INTEGRAN
TECHNOLOGIES U.S.A. INC.

2541 Appletree Drive, Pittsburgh, PA 15241
Phone: 760-607-0436 - Fax: 760-607-0414

NIH SBIR PHASE I:
UFG-COPPER-ENABLED AIR FILTERS FOR HEALTH CARE WORKER PROTECTION

REPORT TITLE:
FINAL REPORT

CONTRACT NUMBER:
1R43OH009929-01

ISSUING GOVERNMENT ACTIVITY:
DEPT OF HEALTH AND HUMAN SERVICES
CENTERS OF DISEASE CONTROL AND PREVENTION
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH

Table of Contents

1 List of Terms and Abbreviations

HCW - Health Care Workers

IAQ - Indoor Air Quality

PPI - Pores Per Inch

UFG-Cu - Ultra Fine Grain Copper

VHN - Vickers Hardness Number

2 Abstract

Indoor air quality (IAQ) is extremely important in health care facilities. In such facilities, health care workers (HCW) are at a much greater risk of exposure to pathogenic airborne microbes than in typical indoor environments. In addition, many patients in hospitals or long term care facilities have compromised immune systems. As a result, airborne microbial contaminant concentrations that would normally be safe to an otherwise healthy individual can cause illness or infection. Through daily contact with immunocompromised patients, HCW are placed at an even higher risk of exposure to infectious agents. Thus, to achieve safe IAQ in health care environments, the reduction of microbial contaminants below normal ambient levels is required. While relatively large airborne particles may naturally settle out of the air, micron sized particles can remain airborne for several hours, and natural decay rates are far too slow to render infectious microbes non-contagious. This means that engineering controls are required to maintain high IAQ in healthcare facilities. HVAC units are critical for IAQ as they heat, cool and provide air circulation. Current antimicrobial solutions in HVAC systems include pressurization control, HEPA filters and UVGI. There are limitations, however, and much room for improvement.

The development of a low-cost antimicrobial solution for incorporation into HVAC air filters would provide an effective way to limit the spread of biological air contaminants, decrease HVAC maintenance costs and improve IAQ. Integran USA has two technologies which may create such an antimicrobial filter solution: 1) the ability to coat low-cost polyurethane open-celled foams with nanocrystalline metal coatings (Nanometal foams), and 2) UFG-Cu, a natural, recyclable metal coating that exhibits excellent antimicrobial activity against all forms of microbes (including spores).

In addition to its enhanced mechanical properties compared to conventional coarse-grained Cu, Integran USA’s UFG-Cu also demonstrates excellent antimicrobial activity due to its ultra fine grain sizes. Reducing material grain size has been previously demonstrated to significantly enhance the efficacy of other known antimicrobial metals.

For the Phase I of this project, Integran USA has successfully developed a process to create UFG-Copper enabled filters using electrodeposition on polymeric substrates. Final results show complete encapsulation of substrate ligaments, smooth and uniform deposit, and proposed hardness achieved. Studies were conducted to characterize thickness uniformity in terms of center to edge thickness ratio. Due to the electrodeposition process, materials tend to deposit less inside the sample than on the surface. The center to edge thickness ratio gives a way of characterizing how uniform the deposit is with respect to within foam samples for small scale (2" x 2") as well as large scale (12" x 12") with reasonable center to edge thickness ratio. These numbers range from 50% (for thick and dense samples) to close to 100% (for thin and porous samples). Cost market studies suggest a 400 times increase in value in using UFG-Cu enabled filters versus comparable conventional filters due to the reusable nature of Integran USA's filters.

