Cosolvent Selection and Modification of Spray Pyrolysis Process for Pure Metal Particles

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ABSTRACT

Used in a variety of electronic applications as well as powder metallurgy applications, micron-sized metal powders are generated with a number of different techniques. One of the most common techniques is ultrasonic spray pyrolysis. Spray pyrolysis is a rapid, simple method that requires fewer steps in comparison to other atomization techniques. It allows for continuous processing and it is a process that allows for a quick and easy scale-up. Finding a better cosolvent for the precursor solution was the most recent objective in the research involving spray pyrolysis of pure metal particles and is what will be discussed for the bulk of this report. Primarily, cosolvents with low health hazards, high production rates and those that make solid, dense particles were considered. This report will elaborate on how new cosolvents were evaluated and selected and what the future plans of the lab group are.

INTRODUCTION

Used for a number of applications, micron-sized metal powders are especially useful in electronics and powder metallurgy. More specifically in industry, these metal powders might be used for integrated circuitry, multilayer ceramic capacitors or as the interconnect in solar cells. In addition, they might be used in impact energy absorbers or simply in structural materials because of their property differences from solid metal. For the purposes of this project, metal powders were generated and analyzed specifically for use in electronic applications.

To generate particles, the process of atomization is commonly used. Atomization is the disintegration of a liquid sheet into fine droplets in a gas phase. There are a variety of techniques used to atomise liquids, however, the conventional method include forcing the fluid through a small opening, a nozzle, at a high speed. Conventional nozzles are simply too large to produce very fine particles, as the size of the droplet is very dependent on the size of the opening in the nozzle. Therefore, in order to create micron-sized particles, ultrasonic atomization must be used (Rajan and Pandit, 2000).

Ultrasonic atomization, also referred to as ultrasonic spray pyrolysis, is associated with two different methods of atomization. The first is to pass the liquid over an ultrasonic wave and the second is to place it over a transducer (Barreras et al., 2002), which produces ultrasonic vibrations to excite the liquid inside the particle generator (labeled below as the Ultrasonic Nebulizer). A few other common names for the ultrasonic spray pyrolysis method are Aman's process, spray roasting, evaporative decomposition, mist decomposition, spray calcination or liquid aerosol thermolysis (Jain et al., 1997). Typically, ultrasonic spray pyrolysis is useful in making spherical metal or metal oxide particles (Park et al., 2003) and is most useful because it is simple and scalable (Suh and Suslick, 2005). The particle generator experimental set-up used for the experiments described in this report is shown below.

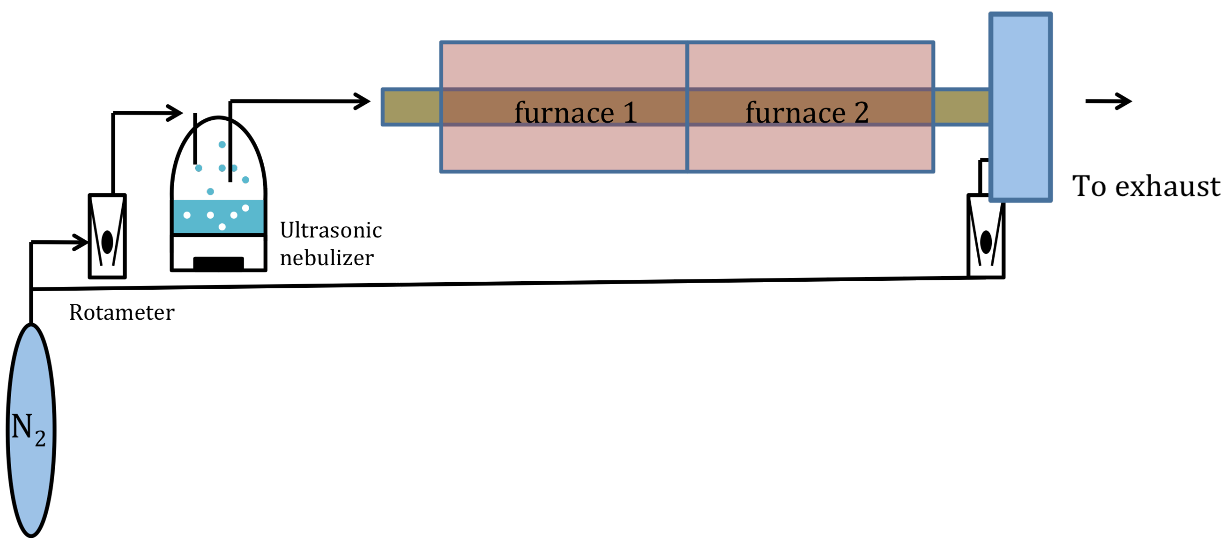

Figure 1: Experimental set-up for particle generation at the University of Maryland.

