Production of Highly Spherical, Copper Coated Anthracene Microparticles

by

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A thesis submitted to the

Faculty of the University of Colorado

in partial fulfillment of the requirements

for the award of Departmental Honors

in the Department of Physics

April 2, 2025

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Thesis directed by Professor Tobin Munsat

Impact ionization mass spectral data is essential for studying dusty space environments. Results obtained from impact plasmas' mass spectra often differ from those generated by other ionization methods, making the ability to study these impacts crucial for the development of flight mass spectrometer instruments. This research is typically conducted using electrostatic dust accelerators, such as the one at the IMPACT Lab at the University of Colorado. However, studies in these accelerators are currently limited to materials that can be charged and electrostatically accelerated—primarily those made of conductive materials or those whose spectral data are not obscured by a conductive polymer coating. There is a need for developing methods to create accelerable forms of materials commonly found in dusty space environments, such as silicates and hydrocarbons. In this thesis, I present work in applying a copper coating to anthracene microparticles, as well as a comprehensive method to produce controllably sized, nearly spherical microparticles from brittle materials, including anthracene.

Dedication

to Kate Timothy

Acknowledgements

I would like to begin by thanking all the wonderful folks at IMPACT Lab. The importance of community and teamwork when working on multi-stage projects cannot be understated and, without the support of everyone at IMPACT, I would have never created this thesis. A special thanks to Grace Owens, Vladimir Gorokhovsky, and John Fontanese, whose tireless work has made this entire project possible.

Additional thanks goes to my research advisor, Dr. Tobin Munsat, who has provided invaluable direction, advice, and opportunities throughout every stage of my undergraduate career.

Thank you.

Contents

Chapter 1

Introduction:

The study of dusty space environments is critical to future space flight missions, particularly those dedicated to detection of exospheres surrounding airless planets and moons, and analysis of the interstellar medium. Much of this medium is populated by polycyclic aromatic hydrocarbons (PAH's). Not only do these PAH's represent a significant portion of all cosmic carbon, but they also represent a fundamental building block for many organic molecules. Dust accelerators, such as the linear electrostatic accelerator at the University of Colorado's Institute for Modeling Plasmas, Atmospheres, and Cosmic Dust (IMPACT) lab are crucial to the modeling of these dusty environments in the lab. They enable the study of these compounds via hypervelocity impact and resulting plasma mass-spectra.

Significant research has been conducted on hypervelocity dust impacts [5][8], though this research has been limited by challenges in creating particles suitable for acceleration. In order to accelerate particles in an electrostatic accelerator, they need to be conductive in order to hold an electric charge. This has limited studies to conductive materials. For this reason, work regarding PAH's has been limited to the study of vinyl polymers. Acceleration has also been achieved through the application of conductive polymer coatings. Recently, Rebecca Mikula et al. studied impact ionization of another PAH, anthracene, for the first time through the usage of a polypyrrole coating and found that the spectra generated from impact plasmas differed

significantly from other methods of study [6]. These conductive polymers, though, often leave artifacts within ionization data that are difficult to distinguish from novel discoveries. Thus, a method for coating particles in conductive materials such as pure metals whose ionization data can be easily discerned from the target and/or impactor material is needed.

The technology to apply thin, metallic coatings to large objects exists and is well established. Commercial services to apply such coatings are quite prevalent, and it was initially hoped that suitable particles with conductive coatings could be acquired commercially. After thorough investigation, however, no such opportunities were found. This is because, while methods exist to apply nanoscopic coatings to macroscopic objects, these methods cannot be applied to microscopic particles. When they are, they most commonly result in only one side of the top layer of particles being coated. Clearly, a method of applying a metallic coating to a continuously agitated bed of microparticles is needed.

Such a method is currently under development at IMPACT labs: a coating device which has adapted various deposition methods to function on an agitated powder base has been developed. This coater is capable of applying metallic coatings with thicknesses varying from 1-100nm. These metallic shells, which can be comprised of copper, titanium, or tungsten, can be easily identified on a spectral graph.

In Chapter 2 of this thesis, work using this coating device to apply a thin copper coating to a sample of anthracene microparticles is presented, beginning with an overview of the coating device as well as a description of its agitation mechanism. Various trials with differing metal deposition methods are then discussed, concluding with the results of a successful trial utilizing thermal evaporation to produce copper-coated anthracene microparticles.

Due to the mechanics of the coater's agitation mechanism, the particles must be significantly rounder than might be achieved via normal breakage mechanisms in order to avoid undesirable effects such as clumping or uneven coatings.

In Chapter 3 of this thesis, work in developing a method of producing rounded microparticles using a device called a "planetary ball mill" is presented. First, an overview of planetary ball milling is provided, followed by a discussion of work developing a model with olivine. Next, work with dry milling as well as work with wet milling is presented. Then, research developing a system for sorting and cleaning particles is discussed. Finally, a demonstration of the milling system's viability is provided by successfully applying it to anthracene.

Chapter 2

Coating

2.1 Overview

Particle coating is accomplished through individual “runs” wherein particles are loaded into the Microparticle Coating Device (MCD), a vacuum is established, the agitation and deposition mechanisms are run, and the particles are then harvested. Due to the mechanical and physical restrictions of the coater itself, these runs can take days to complete, with the deposition portion taking anywhere from 30 minutes to several hours, depending on the deposition source, particle content, agitation method, and other factors. The intended result of these runs is to coat micron-scale particles with a metallic layer of controllable and consistently sized thickness. Common effects seen during the coating process which prevent such a layer being applied include melting, carbonization, and particle compaction.

The primary variables involved in a given coating run are duration, deposition method, agitation media size and volume, powder composition and volume, and deposition material. Far beyond a simple success or failure, these variables control nearly every aspect of a coated product. Through mastery of these inputs, one can produce everything from tungsten coated ceramic pieces to carbon aerogels coated in a single nanometer of aluminum.

A vapor deposition system for coating micron-scale particles consists of several key components. Though individually straightforward, the operation of these components can interact with each other in complex ways. The first of these essential components is a vacuum

chamber. The vacuum chamber is essential to the production and application of metal vapor, and serves several other purposes such as preventing influx of contaminants and providing a basic housing and structure for all other components. The next essential component is a vapor deposition source. This project employs both cathodic arc deposition, as well as thermal evaporation deposition, and both are discussed later in the "Deposition" section. The third essential component for coating micron-scale particles is an agitation mechanism. Continuous agitation of the particles being coated prevents undesirable effects such as clumping or only coating a single layer of topmost particles. Agitation will be discussed further in the "agitation" section. The final component required is a cooling system. Metallic vapor production and deposition sources produce intense heat resulting in temperatures well over 1400^{o} C. A heat extraction system regulates temperatures and prevents melting, carbonization, or other undesirable effects within the microparticles or the coating system itself. Thus, while the coating device consists of hundreds of components from stepper motors to water valves, each can be classified into 1 of 4 core systems: a vacuum chamber, a deposition source, an agitation mechanism, and a cooling system.

