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Full Length Article

Effect of size, morphology, and synthesis method on the thermal and sintering properties of copper nanoparticles for use in microscale additive manufacturing processes

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ABSTRACT

Additive manufacturing using nanoparticles (NPs) is a growing field due to the ever-increasing demand for parts with smaller and smaller features. Of particular interest are copper nanoparticles (Cu NPs) due to the ubiquitous use of Cu in microelectronics applications. There are numerous methods currently available to synthesize Cu NPs in both powder and ink forms. However, the effect of how the NPs are manufactured on the sintering properties of the NPs produced is not well understood. This paper shows that NP size, morphology, and synthesis method can have a significant effect on the sintering temperature and sintering quality for Cu NPs. In addition, surface coatings and surfactants used in Cu NP inks can help to reduce agglomeration in the dried NP samples, prevent oxidation of the Cu NPs, and restrict the sintering of the Cu NPs at lower temperatures due to the need to thermally remove the surface coatings before sintering can occur. Therefore, these coatings improve the Cu NP packing density and increase the temperature required for necking to occur which leads to better sintering of the Cu NP ink samples. It is also observed in this paper that most of these surface coatings are removed during the sintering processes leaving the sintered parts with a much higher Cu percentage than contained in the original NPs. However, at temperatures near the melting temperature of the Cu NPs, the surface coatings can start to graphitize and hinder the fusion of the NPs. Therefore, the optimal sintering conditions for Cu NP inks are at temperature high enough to break down the polymer surface coating on the NPs but low enough that the Cu NPs do not start to melt and that graphitizing of the surface coatings does not start to occur.

1. Introduction

In most commercial sintering applications, powders with particle size on the order of tens of microns are used as raw materials and do not require an extensive study of the material properties as their properties are similar to the bulk properties of the material. However, as the size of particles decreases to less than a micron, the divide between the bulk material properties and nanoparticles' (NPs') properties becomes wider and many new phenomena are encountered too. Thus, to achieve good quality sintered parts using NPs, it is important to have an understanding about the different phenomena that are specific to only NPs like agglomeration of NPs, melting point depression, early onset of sintering and so on. This study was primarily directed towards that objective i.e. to determine the effect of size, morphology, surface coating and synthesis methods on the physical, chemical and thermal changes that these particles undergo while being heated during the sintering reaction.

Metal selective laser sintering (SLS) is an additive manufacturing technology that uses a high-power laser to locally heat and fuse metal particles together into a mass that has a desired three-dimensional shape. In this process, the metal powders are initially spread into a thin layer to form a metal powder bed. The laser then selectively scans the powder bed and fuses the metal powders on the surface of the powder bed together at selected locations based on a previously generated CAD file. After one layer of the metal powder is sintered, the powder bed is lowered by one layer thickness. Another layer of the metal powder is spread onto the powder bed creating a new metal layer that can be scanned and sintered. The process is repeated until an entire three dimensional part is built up [1,2]. The smallest feature sizes that commercially available sintering machines can currently typically achieve are on the order of hundreds of microns due in part to the microscale powders typically used in the sintering operation. To produce parts with finer feature sizes, the use of nanoscale powders will be required. Therefore, this study is focused towards analyzing the thermal and

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physical properties of nanopowders within the powder bed of a microscale selective laser sintering (μ-SLS) system that is designed to be able to achieve 1 μm feature sizes [3,4]. The primary application for the μ-SLS system is microelectronics packaging including the fabrication of solder bumps and 3D interconnect structures [3]. Hence, Cu has been chosen as the material to study because of its wide application as interconnection metal in integrated circuits due to its good electrical conductivity and lower cost compared to silver and gold. Also, Cu lines show at least a 40% reduction in resistance for interconnects as compared to aluminum lines and hence decreases the time constant product (RC) value which reduces the interconnect delay and enhances the performance of the chip [5].

To get feature sizes of 1 μm, it is required to use particles at least an order of magnitude smaller than the feature size and hence, NP based powders are used within the μ-SLS system. However, NPs have their own limitations including excessive agglomeration and oxidation. Nanoscale powders possess high surface energies and, therefore, tend to agglomerate in order to reduce the surface energy of the system. Also, since NPs have a high surface area-to-volume ratio, oxidation becomes unavoidable in contact with air and thus, a high vacuum is sometimes required for sintering the nanoscale powders. In addition, van der Waals forces dominate over gravitational forces at the nanoscale which changes the sintering properties of the NPs. It is because of these reasons that the properties of these NPs are significantly different from the bulk properties of the microscale powders [2,6]. Therefore, a thorough analysis of the physical, thermal, and sintering properties of these NPs is required to accurately model the heat transfer that occurs within the NP-based powder bed during the sintering operation and to be able to estimate the power requirements for sintering depending upon the spot size and layer thickness. This analysis is critical in being able to optimize the microscale selective laser sintering process to produce high quality, micron scale features.