3 Section 1

3.1 Significant Findings

Phase I of this SBIR initiative has been successfully completed, and with promising results. The following objectives were completed:

- Polymeric foam substrates were selected for the electrodeposition process
- Successfully activated polymeric foam substrates for electrodeposition and promotes adhesion
- Polymeric foam substrates were completely encapsulated without any cracks, pits, or pores.
- Surface characterics were smooth and uniform, with Vickers Hardness above 80VHN (91 VHN at current density of 15mA/cm^2, and 115 VHN at current density of 30mA/cm^2)

From the results of small scale testings, deposit thickness of 2" x 2" samples shows that plating at current density of 15mA consistently provides a more uniform coating thickness, except for the case of 5ppi, 1” thick, and 8” anode spacing, and 25ppi, ½” thick, and 2” anode spacing. Anode spacing does not affect coating uniformity. Thinner samples (1/2”) will have better coating uniformity compared to thicker samples (1”). Regarding porosity, higher ppi samples (pores per inch) will have worst coating uniformity compared to lower ppi samples. 5 ppi samples do not seem affected drastically by thickness of sample, current density, or anode spacing.

From the results of scale up feasibility, deposit thickness of 12" x 12" samples shows plating thickness uniformity is better at lower ppi. Substrate thickness does not affect plating uniformity compared to small scale experiments. Sample thickness does not affect plating uniformity compared to small scale experiments

3.2 Translations of Findings

The first set of objectives was to validate Integran USA's process of electrodepositing UFG-Cu on a specific polymeric foam substrate. In this particular case, polyurethane. The process was designed to activate the foam substrate in order to electrodeposit UFG-Cu onto its surface. The plating must completely encapsulate the ligaments of the foam with a smooth nature without any voids of cracks. These were successfully done with the first set of findings.

The second set of objectives was to utilize the process developed to plate small samples. Results of this task were as expected. The thicker the sample, the less likely it is for the middle of the sample to be plated as thick. The denser the sample, or higher ppi, the less likely it is for the middle of the sample to be plated as thick. Anode spacing do not affect the deposition of Cu, enabling Integran USA to discard anode spacing as a variable for plating uniformity. With a lower uniformity, a larger amount of Cu will be deposited on the surface of the foam, lowering efficiency in production. The part of the project was successful in identifying the most efficient set of plating conditions for producing UFG-Cu filters.

The third set of objectives was to replicate and scale up what was achieved in the small scale experiments. This time, sample sizes were 12" x 12". In these experiments, only porosity of the sample affected the plating uniformity. There was little to no effect on plating uniformity with varying sample thickness and plating current density.

3.3 Outcomes/Impact

Findings of this phase I of this project suggest a very promising product. Complete encapsulation of filter ligaments as well as optimum plating conditions identified. With a complete encapsulation of the foam substrate, the highest amount of surface area is ensured, thus enabling the filter to perform at its highest level in terms of antimicrobial property. The deposit was validated with high Vickers hardness, which suggests an ultra-fine grain size morphology, thus suggesting a higher antimicrobial properties than conventional copper as well. Optimum plating and sample size conditions identification leads to a possibility to produce UFG-Cu enabled filters at a reduced cost while maintaining the highest level of performance.

Market studies show that matching the cost of production of Integran USA's UFG-Cu to the price of commercially available antimicrobial treated paper filters, Integran USA's filters present a much better value due to better performance of antimicrobial properties of UFG-Cu, as well as the ability to be cleaned and reused. Cost to produce filters at the recommended plating conditions ranges from $1.41 to $24.68, and represents a 400 times value compared to a disposable commercial product, a saving of about $10,000 over the lifetime of the filter.

4 Section 2

4.1 Backgrounds

Indoor air quality (IAQ) is extremely important in health care facilities. In such facilities, health care workers (HCW) are at a much greater risk of exposure to pathogenic airborne microbes than in typical indoor environments. In addition, many patients in hospitals or long term care facilities have compromised immune systems. As a result, airborne microbial contaminant concentrations that would normally be safe to an otherwise healthy individual can cause illness or infection. Through daily contact with immunocompromised patients, HCW are placed at an even higher risk of exposure to infectious agents. Thus, to achieve safe IAQ in health care environments, the reduction of microbial contaminants below normal ambient levels is required . While relatively large airborne particles may naturally settle out of the air, micron sized particles can remain airborne for several hours, and natural decay rates are far too slow to render infectious microbes non-contagious. This means that engineering controls are required to maintain high IAQ in healthcare facilities.