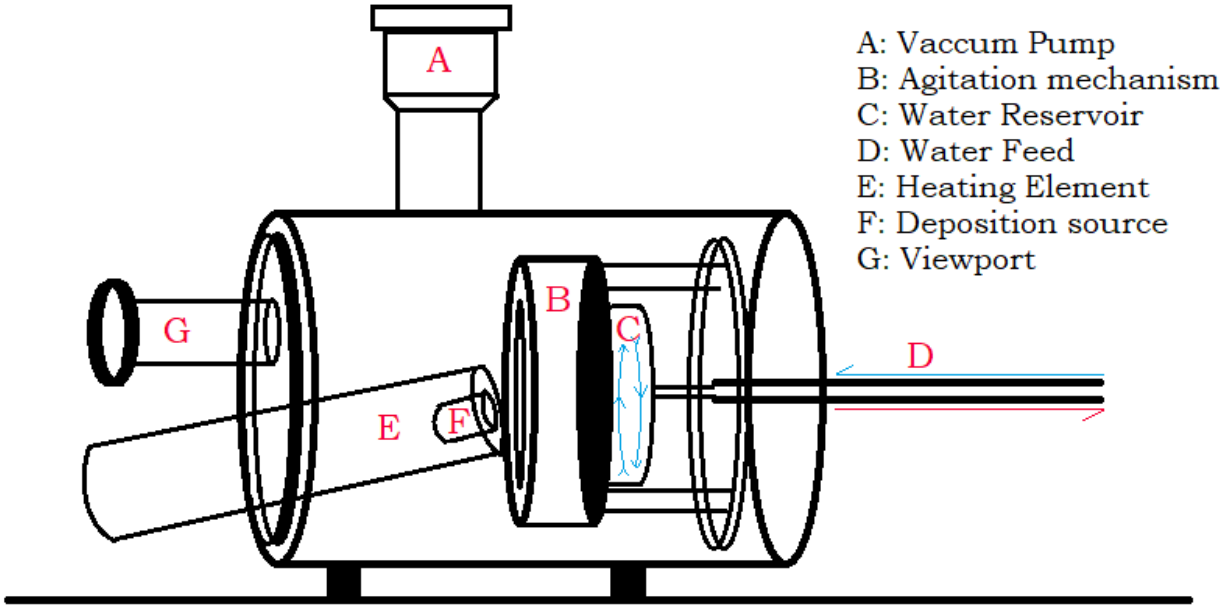

Fig 2.1. Basic Diagram of the essential components of the coating device

2.2 Cooling

One significant problem faced in attempting to coat anthracene in copper lies in the buildup of heat during the coating process. Both coating methods used involve extremely high temperatures. This, in combination with anthracene's melting temperature of 100 degrees Celsius results in significant cooling being required for the duration of a coating run to prevent melting or carbonization. The MCD achieves this through the employment of a water-cooling system that mitigates unwanted thermal buildup in the deposition source, the vacuum chamber, and the particles themselves. This system involves dozens of water lines which provide cooling to all heat-facing components, but only the water reservoir (C) seen in figure 2.1 prevents thermal buildup in the particles. As seen in figure 2.1, this reservoir attaches directly to the agitation mechanism and is circulated by a current of cold water flowing through the rotation shaft (D). Thus, cold water flows into the reservoir, contacts the barrel and absorbs heat, and is then

replaced by more cold water. Additionally, as pictured in figure 2.2, there exists a baffle within the reservoir itself.

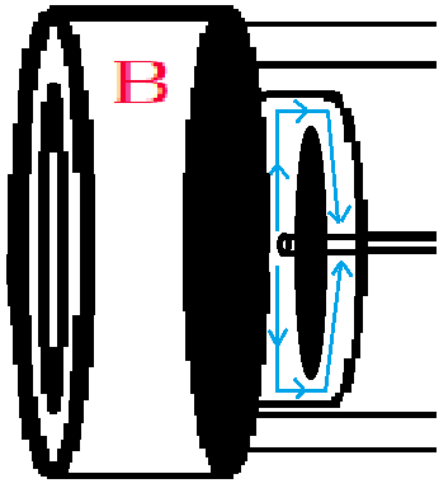

Figure 2.2, Agitation barrel and water reservoir with baffle

This baffle prevents eddies within the water, ensuring even cooling to all parts of the barrel. Additionally, it forces the water to spread evenly across the back of the barrel, ensuring maximum thermal transfer.

Successful cooling of the agitation barrel does not guarantee acceptable thermal regulation within the particles themselves, as there is little heat transfer between the particles themselves. In the vacuum conditions required to operate the vapor deposition sources, particles cannot transfer heat via convection, as there is no significant atmosphere to interact with. Additionally, while the deposition sources themselves reach high enough temperatures to expel heat via radiation, the particles themselves do not. Thus, under coating conditions, particles will only shed heat via contact conduction. Because of this, as well as anthracene's poor conductivity, effective cooling occurs primarily in particles directly touching the walls or fins of the barrel.

Therefore, without some method of particle agitation, heat will build up in the topmost particles far faster than can be transmitted to the barrel walls for disposal, and the anthracene will be carbonized.

2.3 Agitation

The specialty of the Microparticle Coating Device (MCD) lies in its ability to mechanically agitate a bed of particles while applying a metallic coating. Though systems to apply metallic coatings, such as sputter coaters, are commercially available, none have the ability to continually agitate contents under vacuum. At a glance, this may seem a bit pedestrian, but the difficulty in agitation while coating comes from the necessity of operating within a vacuum chamber. Additionally, the high temperatures and buildup of metal layers within such vacuum chambers provide significant challenges to the operation of mechanical devices. To deal with these difficulties, the MCD utilizes a rotating barrel to agitate its particles, as seen in figure 2.3.

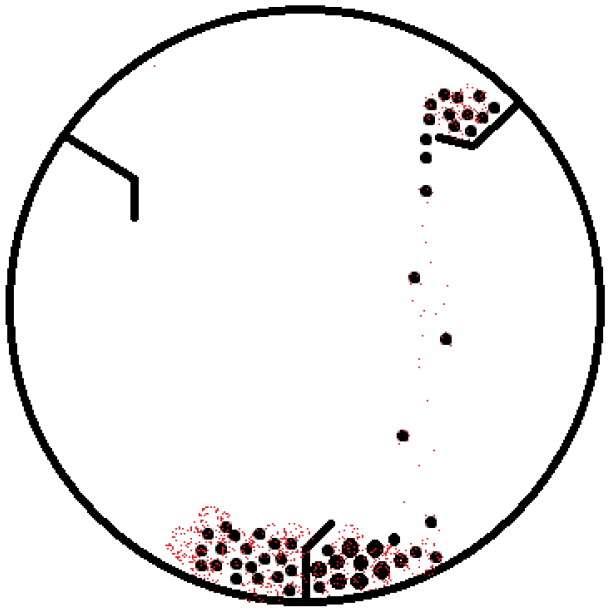

Figure 2.3, Barrel diagram with agitation media.

The barrel agitation system uses a cylindrical barrel (Component B in Figure 2.1) which is vertically mounted on a rotating rod (component D in Figure 2.1). Through the usage of a ferrofluid bearing, this rod passes through the wall of our vacuum chamber and is able to rotate while preserving vacuum conditions. Thus, the rotation of this rod is transferred to the barrel and allows for agitation of the powder within.

In addition to barrel rotation, the particles are agitated in several other ways. The first of these ways is a series of fins mounted within the barrel, as seen in figure 2.3. Depending on the particles being coated, as well as the coating mechanism being employed, these fins are varied in number, spacing, shape, size, and composition. For the purpose of this project, the barrel is configured with 3 evenly spaced 1-inch fins made from 12 gauge stainless steel. In addition to fin configuration, ceramic ball bearings, referred to as “agitation media”, are utilized to further agitate the particles and prevent clumping. Ceramic was chosen as a material for its high heat resistance, as well as its low density; steel balls were initially used, but would often lead to particle compaction within 10 minutes.

2.4 Agitation Tuning

While seeming quite simple, the interactions between fin configurations and agitation media composition can have drastic effects on the results of a coating run and are made quite complex with the addition of a growing metallic layer on all internal faces. Properly calibrated media and fins can increase thermal performance, prevent particle clumping, and ensure even particle coating. Improperly calibrated media will lead to high levels of particle compaction and inconsistent coatings being applied. During compaction, the weight of the agitation media will compress particles together and adhere them to the walls and fins of the barrel. Particles that become attached in such a way are no longer agitated and, as a result, quickly become coated

together into ever-growing layers. In general, an increase in particle agitation leads to an increase in this adherence and compaction. Thus, a balance exists: too little agitation will cause particles to be coated improperly and overheat, but overly intense agitation will increase the rate of particle compaction.

The main variable at play for fin configuration is the angle at which the fins are mounted. At high angles, the fins act as scoops, lifting particles and vertically dumping them after a time. Lower angles, however, act more as ridges, serving mostly to “stir” a bed of media and particles. Higher angles are much better at agitating, and particularly at helping to coat all sides of a particle, but at the cost of decreased compaction time. For this project, a 45 degree angle was chosen for our 3 fins. This is high enough to induce a vertical cascade, but low enough that particles would not be immediately compacted.