Seven samples of Cu NPs were tested for this study. Four of these NPs were received in powder form and the rest of them were received in ink form. These tests were done to comprehensively characterize the different NPs produced by different techniques such as electric explosion of wire, laser ablation synthesis, chemical reduction, and other chemical synthesis methods. The different coatings on these NPs including passive oxide layer, carbon coating, and polyvinylpyrrolidone (PVP) coating also affect the properties of these NPs and hence, the need for these studies to identify the best candidate for use in μ-SLS systems. Certain desirable properties which are sought in the NPs included an average particle size of less than 100 nm with the largest particles not being greater than 200 nm to achieve 1 μm resolution on the final part, low agglomeration tendencies, low levels of impurities so that the sintering process is uniform, low oxidation, and a morphology of the particles that is spherical or close to spherical to improve the specific heat capacity and thus, reducing the total energy required by the particles to sinter [7].

2. Background

The morphology of particles i.e. the shape, size and distribution of particles has been shown and widely reported to affect the mechanical properties of additively manufactured parts. Smaller particle sizes have been shown leading to increased particle packing efficiency in the bed which in turn leads to density closer to the bulk material density and lower surface roughness [8,9]. However, as the particle sizes are reduced, they tend to agglomerate in powder samples. The presence of agglomerates in the bed has been found to negatively affect the flow behavior [10], increased balling up of particles [11], increased porosity and thus lower part density. Similarly, samples with irregular shaped particles have been shown to have higher interparticle friction compared to samples with spherical particles. This higher interparticle friction severely degrades the flow behavior leading to poor layer densities [12]. Since these morphological properties of particles are directly linked to their synthesis process, the synthesis method plays a pivotal role in determining the final properties of the AM part. In addition to the morphological properties, the microstructure and phase evolution of particles and ultimately that of the final part is also highly dependent on the synthesis method as shown by Rafi et al. [13] and corroborated by Slotwinski et al. [14] that the microstructure of the final part depended primarily on the microstructure of the parent powder which was affected by the gas used for atomization in their synthesis process. The variation in microstructure evolution of nanoparticles depending on the synthesis parameters has been an interesting area of study for researchers [15,16] and can be useful in explaining the properties of the final part.

Many different methods are commonly used for the synthesis of Cu NPs and these methods can be characterized into the following categories: 1) chemical synthesis methods, 2) physical synthesis methods, and 3) biological synthesis methods [17]. The common chemical synthesis methods include chemical reduction [18], sono-chemical reduction [19], hydrothermal assisted [20], electrochemical [21], and micro-emulsion assisted techniques [22]. Laser ablation synthesis [23], electric explosion of wire [24], vacuum vapor deposition [25] and mechanical milling [26,27] are some of the more commonly used physical methods. Biosynthesis of NPs primarily involves oxidation/reduction as the main reaction during the production. In biosynthesis methods, metal compounds are usually reduced into their respective NPs by microbial enzymes or by plant phytochemicals with antioxidant or reducing properties [17,28]. In addition, Cu NPs are often coated with protective polymers [29,30] or surfactants [31–33] to prevent their oxidation and agglomeration. Usually, chemical synthesis methods are more effective than physical synthesis at producing uniform NPs because chemical synthesis methods provide better control over the size and morphology of the particles that are produced than the physical methods.

Some of the most commonly used techniques for mass production of NPs are chemical reduction, laser ablation synthesis and electric explosion of wire (EEW). In the chemical reduction techniques, a copper salt is reduced by a reducing agent such as sodium borohydride, hydrazine (N_2H_4), ascorbate, polyol, isopropyl alcohol with cetyltrimethylammonium bromide (CTAB), while glucose is used as the stabilizing agent [30,34]. Laser ablation is a commonly used technique for the preparation of Cu NPs in colloidal form in a variety of solvents [35]. Factors that affect the final NPs produce by laser ablation are the type of laser, number of pulses, pulsing time, and type of solvent used in the ablation process. Electric explosion of Cu wires is also used in the production of Cu NPs. In this method, high-voltage (15–30 kV) and powerful (density 10^{11}–10^{12} A/m^2) impulse (duration 10^{-4}–10^{-7} s) flows through the wire causing it to explode into NPs [36]. In EEW low electric densities, $E/E_S = 0.8$–1.5 where E is the comparative explosion energy and E_S is the sublimation energy of exploded material, are typically used. The limitation of EEW as a method of NPs production lies in a great dispersion of particle diameters (nanometers to 10′s of micrometers) produced by this method [24]. The Cu samples that are presented in this study have been prepared by using chemical reduction, electric explosion of wire, and laser ablation synthesis methods. This paper presents a comparative study of the physical and thermal properties of Cu NPs produced by different methods and for μ-SLS applications.

3. Experimental setup and results

3.1. Effect of synthesis method on the morphology of Cu NPs produced

In order to physically characterize the Cu NPs created using different synthesis methods, Scanning Electron Microscopy (SEM) was used to measure the particle size and morphology of the NPs. Both size and morphology of particles are important to achieve good quality sintered parts with the desired micron scale feature size. These SEM