Production of Uniform Bronze Powders
by the
Uniform Droplet Spray Process

by

Wesley Harlan Williams

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Abstract

This study showed the capability of the Uniform Droplet Spray (UDS) process to produce
uniform droplets of high liquidus temperature copper-tin alloys. An apparatus was
designed, fabricated, and utilized to produce uniform powders of bronze

Unlike conventional manufacturing techniques such as gas atomization, the UDS
process produces droplets of uniform diameters with variances of 3 to 4%. Uniform Cu-
20%Sn droplets were produced from 100 μm and 175 μm diameter orifices. The potential
applications for uniform metal droplet sprays include the following: uniform metal powder
production, uniform spray coating, near-net shape forming of billets, metal-matrix
composite production, and fabrication of three-dimensional parts.

Although uniform bronze droplets were produced, the modified system is not as
robust as desired and recommendations are made to solve this problem. The UDS process
of creating bronze powders, though not yet perfect, is a viable one for further development.

Thesis Supervisor: Jung-Hoon Chun
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First of all, thank you, Professor Chun, for teaching me so much these last three years.

The only part of this study that was done entirely by me is the actual running of the redesigned apparatus. I was helped, prodded, shown, and in many cases taken by the hand and guided in all other aspects of the study.

Godard Abel did much of this prodding before he left for the great, exiting world of consulting. In particular, he designed the original system and had the idea of adding the viewports. Also he got me the job with UDS (then DBM) that has me typing here today. I would also like to thank all of the UDS team. Chen-An Chen and Pyong-Won Yim, two aged, venerable sages of the process, helped me in many ways, told me when I was doing well, and laughed at me otherwise. Jeanie Cherng taught me patience.

Craig Blue at Oak Ridge National Laboratories provided me with the Cu-20 wt.%Sn that was finally made into powders. He also provided me with insert drawings.

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1. Introduction

Uniform powders of a bronze alloy, Cu-20 wt % Sn, have been produced through the redesign and fabrication of a high-melting point metal spraying system used by the UDS (Uniform Droplet Spray) team at the Laboratory for Manufacturing and Productivity at MIT. Similar to the process used in ink jet printing, the UDS process consists of imposing forced vibrations on a laminar jet of molten metal. These vibrations cause the jet to break up uniformly, whereupon each droplet is charged so that they repel each other as they solidify. The result is metal powders that have uniform diameters with a variance of 3 to 4%.

This study had several goals. The first was to modify a system designed by Abel [1992]. Many problems had been encountered in the attempts to use this original system to produce uniform bronze powders. Chief among these was the inability to charge the molten metal droplets, and frequent failure of the apparatus. Another major goal was to make the system as robust as possible while minimizing cost. The redesign consisted primarily of fabricating a new high-temperature furnace that allowed for the monitoring of the molten-metal jet and the utilization of better orifice mounting techniques.

The UDS process eliminates many problems encountered in traditional metal spray forming processes, such as gas atomization in which a high velocity spray of inert gas is used to break up a metal stream into droplets. Gas atomization yields droplets of varying diameters. Owing to its innate uniformity, the UDS process allows precise control of mass and enthalpy flux and ensures that all droplets have similar temperature histories and uniform velocity. These properties make it possible to control the microstructure of spray deposits. The potential applications for uniform metal droplet sprays include the following: uniform metal powder production, uniform spray coating, near-net shape forming of billets, metal-matrix composite production, and fabrication of three-dimensional parts.