The variables at play for agitation media are the volume of media and the volume of particles. Experimentally, we have discovered that a ratio of about 10% particles and 90% agitation media works best. Given the size of the agitation barrel installed in the MCD, the total volume for this combination is typically set at about 50 ml. At this ratio, agitation media functions slightly differently than one might expect. Rather than a bed of powder being stirred by ceramic balls, the ceramic bearings are coated in a fine layer of dust. Then, as they roll around and rub against each other, they exchange particles, rotating and continuously agitating the dust. This agitation method has several advantages: the first is that the particles are constantly in contact with a relatively large piece of ceramic, which greatly aids the conduction of heat away from the anthracene. Additionally, most of the powder being coated on media rather than in a pile makes it significantly harder to compress together, preventing compaction. Finally, having such a large fraction of our particles being in direct contact with the agitation media considerably

decreases the heat buildup within a given run, as the ceramic balls are far better at conducting heat than the anthracene microparticles. Additionally, because the ceramic media are so much larger than the particles themselves, they take much longer to heat up, greatly extending the duration for which deposition can be active before causing significant thermal buildup.

The final variable to be controlled in optimizing particle agitation is the size distribution of the agitation media. 3 separate sizes of ceramic bearing are used: 3mm, 2mm, and 1mm balls. In a given run, however, only 2 sizes will be mixed. Advantages of larger media include slower compaction and better thermal regulation, while usage of smaller media has the advantage of a higher surface area. After analyzing the particles produced under a variety of coating conditions, it was discovered that the particles which coat the agitation media often undergo the most optimal agitation and thermal control and are the easiest to recover. Thus, a higher media surface area often directly translates to a higher yield from each test. Producing mathematical models of this system has proven challenging, however, so the current method of optimizing media sizes involves using a dummy model of the barrel to test out specific combinations of media sizes. This requirement for manual testing is the reason combinations of only 2 media sizes are exclusively used; introducing a third size would complicate the modeling process exponentially and has shown little promise of significantly improving agitation performance. For the combination of anthracene and 3 fins at 45 degrees, a combination of 15 ml of 1mm balls and 35 ml of 2mm balls provided the highest yield while minimizing compaction for 30 minutes–the intended run duration.

2.5 Deposition Sources

The coater operates using one of two deposition sources. The decision was made, for both sources, to coat the anthracene in copper due to its high conductivity and low melting

temperature. The first of these is a cathodic arc target, and the second is a thermal evaporation system. Using high currents and magnetic fields to create and direct metallic plasmas, the cathodic arc system is more commonly used on the MCD, as it applies a more consistent layer of metal with greater precision. The mechanics behind its function allow it to be quickly toggled on and off, allowing for a great degree of control during coating runs. Thus, initial tests were run with the hope of using the cathodic arc deposition system to coat our anthracene. These attempts, failed to produce products with acceptable levels of carbonization. The plasma created by the cathode carbonized all the anthracene in the barrel before any cooling or coating could occur. This was observed both in large pressure spikes during the beginning of the run, as well as an analysis of the coated product particles which were all completely carbonized. It was determined that such excessive heat buildup was beyond our ability to manage via adjustments to run time, agitation media, or other factors. Therefore, thermal evaporation, which produces metal vapor at 1400 degrees, was chosen as a deposition method for future runs.

Rather than generating a plasma which is magnetically directed to adhere to particles, the thermal evaporation source functions by using an induction coil to heat a crucible of metal to melting temperatures. This liquid metal quickly evaporates under vacuum conditions. When this crucible is placed near the bed of test particles, the evaporated metal ions can come into contact with the much cooler particles, and condense, adhering to their surface. Thus, over time, an even coating will build up on the surface of all nearby particles. The main advantage of this system is that the temperature of the copper molecules adhering to the particles is much lower than that of the plasma produced by a cathodic arc, thereby avoiding the previous carbonization issues. The main disadvantage of evaporation, however, is that the crucible can crack if heated or cooled too quickly. As a result of this, several hours are required to bring the evaporator to temperature

before coating can begin, and several more are required to cool the apparatus after the test has concluded. While these long heating periods may lead to particle carbonization, the lack of thermal transfer via convection largely prevents particle heating outside of the evaporation stage. While some heat will certainly be transferred via radiation, but such a level of heating is well within the cooling capacities of the water reservoir and barrel.

2.6 First Test

The first test of the thermal evaporation system involved using 10 ml of milled anthracene, in combination with 10 ml 1mm balls and 40 ml of 2mm balls. The same fin configuration of 3 1-inch fins at 10 rpm was chosen. Rotation was active for the entire duration of the evaporation period, but–to prevent compaction–it was not active during the heating and cooling periods. The test itself took nearly 6 hours. The full temperature and pressure details of the coating session can be seen in figure 2.4.

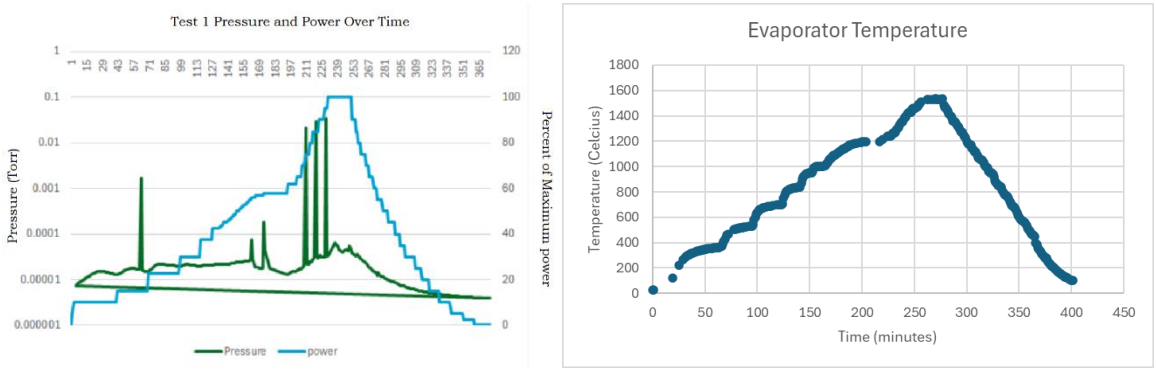

Figure 2.4: Data collected from initial evaporation test.

As copper melts at roughly 1085 degrees Celsius, evaporation was technically active for nearly 3 hours. However, while some copper may have been evaporating as early as T=152, the beginning of evaporation is usually indicated by a sharp increase in pressure as gaseous copper is released into the vacuum chamber. Similarly, the end of evaporation is often signaled by a quick

decrease in pressure as a cease in production of caseous copper allows the vacuum pump to pull out all evaporated copper and quickly restore lower vacuum. Thus, as can be seen from pressure readings, the bulk of evaporation occurred over a 40-minute span from t=197 to t=239. The beginning of barrel rotation uncovers previously buried particles to a high heat environment, causing a sudden increase in outgassing. The effect of this is a large spike in pressure that can be seen at T=211.

The results of this initial test were encouraging. While there was certainly some carbonization in the anthracene microparticles, it was far less than that seen in tests of the cathodic arc deposition system. However, while the evaporation did not cause excessive carbonization, many particles were coated together in large clumps or sheets, as can be seen in figure 2.5.