As shown in Figure 1, liquid (precursor) solution flows into the generator where a transducer excites the solution into liquid particles, which are then carried out of the generator by the carrier gas (nitrogen gas) and through the furnaces. The furnaces are used to evaporate solvent so that the resulting particles caught by the filter are solid metal particles. These particles are easily collected off of the filter paper once the apparatus has cooled. This method, a cosolvent-assisted spray pyrolysis process, was developed specifically to produce pure metal particles. Metal salts, like copper or nickel nitrate, are used along with a cosolvent in the precursor solution fed into the particle generator, which allows elimination of a reducing gas typically necessary for particle formation at lower temperatures (Kim et al., 2003). In an industrial set-up, the particle generator would be larger, containing five to ten to even twenty transducers so that the production rate would match the demands of the company's use.

In the past, those working in Dr. Sheryl Ehrman's laboratory at the University of Maryland have been able to fully understand the properties of the spray pyrolysis technique and interworking of the instrumentation. They have mastered single component particle generation with silver and nickel particles, however atomisation rates were not ideal, which led to further investigation (Ehrman and Zhang, 2011).

The most recent project objective was to find a new cosolvent for use in the precursor solution. In choosing a new cosolvent, there were a few factors to consider. Most importantly, DuPont and those involved at the University of Maryland were interested in the safety of their laboratories so only cosolvents with low health hazards were selected. Also, DuPont was looking for a cosolvent that would increase particle production rate and would produce, solid and dense (not hollow) particles.

METHODS

In order to find a better cosolvent, it was important to understand the ideal conditions necessary to generate the desired particles. Ideal conditions refer to the flow rate of carrier gas, the concentration of the cosolvent in the precursor solution as well as the temperature of the furnaces. To get an idea of the ideal conditions necessary, a series of experiments were conducted.

First, to examine the effects of viscosity, copper particles were generated from a solution of copper nitrate with varied concentrations of glycerol. The precursor solution was placed in a bottle, which was placed on a balance for the duration of the experiment and the particle generator was run as previously described, except the particles were not collected (simply released into the hood) and did not go through the furnaces. For these experiments, the objective was to simply find the rate at which particles were atomizing strictly with respect to viscosity, or how concentrated the precursor solution is with respect to the cosolvent. With the precursor solution continuously on the balance, the mass was recorded every ten minutes in order to determine how quickly particles were atomizing, in other words to determine the atomization rate. A diagram of the experimental set-up is shown in Figure 2 below.

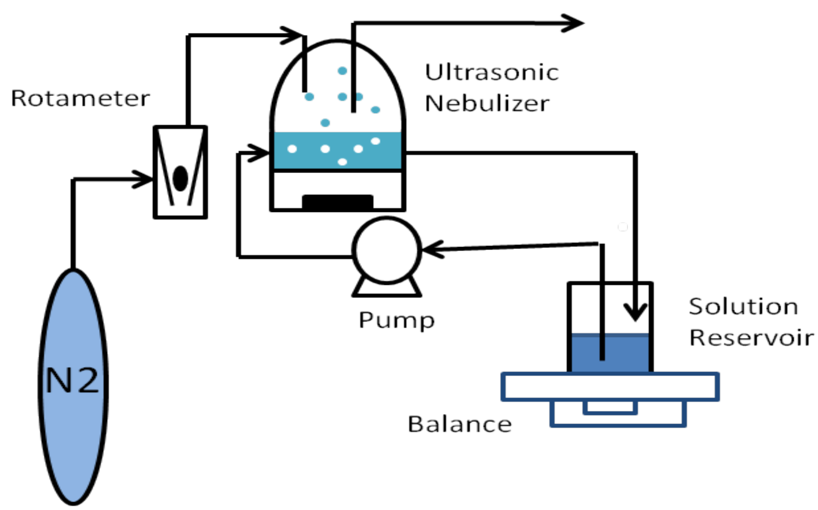

Figure 2: Experimental set-up of atomization experiment.

In addition to testing the atomization rate, research and analysis of different cosolvents was conducted to ensure safety of experimenting with different chemicals. The list was narrowed down to the following, shown in Table 1. To generate this initial list, cosolvents soluble in water were only considered, as this is necessary to create well-dispersed solutions. The group was aware that cosolvents such as ethylene glycol and glycerin could be used to generate particles, so some of their properties were valuable, however, it was these cosolvents that needed replacement. The two properties considered most significantly were flash point and viscosity. A low enough flash point was important to maintain a safe laboratory environment, while a low enough viscosity was necessary to ensure a relatively high production rate. In order to make accurate conclusions from the data, viscosities of each solution were also measured using capillary viscometers.

