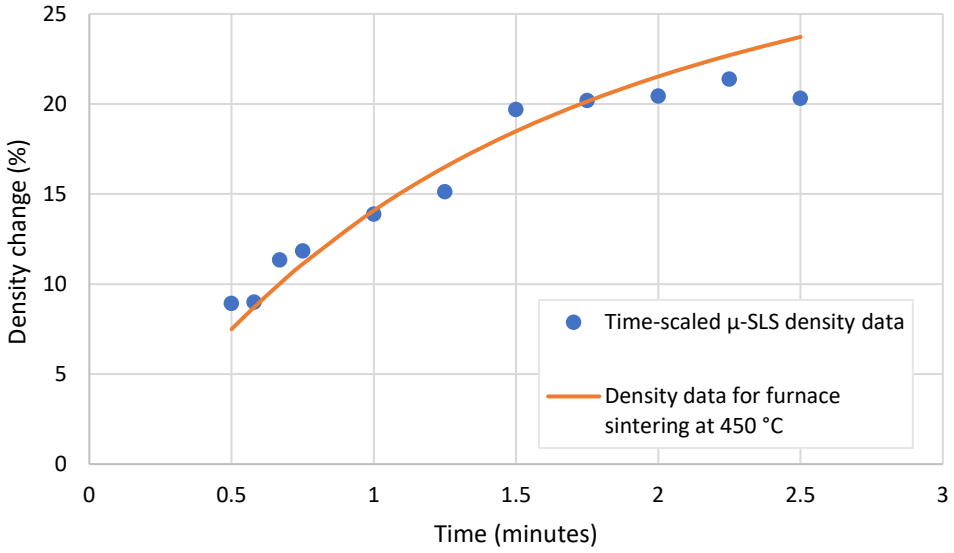

Figure 14. Comparison between the densification from the μ-SLS system and furnace sintering

Conclusion

To gain an understanding of the physical properties of the parts fabricated from the μ-SLS system, it is important to be able to quantify the density of these parts. However, measuring density on parts fabricated from the μ-SLS system is challenging because of the sizes of the manufactured parts. In parts this small, it is easier to measure the electrical resistance. This paper presents experimental procedures to determine the electrical resistance of copper nanoparticles as a function of the density of the parts fabricated from the μ-SLS system. This relationship was used to calculate the density of parts fabricated from the μ-SLS system as a function of laser exposure time. Comparing the resulting density curve to previously measured densification information for the same copper nanoparticles showed very good agreement between the densification measured from the μ-SLS system and the expected densification trends gotten from furnace sintering experiments.

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