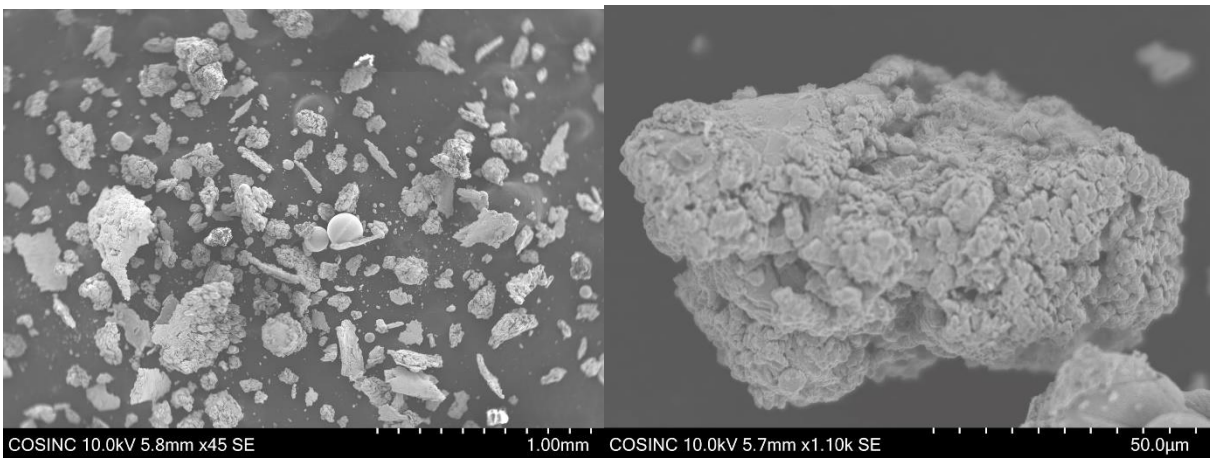

Figure 2.5: Images of copper coated anthracene. Note large clumps which consist of smaller adhered particles.

This adherence is a product of overcoating. Clearly, the particles resultant from this initial test are not yet suitable for acceleration, but they are far more promising than those achieved via cathodic arc deposition.

Thus, the MCD is demonstrated to, at least fundamentally, coat anthracene microparticles. While the process certainly needs further refinement to optimize coating time and further reduce carbonization, the basic ability to apply a metallic coating has been established. Now, however, study is required in the production of the microparticles in the first place.

Chapter 3

Milling

3.1 Planetary Ball Mills

Ball mills function on a simple premise. One puts a substance, or "milling material" that they wish to be crushed into a container full of balls, called "milling media". These jars are then agitated in some way, which leads to collisions between the balls within. Due to their geometry, when spheres contact each other, they do so only across an extremely small area, resulting in extraordinarily high pressures at the point of contact. Upon agitation within a ball mill, the material being milled becomes trapped within the contact points of the milling media and is pulverized. Specifics such as the material's composition, the size and shape of the containers, the makeup of the milling media, and method of agitation all vary greatly across different types of ball mills. For example, "stirred mills" are a type of ball mill which uses a rotating arm to stir jars full of balls, while "shaker mills" rapidly vibrate their jars. In geological research, large steel milling media are used, while for pharmaceutical research, small ceramic media are more often employed. In this project, a type of ball mill called a "planetary ball mill" is employed for its great degree of control over the size of its product particles. Specifically, a model VPMC-4L planetary ball mill is used.

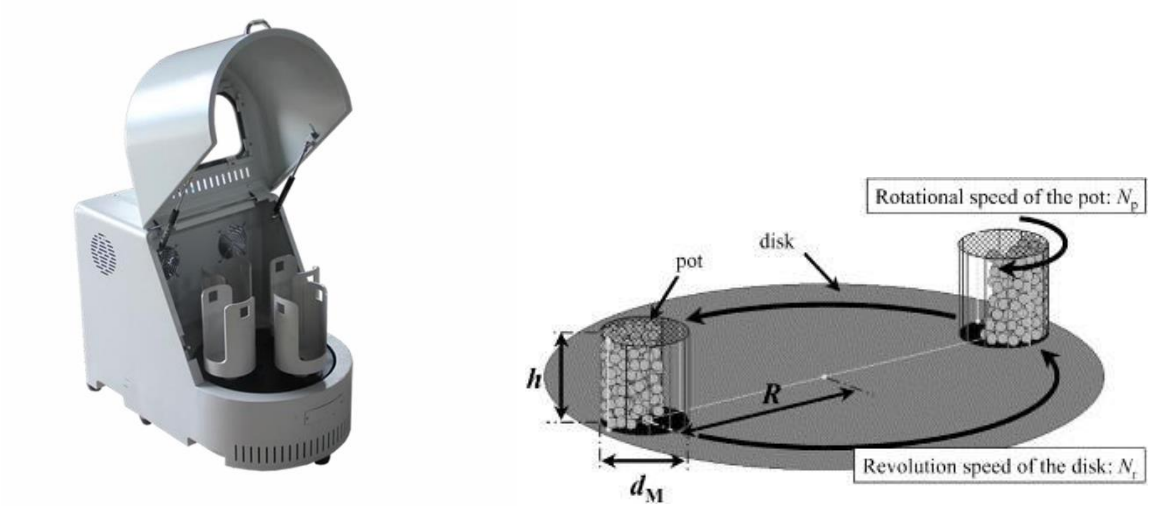

Figure 3.1. Planetary ball mill and accompanying motion. The model pictured is the exact model used in this study. Borrowed from [7].

Planetary ball mills usually consist of several jars secured in a rotating housing which itself is mounted on a rotating plate such that the jars, while rotating, all orbit a central point. See figure 3.1. These jars typically rotate in the opposite direction as their orbit. The centrifugal, Coriolis, and Euler forces present within the jars are often hundreds of times greater than gravity. These high forces allow planetary ball mills to achieve much finer grinding than other types of ball mills. By controlling the rate at which the jars orbit and rotate, as well as the size and composition of the milling media, one can control the energy of these collisions to a significant degree. This control in collision energy, combined with materials' latent property to require more energy to break the more fine grained they become, allows the user to, in theory, precisely control the size of the products produced by ball milling. In practice, many issues, such as material within the jars compacting or the balls milling themselves more than the material, cause such levels of control to be difficult to obtain.

In addition to their control of particle size, planetary ball mills also afford their user a degree of control over their products' shapes. According to commonly established theory, the energy applied by a ball mill determines how small its particles become, and the rate at which that energy is applied controls how round the particles become [3][4]. When the energy is applied slower, i.e. slower rotation speeds over longer periods of time, particles break more slowly but are allowed more time to break, resulting in similar size distributions to comparable quicker, faster trials. One notable effect of slower, longer grinds, though, is that they provide more time in which particles can collide with each other, rather than being shattered by a–comparably massive–milling ball. Particles are often on the size scale of a single micron, while milling balls can be 10mm or larger. Thus, any interaction between a particle and a milling ball will almost certainly result in the particle being shattered into many much smaller–and less round–fragments. When particles collide with each other, though, the interaction is much less violent [3]. Rather than complete shattering–often called a total fracture—these interactions typically result in one or both particles having a corner being broken off. Thus, giving particles repeated opportunities to have corners shaved off will result in, on average, rounder particles. Thereby, a user can balance the speed and duration of a planetary ball mill's grinding time to produce particles of a specific size and shape.

As was quickly discovered during preliminary milling trials, achieving a suitable size distribution presents fewer challenges than achieving a suitable shape distribution. This is largely due to a phenomenon called "over-milling." As previously mentioned, given a certain size of milling media and rotation speed, the milling products' grain size will only get so small. After this, repeated collisions will not serve to reduce the size of specific grains but will typically compact multiple grains together. Very quickly, this causes nearly all grains within a certain jar

to clump up and form a single, dense slab of material. This places an upper limit to the duration for which a substance can be milled, and thereby a ceiling on particle roundness.

3.2 Why Olivine?

Preliminary trials for planetary ball milling were run on quartz samples. The goal of these trials was to compare the physical results of theoretically determined parameters. After a few experiments, several general parameters were established for successful milling. In order to prevent over milling, an optimal rpm range of 350-650 was established. Additionally, a maximum fill content of about 50ml of balls and 10ml of powder was established. These trials also quickly demonstrated significant challenges to controlling particle roundness.

The aim of this research is to develop a set of processes which are applicable to a broad set of materials and will produce spherical or nearly spherical particles on the size range of 0.5-1.5 micron in diameter. The Dust Acceleration Laboratory deals with an incredibly wide range of materials in acceleration, with the goal of accommodating as many more materials as possible. Thus, it would be inefficient to experimentally determine specific milling parameters for individual materials. Rather, it would be far more efficient to work with a substance which is the "worst case scenario", particularly for controlling particle shape. In theory, if milling parameters are found which work well to shape this "most difficult" material, then these milling procedures should be able to, with minimal adaptation, be applied successfully to anything else. Obviously, no one specific set of parameters will work for all sample, but by starting with the worst case and moving on, the process of finding milling parameters for each new sample begins with a procedure that will shape it correctly. The parameters for each new material may then require tuning to perfect product size distributions, but such optimization is significantly easier than perfecting shape distributions.