The next section will describe the UDS process in detail and discuss the original high-temperature system. Section 3 will discuss the limitations of Abel's system and summarize the results attained from its utilization. Section 4 will discuss the redesign of the high temperature system, outlining possible solutions. Section 5 presents the redesign in detail and discusses the solidification rate of the droplets. Section 6 gives the results of the initial testing of the system, as well as the steps taken to eliminate new problems, and
section 7 gives the results of the second testing. The final section gives conclusions and recommends future research on high temperature metal sprays.
2. UDS Process

Figure 2-1 shows a schematic of the UDS process. The first step in this process is to apply heat to a crucible containing metal, causing the metal to melt. The next step is to apply pressure within the crucible, forcing the metal through an orifice at its bottom, creating a laminar jet. This jet is broken up into uniform droplets by the vibration of a shaft immersed in the melt near the orifice. This shaft transmits the vibration via a piezo-electric crystal vibrating at a desired frequency. The vibration creates a disturbance that is sufficient to break up the laminar jet uniformly at the set frequency. The diameter of the droplets can be changed by varying this frequency. The final step is to inductively charge each droplet at the point of jet break up. Underneath the crucible is a graphite charge plate. The charge plate consists of a gap through which the molten metal jet passes. This plate is positioned so that the jet breaks within its gap. The jet is grounded while the charge plate receives a high positive voltage (500-1000V). The droplets are charged by this difference in electric potential and the capacitance between the droplets and the charge plate. All the droplets receive the same negative charge, and therefore repel each other in flight.

Because oxidization of the molten metal jet prevents jet disintegration, the jet must be sprayed in an inert environment, as can be seen in Figure 2-2. The crucible is enclosed in a Pyrex chamber which is slightly pressurized with nitrogen (2-5 psig). The nitrogen provides an inert atmosphere for the spray. After the crucible is heated to a desired superheat it too is pressurized with nitrogen (10-20 psig). The pressure difference between the crucible and the Pyrex chamber forces the metal through the orifice. The metal droplets then solidify while falling through the chamber’s atmosphere.

The piezo-electric vibration is controlled by a frequency generator which is monitored by an oscilloscope. The output from the function generator is amplified and the voltage is stepped down through a transformer before it is connected to the piezo-crystal. The temperature is controlled by an Omega 9000A PID Controller and the voltage on the charging plate is set on a Bertran High DC Voltage power supply (Model #230). Figure 2-2 shows a schematic of the UDS monitoring system. A video camera and a strobe light are used to record the droplet break-up. The strobe light is set at a frequency equal to the droplet break-up frequency so that the individual droplets are captured on the video monitor.
Figure 2-1: Schematic of UDS Process
Figure 2-2: Schematic of Video Monitoring
3. Limitations of Previous System

Figure 3-1 shows a schematic diagram of the original high temperature melt-vibration system. The system was designed to melt metals with melting points up to 1100 °C. The crucible is made of graphite and the heating element is a Thermacraft clamshell electric resistance heater (Model RH251) with an inner diameter of 75 mm and an outer diameter of 100 mm. The heater runs on 115 V and provides 720 W of power. The heater is embedded in a ceramic fiber insulation package that has a 38 mm hole machined into the bottom to allow the metal jet to pass through. The insulation and heater are inside a cylindrical 304 stainless steel section with an outside diameter of 250 mm. This section has two ISO Type-F vacuum flanges welded to it. These flanges provide input for heating and charging. The heater is controlled by an Omega 9000A PID temperature controller. An Omega solid-state relay is used to switch the heater. The temperature is measured by an inconel-sheathed type K thermocouple which is immersed in the molten metal. The piezoelectric transducer is separated from the melt, since the transducer can only function up to half of its Curie temperature, about 200°C. If the crystal is heated to above this temperature, then it loses its piezo-electric behavior. The shaft and disk of the vibration transmitter are made of alumina and are immersed in the molten metal to transfer the vibration.

This system performed over twenty runs with limited success. Of these, the vast majority were failures because of two main problems. The first and most prominent was the inability to perform adequately of the graphite adhesive that was supposed to hold the ruby orifice in place. Although it was rated for temperatures up to 1100 °C, the orifice was blown out of its pocket in most of the runs because the combination of pressure and temperature was too much for the adhesive. The second problem was the inability of the system to monitor jet break up. This meant that on the few runs where the adhesive did not fail, the droplets could not be inductively charged, since there was no clear evidence of where the breakup occurred.