Typically, combined engineering approaches to maintaining IAQ are currently used. HVAC units are critical for IAQ as they heat, cool and provide air circulation. Current antimicrobial solutions in HVAC systems include pressurization control, HEPA filters and UVGI. In practice, these techniques are mostly reliable and effective. There are limitations, however, and much room for improvement. For example, inadequate ventilation and malfunctioning systems are, in most cases, found to be the root cause of HCW infection by influenza and mycobacterium tuberculosis (TB). One limitation to current antimicrobial solutions in HVAC systems is that they rely on each component of the combined approach to achieve required IAQ. Minor deficiencies or failures of any given component may not have a large impact on IAQ, but these deficiencies are additive and can lead to appreciable negative results in a multi-component system. Often, the effect is large enough to measurably affect IAQ. As an example, it is typically recommended that there should be 10-12 air changes per hour (ach) in high risk areas in hospitals, such as operation rooms. However, on average, there are typically only about 6 ach in such areas. The rate of air change in common areas such as waiting rooms is even lower. While there are no official guidelines for acceptable levels of airborne microbials in health care facilities, the World Health Organization conservatively recommends maintaining an average level which is less than 100 cfu/m^3 (cfu stands for colony forming units of bacteria). However, many facilities do not even meet this conservative standard. In fact, average ranges of 150 – 250 cfu/m^3 are common. Deficiencies in ach are most likely the cause of increased concentrations of cfu, creating a weak link that limits the efficacy of the entire system. Any increase in antimicrobial effect that a HVAC system may have will help increase the efficacy of the system, and decrease the risk to HWC, regardless of the ach rate. As another example, pressurization control is often used in high risk rooms to maintain high IAQ. These rooms are referred to as airborne infection isolation rooms (AIIR). In a recent study of such rooms, only 32 % of 678 rooms tested met the desired negative pressure level. It is difficult to quantify the effect of such a deficiency, but it is obvious that on average, many HCW are exposed to significantly higher levels of airborne pathogens than what is recommended.

There are other limitations to the current antimicrobial solutions in HVAC systems. The current techniques provide limited protection against all microbe classes, are expensive and/or are not appropriate for use in all systems. For example, pressurization protection is generally only used in biohazard facilities and isolation rooms. HEPA filters often result in increased energy consumption (due to higher air pressures through the system) and thus are not always economical. As well, UVGI systems, in which the air is forced past sterilizing UV lamps, are effective against viruses and bacteria but not spores. Air purifiers (either incorporated into the HVAC unit or as stand-alone units) can be used to remove particulates from the air. However, these units may be noisy and not affordable (for efficient air purifiers) for the average application. Preventative maintenance is very important for the proper functioning of an HVAC unit to maintain appropriate IAQ, but it is costly. Common maintenance practices (performed by HVAC professionals) include: using compressed air to blow dust and debris out of the ductwork, using a rotary brush to physically dislodge debris in the system, and vacuuming interior duct surfaces. These methods not only stir up hazardous bioaerosols but also rely on visual inspection to determine the cleanliness of the system, which is insufficient to effectively evaluate microscopic microbes. Regular HVAC maintenance also includes the cleaning and/or replacement of air filters every few months or years, which is a significant cost for HVAC system users. In addition, HVAC units provide moist, dark environments which are ideal breeding grounds for biological contaminants such as mold, mildew, bacteria and viruses. Microbes can grow in multiple areas of HVAC systems, including on the air filters themselves (Figure 1). Infectious airborne diseases can be transmitted through dirty HVAC systems, including Legionnaires' disease, influenza, measles and chicken pox. Molds and mildews growing in HVAC units can also release toxins, causing asthma, hypersensitivity and humidifier fever. Some species of fungi and bacteria found in HVAC units produce spores which are highly resistant to heat and UV radiation and form a significant proportion of non-communicable diseases. In addition to transmitting disease, biological growth within HVAC systems also causes structural damage to system components and the growth of foul smelling microorganisms.