This is where olivine comes in. Olivine is a mineral but does not have one specific chemical formula. Rather, it represents a spectrum of iron- or magnesium-imbued silicates with the same properties. The generalized chemical formula for olivine is $(Mg,Fe)_2SiO_4$. Olivine undergoes a brittle fracture. It has a Mohs hardness of 7 and does not break along any fracture planes. Rather, it has a conchoidal fracture pattern—it shatters like glass. Essentially, olivine is extremely tough and when it breaks, it shatters into shards. All of these factors individually make olivine difficult to mill into spheres. Together, they make it a "worst case scenario" for grinding into spheres. Olivine was chosen as a starting material for these reasons, as well as the abundance of olivine both terrestrially and in dusty space environments.

One notable effect for grinding olivine, as well as other brittle materials is called the "comminution limit." At a certain size, brittle materials will stop undergoing brittle fracture patterns, such as cracks propagating or chips forming, and instead begin to follow ductile deformation. This happens because the total energy holding a particle together is not high enough to propagate a crack, and thus the particle undergoes plastic deformation instead [1]. Practically, this means that, without milling at a much higher energy, eventually all our particles will hit this "comminution limit." Additionally, because of the nature of plastic deformation on particles small enough to hit their comminution limits, it is expected that all particles at this size should be highly spherical. During the work, it was observed that the comminution limit of olivine is about 0.1 micron. While such particles are too small to be used in acceleration studies, they are large enough to be processed (washed, sorted, etc.) by the same methods as particles on the single micron scale.

3.3 Dry Milling

Initial trials of olivine milling involved simple tests to confirm and quantify theoretically established effects of differing parameters such as milling speed and time. The first test consisted of 2 jars with 40x10mm steel balls and 10ml of olivine powder each for 80 minutes of grinding at 500 RPM. This resulted in a heavy degree of over-milling and very jagged particles across a wide distribution of sizes. This can be seen in figure 3.2. The sample compacted significantly, limiting how much the particles could be milled before they became pressed together. Despite this, however, many of the product particles lie within acceptable size ranges, thereby establishing planetary ball milling as a feasible method for milling olivine to size.

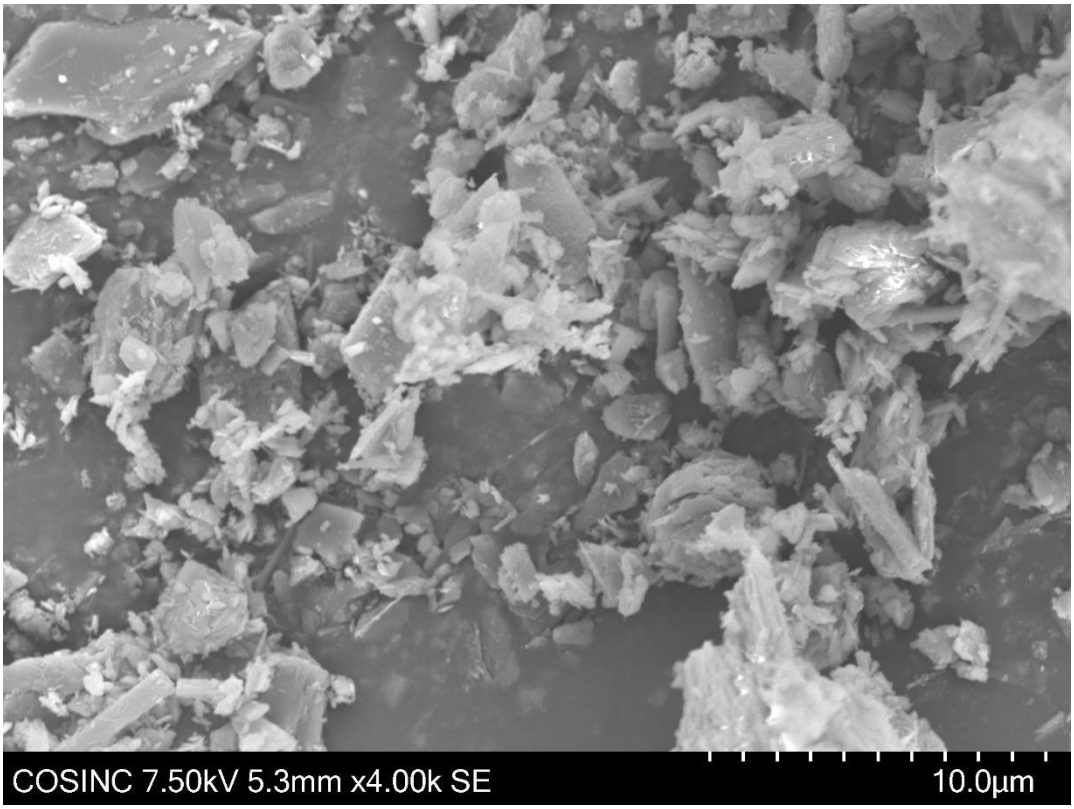

Figure 3.2**.** Initial results of olivine dry grinding using 40x10mm steel milling balls at 500 rpm for 80 minutes. Particles are jagged and not consistently sized.

It was then hypothesized that further milling may break up compacted pellets. In the process of such re-grinding particles would continue to round out, reducing the possibility of further clumping. Thus, it seemed possible that the over-milling issue may subside with sufficiently long runs. This was tested by agitating the milling products and, employing a slightly lower speed to mitigate thermal buildup, milling the product olivine for a further 330 minutes. The composition of the jars was checked after every 30 minutes of milling and a decrease in compaction was never observed. In fact, the final product was so densely pressed together that it was impossible to properly separate for study with an electron microscope. It was concluded that the compaction behavior of olivine during sufficiently long mill times had been thoroughly explored.

Finally, it was hypothesized that the usage of extremely small (1mm) milling media in combination with large 10mm milling media would help to prevent over-milling pellets from forming. The premise was that the smaller media would fill the voids between the larger balls, so pellets forming in these spaces, would absorb the smaller media. Because the jagged olivine was observed to stick to itself far more readily than it stuck to the milling media, it was theorized that these 1mm inclusions would serve to disrupt the binding structure of these pellets. Thereby, the formation of these compaction pellets would be prevented before they became so large as to prevent milling by the large media. This hypothesis was tested using 15ml olivine powder, 500x 1mm milling media, and 1x 10mm milling ball (to help break up larger grains/ compaction pellets) at 250 rpm for 300 minutes. Here, a much lower speed was employed in hopes of preventing high-energy impacts which may cause compaction. At such speed and sizes, the milling media serves to agitate the product more than it does to crush the olivine. Rather, the attrition (particle on particle) interactions are what prevail in such conditions and are also what

contribute to rounder corners. The results of this test, however, did not yield rounded particles. The product particles were extremely over-milled, demonstrating that smaller milling media will not prevent compaction.

A few more deviations were run on this test, all trying different combinations of milling speed and media composition. Eventually it became clear that, while small sizes could be achieved with dry milling, dry milling a material as brittle as olivine will always see compaction in its products before rounded particles are produced.

3.4 Wet Milling

One common step to avoid the issue of over-compaction is introducing fluid to the milling product and media. By milling a slurry rather than a powder, the issue of compaction can be almost entirely avoided. The reason that wet milling was initially explored is that it is a degree more complex than dry milling. At a minimum, one must figure out the correct type and volume of fluid, as well as a way to dry their particles after milling is completed.

Exploration into wet milling began by using water as the suspension fluid. Water was chosen for its advantages of non-flammability, as well as its availability. The goal for the first trial with water was to establish a median set of milling parameters which would work to both mill particles to size and avoid compaction. For this, 3x10mm steel balls with 5ml of previously ground olivine in 5ml of water were used for approximately 15 minutes at 600 RPM. Previously ground olivine was employed as the viscosity of water impedes the movement of milling media, resulting in decreased ability to break apart large particles. As can be seen in figure 3.3, this test resulted in particles being milled to proper size but still retaining their angularity. However, the

faces and edges of the resultant particles, while still angular, were much smoother than the products of other dry trials.