The orifices are mounted in a 2.38 mm diameter, 0.635 mm deep pocket machined into the bottom of the graphite crucibles. Orifices are glued into the pocket with a high temperature, graphite based adhesive. The adhesive that was originally used, (Graphibond 668), proved unstable at the temperatures reached in his runs. Like many adhesives, it is a two part mixture consisting of an uncatalyzed base material and a hardener. It can be mixed to any consistency, yielding varying strengths upon solidification and curing. There are
two possible causes of the adhesive's failure. The mixture used could have been too thick to adequately surround the orifice and adhere it to the side of the pocket as well as the bottom of the crucible. In addition, there was no attempt to increase the strength of the bond on the bottom of the crucible by layering many coatings of adhesive or by pocking the surface. The problem of holding the orifice in place was a major focus of this study.

Figure 3-1: Schematic Diagram of High-Temperature Apparatus
[Abel, 1992]
As previously stated, jet monitoring is an essential part of the UDS process. Abel's original design yielded jet breakup inside the stainless steel furnace (see Figure 2-2). This meant that the jet could not be monitored. It is important to be able to monitor the jet for three main reasons. The first is the stabilization of the jet. This means finding a pressure that will yield a laminar jet. The second is the characterization of the jet. This means finding the right frequency and amplitude for uniform breakup, given the material and orifice size used. The last, and most important of the three reasons for monitoring the jet is inductive charging of the droplets. This entails knowing where the jet is going to actually break up, so that the droplets can be inductively charged. If the point of jet break up is not visible, then there can be no clear idea of where to put the charge ring.

Owing to the aforementioned problems, the first attempts at spraying bronze had very limited results. Figure 3-2 shows a picture of droplets collected by Abel. Because the droplets were not adequately charged, it is apparent that some have merged together. If this merging occurs early in the droplet's flight path, the results are droplets of varying size, and if the droplet is partially solidified upon merging, the result is attached droplets. Both features can be seen in Figure 3-2.

![Figure 3-2: Merged Droplets from Previous System](image)

**Figure 3-2: Merged Droplets from Previous System**
4. Redesign of the High-Temperature UDS System

In order to spray high temperature metals such as bronze consistently, a new design was needed that would be free of the limitations of the previous system. Many possible solutions were considered. In the new design process, minimizing cost and maximizing ease of manufacture were major objectives.

4.1 Jet Monitoring

One solution to the problem of not being able to monitor the metal jet, and thus not charge the droplets consistently, was simply to put a charge plate at a distance close enough to the orifice so that any jet sprayed would break up inside of it. This was tried with the original system, but was discouraged thereafter, as it still did not allow for the stabilization and characterization of the jet. Also, this method required that the charge plate be very close to the grounded crucible bottom, increasing the probability of arcing across the air gap between them, and thus the loss of the capacitance of the charge plate. For these reasons, it was decided to incorporate into the redesign actual video monitoring of the jet.

It was hypothesized that adding two viewpoints on either side of the stainless steel furnace section encompassing the region where the metal leaves the crucible and enters the charge plate would be the simplest and most practical solution the problem of monitoring the jet. The existing system lacked the space for the addition of these viewpoints, so this design would call for a new furnace section. Also, the addition of these viewpoints would require that the insulation in the line of sight between them be removed, and there was concern as to whether such a modification would produce a system that could still melt copper alloys.

4.2 Orifice Mounting

Solutions to the problem of holding the ruby orifice in place did not manifest themselves as quickly as the jet monitoring solutions. One idea was to design an orifice or orifice holder that was inserted into the bottom of the crucible and held with fasteners other than adhesive, such as a bolt circle around a gasket, or an insert that threaded into the crucible bottom. Such a design can be seen in Figure 4-1.
Figure 4-1 Schematic of Orifice Insert

Although a mechanical solution was appealing, the technique of using adhesive had proven to be quite robust at moderately high temperatures, and in order to maintain the modularity of the systems in the laboratory it was desired to use a similar method for high-temperature applications. Also, after several tries to make the graphite adhesive work for the spraying of aluminum jets, (at temperatures above 700°C), Jeanie Cherng of the UDS team had evolved a technique of applying the adhesive that was reliable for those temperatures. Finally, the lower cost of using the adhesive over manufacturing an insert was another pertinent factor, and it was decided that a technique similar to Cherng's would be employed in an adhesive application.