Table 1: Table of possible options for cosolvents, limited by factors especially viscosity and flash point.

Possible Options for Cosolvents						
Name	**Molecular**	**MW**	**Density (g/cm^3)**	**Flash Point (°C)**	**Viscosity (cp)**	**Solubility**
Ethylene Glycol	$C_2H_6O_2$	62.07	1.115	111	16.1	miscible
Glycerin	$C_3H_3O_3$	92.9	1.261	160	14.1	miscible
Tripropylene Glycol Methyl Ether	$CH_3O[CH_2CH(CH_3)O]_3H$	206.3	0.798	121	6	miscible
Diethylene Glycol Butyl Ether	$C_4H_9OCH_2CH_2OH$	162.2	0.788	106	4.7	miscible
Diethylene Glycol Ethyl Ether	$C_2H_3O[CH_2CH_2)]_2H$	134.2	0.821	102	3.6	miscible
Triethylene Glycol Methyl Ether	$CH_3O[CH_2CH_2O]_3H$	164.2	0.868	135	6.2	miscible
Triethylene Glycol Ethyl Ether	$C_2H_5O[CH_2CH_2O]_3H$	178.2	0.848	129	6.8	miscible
Triethylene Glycol N-butyl Ether	$C_4H_9O[CH_2CH_2O]_3H$	206.3	0.819	138	7.9	miscible

Other important factors to consider were temperature and flow rate. A series of experiments were also conducted, taking temperature as the dependent variable. For these experiments, the particle generator was run with the normal set-up shown in Figure 1; the temperature of the furnaces was the only variation made between experiments. Once the ideal temperature was established, the flow rate was varied as well, to determine if more dense particles could be generated with a lower flow rate than what is typically used (2.5 L/min).

RESULTS and DISCUSSION

The first series of experiments conducted were those examining the atomization rate for a set of solutions of varying viscosities due to variations in concentration of cosolvent. The solutions were made with 1.2 M copper nitrate, deionized water and glycerol in different concentrations measured in volume percentages. The experiment was completed and repeated to ensure that accurate conclusions could be made about the experiment. As is shown in Tables 2 and 3 below, the trends are the same; as viscosity increases, the atomization rate decreases. Therefore, solutions with lower viscosities are preferred as a way to increase particle production rates.

Table 2: First Round of Atomization Experiments Conducted.

First Round of Atomization Experiments		
Solution	Viscosity (mm^2/s)	Atomization Rate (g/min)
1.2 M, 10 vol% glycerol	1.7	0.43
1.2 M, 20 vol% glycerol	2.3	0.22
1.2 M, 40 vol% glycerol	6.5	0.12

Table 3: Second Round of Atomization Experiments Conducted (repeated experiment to ensure repeatability and correct conclusions).

Second Round of Atomization Experiments		
Solution	Viscosity (mm^2/s)	Atomization Rate (g/min)
1.2 M, 10 vol% glycerol	1.7	0.43
1.2 M, 20 vol% glycerol	2.3	0.34
1.2 M, 40 vol% glycerol	5.8	0.08

There seems to be a small deviation in the viscosity measurements of the 40 volume percent solution, with the first round of experiments showing a viscosity of 6.5 mm^2/s and the second round of experiments reporting a viscosity of 5.8 mm^2/s. This error could be attributed to the fact that different solutions were made for each set of experiments so there must have been a human error associated with the measurements in making that particular solution. However, determining this obvious trend between viscosity and atomization rate still makes a significant difference for determining a new cosolvent.

In further analysis of the list of cosolvents and their viscosities and flash points, the list was narrowed down to three potential cosolvents for further experimentation - triethylene glycol ethyl ether, tripropylene glycol methyl ether and diethylene glycol ethyl ether. These cosolvents seem to be good matches for the following reasons: they have low enough flash points and viscosities and minimal health hazards. In more detail, triethylene glycol ethyl ether has a health hazard rating of one and a flash point of 121 °C while tripropylene glycol methyl ether and diethylene glycol ethyl ether both have health hazard ratings of zero and flash points of 102 °C and 129 °C, respectively. These cosolvents have been ordered and will be used in further experimentation.

After choosing new cosolvents to experiment with, additional ideal conditions for the experiments were determined. Scanning Electron Microscope (SEM) photography was used to analyze the particles generated in the series of experiments conducted to find trends related to temperature and carrier gas flow rate. Scanning Electron Microscopy is a method that "uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens" (Swapp, 2011). In analyzing the SEM photos shown in Figure 3 below, it becomes obvious that simply decreasing the flow rate of the carrier gas and increasing the temperature of the furnaces can generate denser, less porous particles. Therefore, in future work, particles will be generated with cosolvents of lower viscosity, using lower carrier gas flow rates (still keeping in consideration that a significant production rate is necessary), and higher furnace temperature settings.