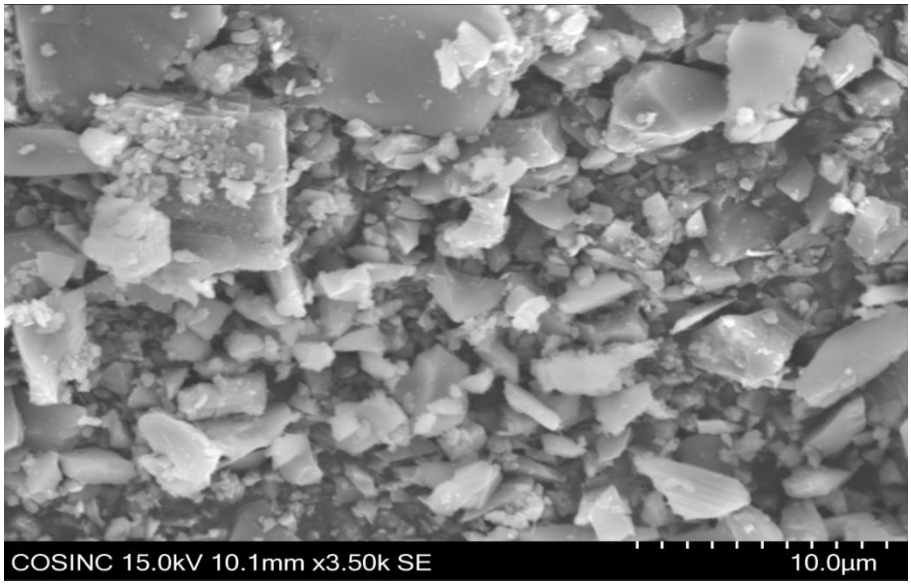

Figure 3.3**.** Initial results of slowly, wet ground olivine. Particles were produced via 20 mins of dry milling at 450 rpm using 40x10mm steel milling balls. Then, particles(5ml) were suspended in 5ml of water and ground with 3x10mm milling balls for 15 minutes at 600 rpm. Note the smooth faces of large particles.

This smoothing implies that wet milling can be modeled, at least at speeds achievable in a VPMC-4L planetary ball mill, as both crushing large particles and polishing smaller particles. Conceptually, this dynamic is similar to that seen in a typical rock tumbler, albeit with different sizes and forces. With this in mind, the next test was designed to wet mill olivine as fast and long as possible, with the intention of exaggerating this polishing effect to a degree where it might begin to round particles. So, using the same parameters (with the exception of duration) as before, a milling test was run for an hour and a half rather than 15 minutes. This results of this can be seen in figure 3.4. Aside from particles being smaller and somewhat rounder than the initial product, found thin, needle-like structures were also produced. This result implied the presence of unknown interactions, as no structure so delicate could possibly survive or be

produced by the violent process of wet milling. After undergoing a spectroscopy test, the needles were found to have no irregular chemical composition, dismissing the possibility of their presence being explained by contamination.

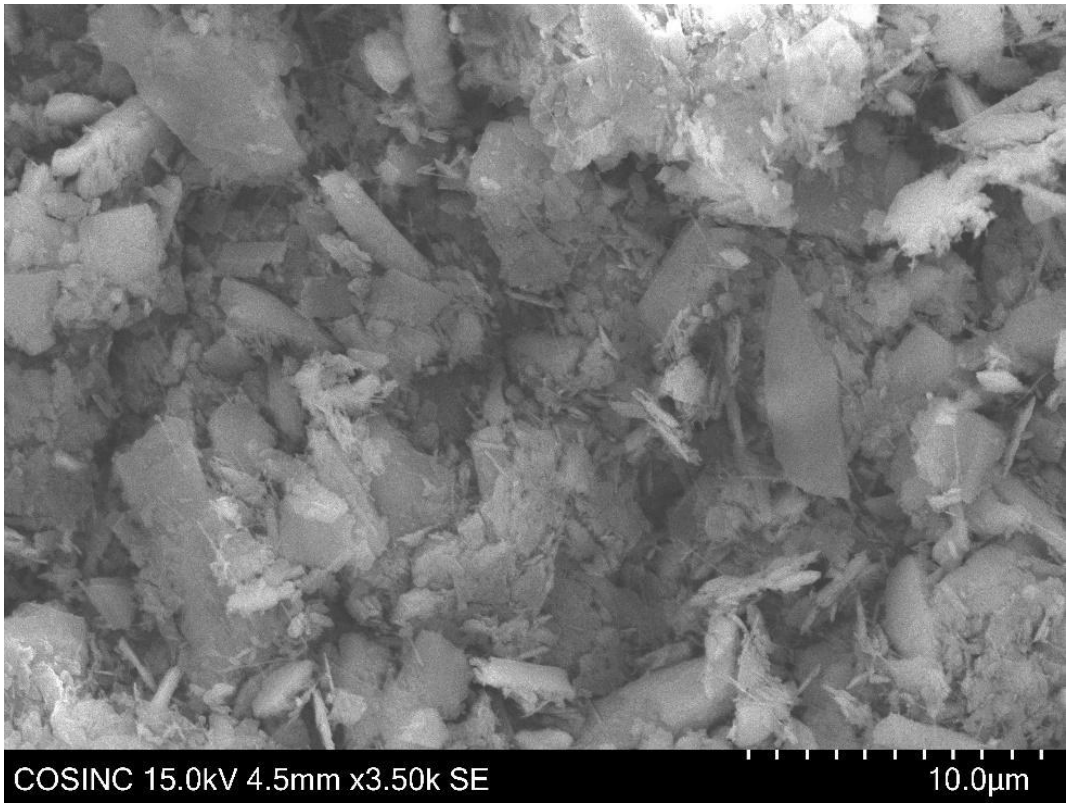

Figure 3.4**.** Results of slowly, wet ground olivine. Particles were produced via 20 mins of dry milling at 450 rpm using 40x10mm steel milling balls. Then, particles(5ml) were suspended in 5ml of water and ground with 3x10mm milling balls for 90 minutes at 600 rpm. Note the presence of fine, needle-like structures.

A brief review of literature regarding interactions between olivine and water [2] led to the hypothesis that some of the olivine particles were reacting with the water in the jars in a process called “serpentinization”. Serpentine, like olivine, does not have one specific mineral composition but rather represents a collection of slightly varying compositions with similar properties. Serpentinization is a generalized term describing the hydrolysis of ultra-mafic

compounds. In the case of olivine, serpentinization occurs when olivine interacts with heat and water to form serpentine [2].

$$(Mg,Fe)_2SiO_4 + 2H_2O + Heat = (Mg,Fe)_3Si_2O_5(OH)_4$$

Because of the high similarity of the two compounds, the chemical difference is nearly impossible to identify, especially on a simple so thin as the needles previously observed. To mitigate this, the usage of ultra-pure ethanol was suggested. This, however, was quickly ruled out as it was determined that the interaction between ethanol, high temperatures, and sealed jars was less desirable even than serpentinization. Rather, the serpentinization hypothesis was addressed by removing the heat necessary to induce the reaction. This was accomplished by exclusively milling in short, 5-minute bursts which were separated by long (30+ minute) breaks exposed to an air-cooling system. This resulted in an elimination of the serpentinization issue, as no more needles were observed.

With serpentinization resolved, work resumed on the prospect of running long trials in hopes of maximizing particle attrition and smoothing effects. For this, more dry stock was used. This stock was produced via 20 mins of dry milling at 450 rpm using 40x10mm steel milling balls. Then, particles (5ml) were suspended in 5ml of water and ground with 3x10mm milling balls for 200 minutes at 600 rpm. The intention of using such a low volume of milling media was to minimize the size reduction in particles while maximizing particle-particle contacts. Thus,

only enough media was included to continually stir the particle suspension. This resulted in significantly rounder particles, as can be seen in figure 3.5.