Cherng's technique consisted of pocking the surface around the pocket to increase surface area of the crucible bottom that the adhesive touches, and layering several coatings of the adhesive to increase the strength of the bond. Also, skill is required to make sure that any space between the pocket wall and the side of the ruby orifice is filled with adhesive. It was hoped that by taking these steps to make the adhesive bond as strong as possible would result in a satisfactorily robust orifice mount.

The final design consisted of lengthening the stainless steel furnace section to 250 mm and adding two viewpoints as discussed in section 4.1, as well as using a better orifice mounting technique.
5. Detailed Design of Modified High-Temperature System

Figures 5-1 and 5-2 show the modifications made to the high temperature furnace. Figure 5-1 shows a top and side view of the modified stainless steel furnace section. The furnace has been lengthened and jet monitoring was made possible by welding on the two 7.62 cm long conflat flange half-nipples. Onto these half nipples bolt Kurt-Lesker 7 cm Conflat flange quartz glass viewing ports (model # VPZL275) were mounted. Figure 5-2 shows a schematic of the entire modified system. The added viewpoints (not show in cross-section) allow for the viewing of the circled section. These were the only modifications to Abel's original system: all other components remain as described in Section 3.

**Figure 5-1:** Modified Stainless Steel Furnace Section (Dimensions in inches)
Figure 5-2: Modified Design of Furnace
Figure 5-3 shows the pocking technique to increase bond strength around the orifice pocket. The grooves can be machined in, or, owing to the softness of graphite, scratched in by hand. Care must be taken to insure that the grooves do not break the orifice pocket wall, as this would lessen the robustness of the bond, and defeat the purpose of making the grooves.

![Orifice Pocket](image)

**Figure 5-3: Modified Design for Orifice Mounting**

5.1 Droplet Solidification Rate

To determine the flight distance needed for the solidification of roughly 200 μm diameter droplets, a simple heat transfer model derived by Passow [1992] was used. The droplets are modeled as spheres with a constant velocity air flow over them. Forced convection and thermal radiation are the two sources of heat loss considered. Equation 5.1 [Mills, 1992] shows this model. The first term represents heat loss through convection, while the second represents radiative heat loss:

\[ Q = h A_d (T_d - T_g) + \sigma \varepsilon A_d (T_d^4 - T_g^4) \]  

(5.1)

where \( h \) is the heat transfer coefficient, \( A_d \) is the surface area of the droplets. The \( \sigma \) is the Stefan Boltzman constant and \( \varepsilon \) is the emissivity of the metal. The heat transfer coefficient is taken for the empirical correlation for forced convection around a sphere [Mills, 1992].
\[ h = \frac{k_g}{d_d} (2.0 + Re^{1/2} Pr^{1/3}) \left( \frac{c_g(\text{avg.})}{c_g} \right)^{26} \] (5.2)

\( k_g \) is the thermal conductivity of the gas, \( d_d \) is the droplet diameter, \( Re \) represents the Reynolds number and \( Pr \) is the Prandtl number. \( C_g \) is the heat capacity of the gas at room temperature and \( c_g(\text{avg.}) \) is the heat capacity of the gas at the average temperature of the droplet and the gas.