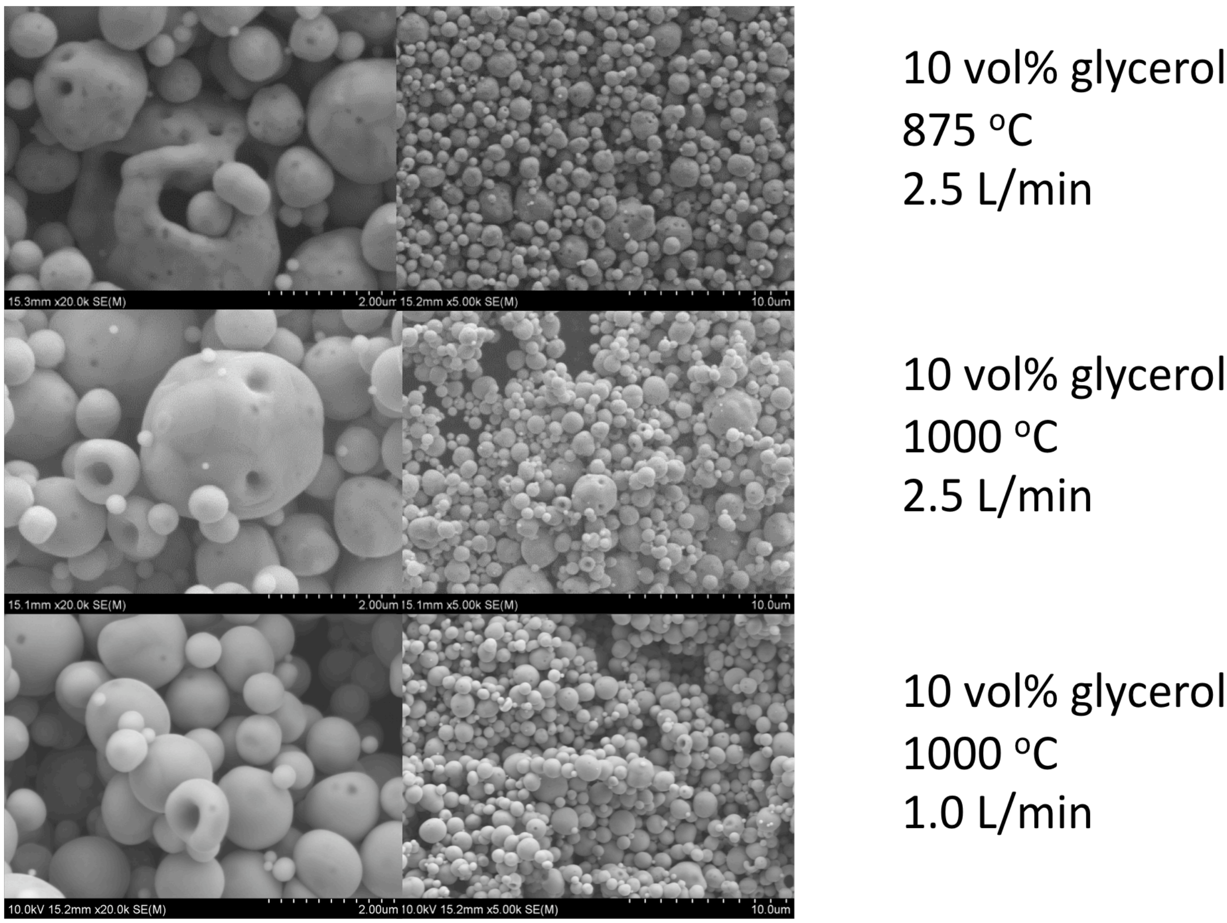

Figure 3: SEM photographs of Copper particles at varying furnace temperatures and flow rates.

CONCLUSION

In summary, ultrasonic spray pyrolysis is an atomization technique that allows quantitative as well as qualitative experiments to be conducted in order to make conclusions about particle generation. In experiments used to generate pure metal particles, it became clear that decreasing viscosity and carrier gas flow rate while increasing furnace temperatures allowed particle production rates to increase with more desirable properties – dense, non-porous, solid metal particles. These findings are consistent with other experiments done by other lab groups, including scientists at the Korea Research Institute of Chemical Technology. They have found that “it is clear that various operating conditions such as temperature, [and] concentration, …influenced the size and morphology of the final particles” in their study of atomization of pure nickel particles from nickel nitrates (Park et. al., 2003). These conclusions will be incorporated in further experimentation with the new possible cosolvents in order to find a more ideal cosolvent for the precursor solution.