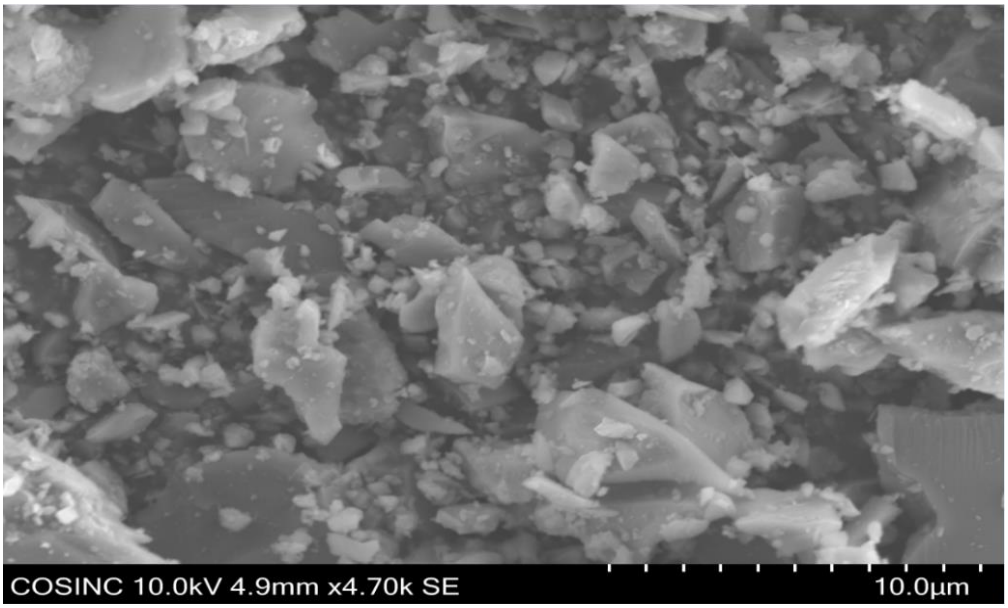

Figure 3.5. Initial results of prolonged, wet ground olivine. Particles were produced via 20 mins of dry milling at 450 rpm using 40x10mm steel milling balls. Then, particles (5ml) were suspended in 5ml of water and ground with 3x10mm milling balls for 200 minutes at 600 rpm. Intervals were allowed every 5 minutes to allow for sufficient cooling of milling media.

Note the roundness of the smallest particles. These results demonstrate the feasibility of using high-attrition wet milling trials over long periods to produce rounded particles. As over milling is no longer a concern, the only thing restricting this process is the time it takes; allowing for up to an hour of cooling for every 5 minutes of milling with the requirement of continuous supervision leads to trials taking place over the course of weeks. Thus, one final trial was designed in which the same parameters would be used, but for 350 total minutes rather than 200. This resulted in samples whose particles on the 0.5-1.5 micron scale were round enough to be considered for coating and further acceleration.

3.5 Particle Sorting

While the last trial produced particles on the single micron scale round enough to be considered for acceleration, these were interspersed with larger particles unsuitable for study. An ideal sample would contain particles within a narrow size and shape distribution. Such a sample would be impossible to produce in a ball mill, so instead the decision was made to sort the results of wet milling trials. If a method could be developed to separate the "good" (small and round) particles from the "bad" particles (not small or not round), a sample could be produced, albeit of drastically reduced volume, of all desirable particles. Then, all that would remain would be to process a large volume of olivine in such a manner. To achieve this separation, the fact that larger particles settle out of suspension quicker than small particles was employed. A benchtop centrifuge was used to control the exact rates at which particles of varying sizes settled. In theory, one could spin a sample of mixed particles such that only particles smaller than 1 micron remained in suspension. Then, by removing this suspension and evaporating the water, one could "sort out" all particles larger than 1 micron. An initial proof-of-concept test was run, spinning particles in a water suspension at 500 xg (500 times gravitational acceleration) for 10 minutes. The fluid was removed and evaporated onto a microscope slide, where it was observed that only particles under 0.5 micron in size had remained in suspension. Thus, the feasibility of such a sorting method was established.

Knowing that the 500xg was too fast to obtain 1-micron particles, a test was designed where a sample would be spun in successively faster trials in increments of 10xg, each with a duration of 10 minutes. After each interval, droplet samples were taken to analyze particles still in suspension.

Through analyzing these samples for particle size, an optimal spin rate in which the particles left in suspension were all smaller than 1.5 micron in diameter could be determined. The results of this experiment yielded an optimal spin rate of 50xg for 10 minutes. With this method, the results of the last wet milling trial were processed. A total of about 0.5 ml of particles under 1.5 micron in diameter were extracted through multiple rounds of centrifuging. These particles were further processed at 1000xg for 5 minutes, in order to separate out undesirably small particles. The remaining product contained only particles of desired shape and size, as seen in figure 3.6. Thus, a method for reliably developing small, round olivine is established.

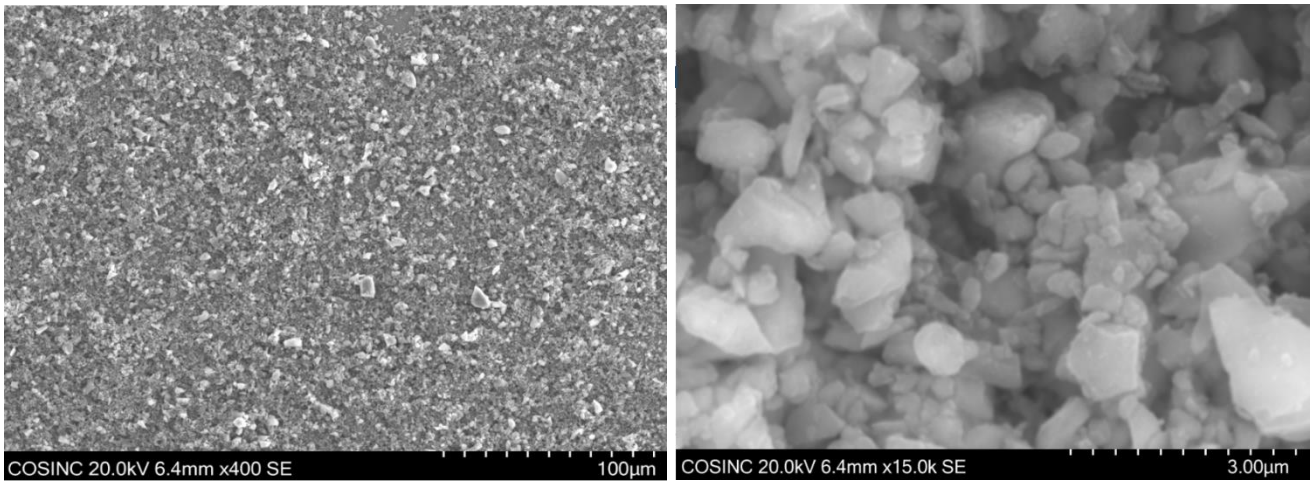

Figure 3.6. Product of particle separation method on sample. Particles were separated for 10 minutes at 50xg.

3.6 Particle Washing

Finally, these suitable particles must be prepared for coating and acceleration. The biggest issue to overcome here is drying samples while avoiding clumping or compaction. Various methods were employed to combat this effect, from evaporation in ultrasonic conditions to flash boiling off any liquid, but none avoided the issue completely. After a closer inspection of

the particles, it was hypothesized that some substance must be adhering the particles to each other, as the particles themselves were too round to have interlocked and were adhered with too much force for the issue to have been caused by electrostatic buildup. A spectral analysis of a clumped sample revealed that traces of iron could be found between particles, as seen in figure 3.7.