Abel [1992] demonstrated that, for a 175 \( \mu \)m copper droplet with an assumed initial velocity of 7 m/s, the initial forced convection term is approximately six times greater than the radiation term, assuming ideal black body radiation from the droplet to the chamber. This validates dropping the radiation term in equation 5.1. Using Passow’s model, Abel showed that 178\( \mu \)m bronze droplets solidify completely in approximately 0.8 m. With a spray chamber length of 1 m the droplets should be completely solidified before they reach the bottom of the chamber.
6. Results of Initial Testing

Once the new furnace was fabricated, an attempt was made to spray a bronze alloy consisting of 90% Cu and 10% Sn, which has a liquidus temperature of 1030°C. Figure 6-1 shows the temperature vs. time curve for this furnace. Note that the furnace was unable to reach the liquidus temperature of the Cu-10%Sn bronze alloy, attaining a steady state temperature inside of the crucible of only 980°C. Because of this, it was impossible to spray the alloy, and consequently, to ascertain the whether the new orifice mounting technique prevented the orifice from coming out of its pocket.

![Temperature vs. Time Curve for Modified Furnace](image)

Figure 6-1: Temperature vs. Time Curve for Modified Furnace

6.1 Acquisition of Lower Liquidus Temperature Alloy

As the system had already been modified, and an experimental steady-state temperature had been obtained, it decided to use a lower melting point alloy of bronze rather than to attempt further alterations to the system. Figure 6-2 shows a phase diagram of the Cu-Sn system. Given that the system could attain temperatures exceeding 900°C in just a few hours, and it was desired to maintain as high a copper content as possible in the selected alloy system, an alloy of Cu-20 wt %Sn whose liquidus temperature is 896°C was chosen.
Figure 6-2: Phase Diagram For Copper-Tin Alloys
[Brandes.1992]
7. Results with Second Alloy

Figure 7-1 shows a picture of uniform powders that were collected using the modified system. Fifteen runs were attempted with this system. At present, a stable jet demonstrating uniform breakup has only occurred twice. The droplets in Figure 7-1 are from these runs. The system had no trouble getting up to the desired spray temperature of 925°C (a superheat of 29°C). The new viewpoints allowed for the anticipated jet monitoring, stabilization, and charging. However, despite the use of the new orifice mounting technique, orifices were blown off during many experiments.

Figure 7-1: Uniform Powders of Cu-20%Sn
8. Conclusions and Recommendations

This study has demonstrated the capability of the UDS equipment to produce uniform bronze powders. The redesign of the furnace section (addition of viewports) and utilization of a better technique for bonding the ruby orifices into their pockets onto the bottoms of the crucibles enabled this successful powder production. There is much room for improvement on the new design, however. The limited heating ability of the system makes it impossible to spray copper-tin alloys with a copper wt.% greater than 80%. Adding some form of insulation to replace what had to be removed for the addition of the viewports is necessary. As this insulation must be translucent, to allow for the monitoring of the jet, one recommendation is to place thick tinted quartz glass or sapphire windows at several positions along the inner diameter of the half-nipples. The window's thickness would lower the conductive heat loss, while the tinting would reduce some of the radiative heat loss.

Another solution to the heating problem would be to design an entirely new furnace, based upon induction heating instead of electric resistance. A water-cooled induction furnace would have little trouble melting any copper alloy. Abel [1992] considered using an induction furnace in his original design, but opted for the electric resistance for cost considerations.

The problem of failed runs due to the failure of the orifice adhesive is still very prominent, as Section 7 suggests, and must be resolved. Since an adhesive solution does not seem to be reliable, a mechanical solution should be investigated. An insert, as discussed in Section 4, is a promising solution. It would, however, require a complete redesign of the crucibles. A simpler solution may be to machine an orifice pocket such that the ruby orifice is inserted from the inside of the crucible. This way, the adhesive would only have to seal around the orifice, not hold it against the applied pressure.

Through attempts to maintain modularity between the low and high temperature systems in the UDS lab, the robustness of the high temperature system has been compromised. The differences between what is robust in the low temperature regime and what is robust at higher temperatures must be properly addressed in the design of future high temperature metal spraying systems.
References