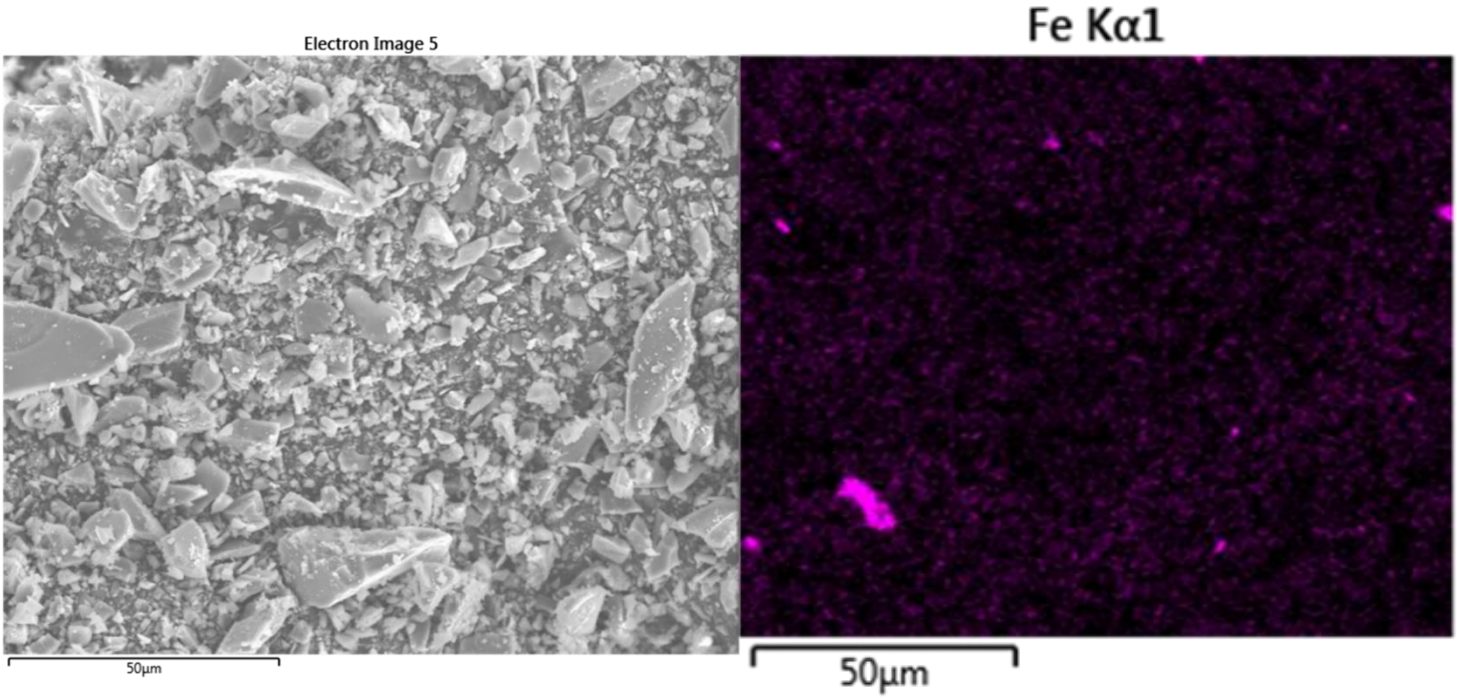

Figure 3.7**.** Electron Dispersion Spectroscopy analysis of unwashed sample. Note the presence of both iron flakes, as well as iron residue between particles.

This iron was determined to have been stripped from the interior faces of the milling jars and media by the highly abrasive olivine particles. As this effect cannot be completely eliminated due to the nature of olivine's hardness, it was determined that this residue would have to be removed after the milling and sorting processes. To do this, a system for rinsing particles was devised. First, the particles were centrifuged at about 2500xg for 15 minutes. The purpose of this step is to settle all particles out of suspension. Next, the water is pipetted out of the sample

and clean acetone is introduced. The solution is agitated on a vibration pad for an hour, and left on a roller/rocker for a further day before the centrifuging and liquid extraction process is repeated and more clean acetone is introduced. In total, 3 such “rinses” with acetone were performed, followed by 3 rinses with isopropanol, intended to remove any residue left by acetone. These, in turn, were followed by 3 rinses with ethanol intended to remove any residue left by the isopropanol. Finally, 3 rinses with ultra-pure water were conducted to remove any remaining residue. These particles were allowed to dry, and were found to no longer clump with significant force, enabling them to be used for coating and later acceleration.

3.7 Anthracene

While this method has only recently been fully developed, its viability has been tested on one substance, anthracene, after its development with olivine. Anthracene is a significant compound for study because it is one of many polycyclic aromatic hydrocarbons (PAHs) which are abundant within the interstellar medium [6]. Because of their abundance, as well as the non-trivial amount of cosmic carbon they represent, the study of impact-plasma mass spectra of hypervelocity anthracene impacts is significant to, among other fields, future space missions [6].

Anthracene is far more plastic than olivine, allowing for much simpler milling methods to be used. Preliminary dry milling trials intended to create acceptable size distributions (but not necessarily shape distributions) produced the highly round particles seen in figure 3.8. These samples still displayed a wide variety in their size distributions, however, so separation methods were still needed. Because of anthracene's comparatively low density (1.13g/cm^3), another test utilizing increments 10xg for 10-minute intervals was conducted. Suitable particles were extracted after separating particles over 1.5 micron in diameter with a 10 minute, 240xg trial and later particles that were undesirably small were removed with a 10-minute trial at 2500xg. Thus, the particle preparation process was successfully applied to anthracene.

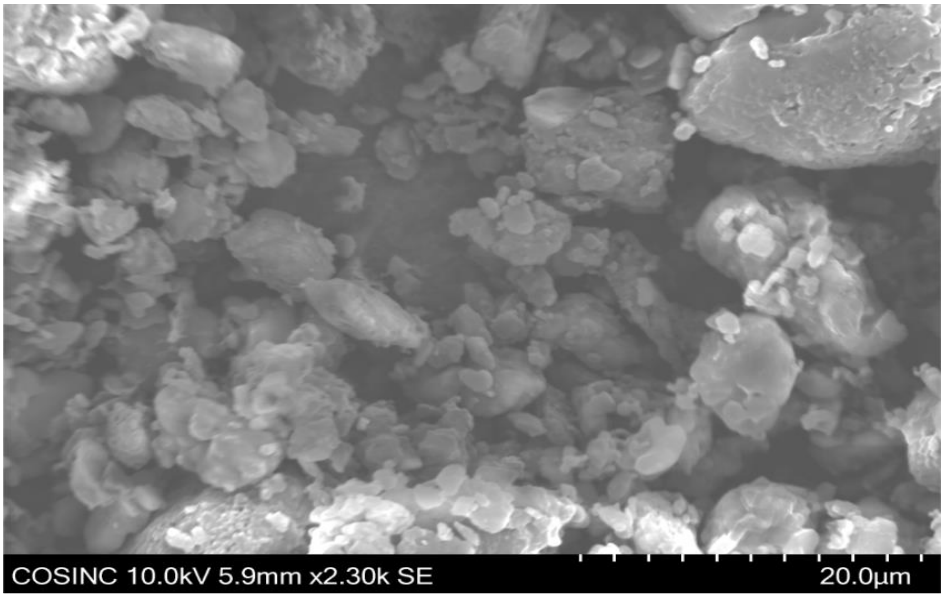

Figure 3.8. Anthracene microparticles produced by a planetary ball mill. 36x10mm milling balls were used in combination with 5ml anthracene powder. The mill was run at 500 rpm for 15 minutes.

Chapter 4

Conclusion

In recent years, highly spherical conductive microparticles have become increasingly important for electrostatic dust acceleration. The key question that motivates this thesis is how to produce these particles. This thesis answers this question by presenting research in the production of round, copper coated anthracene microparticles.

First, a description of the coating device is given. Then, results of preliminary coating trials are presented and discussed. These trials yielded copper coated anthracene, yet the particles were over-coated. Further research and development is required on to determine the optimal coating duration for these particles.

Next, a guide to producing spherical microparticles is presented. First, dry milling is employed to shape the particles. Next, extended wet milling trials, with frequent cooling breaks, are used to achieve the desired particle size. A centrifuge is then used to refine the sample, isolating only the desired particles. Finally, the particles are rinsed to prevent clumping during the drying process.

When applied to anthracene, this method demonstrates that fewer steps may be sufficient. However, further research is needed to explore the broader applicability of this process. With the systematic creation of spherical particles now established, additional work is required to adapt

this technique to a variety of materials found in space dust environments, including other silicates and hydrocarbons.

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