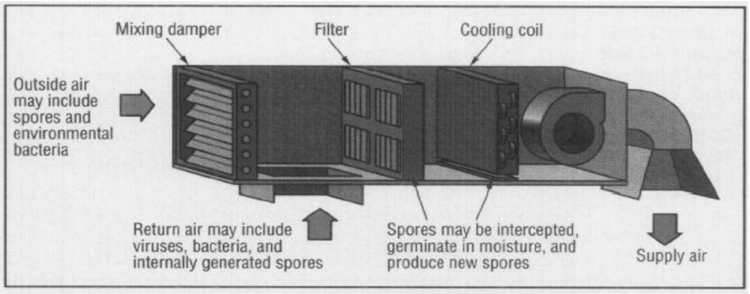


Figure 1: Typical routes of microbial contamination in HVAC systems. Reproduced from [2].

One example of a common airborne pathogen that HCW are exposed to is the influenza virus. Influenza is responsible for approximately 36,000 deaths annually, and the death rate has increased steadily over the last two decades. While the flu is readily spread by respiratory droplets only effective at short distances, there is some indication that there is an airborne component which can cover long distances. Airborne spread of influenza obviously puts HCW at risk. Typically, vaccines are relied upon to mitigate this risk. However, flu vaccines are not mandatory for HCW - in fact, typical HCW immunization rates are only 40 % - 56 %. In addition, vaccination does nothing to directly mitigate the spread of airborne pathogens. Low vaccination rates, coupled with inadequate IAQ, result in many HCW being exposed to influenza. If everything else in an HVAC system were to remain constant, adding antimicrobial capability to the system would lead directly to decreased exposure of HCW to pathogenic viruses such as influenza. Based upon the typical ach rate of 6 (as opposed to the desired ach rate of 10-12 in healthcare facilities), it can be estimated that HCW are being exposed to twice as many airborne pathogens as the expected limit. A relatively inefficient antimicrobial filter capable of killing only 50 % of viable pathogens would be enough to reach desired limits. Any further antimicrobial efficacy would only serve to further reduce risks to HCW.

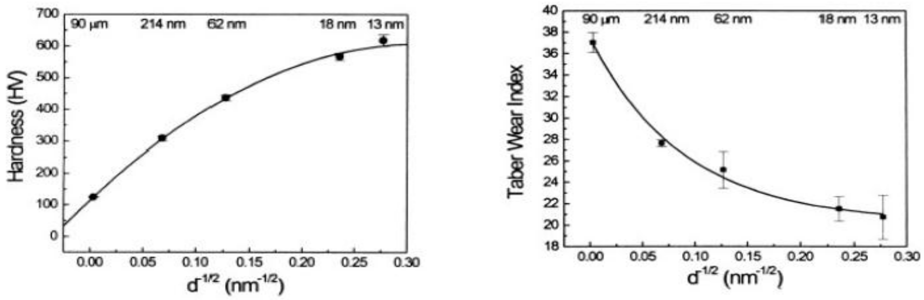
Another common airborne pathogen that HCW are exposed to is *Mycobacterium tuberculosis*, or TB. TB is a serious bacterial disease that most often affects the lungs and can be fatal. Airborne spread of TB to HCW workers is obviously a concern. To mitigate the threat of TB to HCW, AFSCME logically recommends that the number of airborne infectious bacteria should be reduced . Currently, a combination of HEPA filtration and air pressure control is used to control the amount of infectious TB bacteria present in healthcare facilities. As mentioned previously, there are several drawbacks to the current approach, including insufficient system reliability and potentially large costs. Any failures in the current antimicrobial system because of unreliability can lead to great health and financial costs. In one study, a mother and child with undiagnosed TB exposed many infants and HCW in a pediatric ward to TB. After exposure, approximately 2 % of the HCW showed positive TB skin test results . Even this small amount of infection can lead to great costs, including treatment and costs associated with lost work-hours. In addition, ethical considerations dictate that HCW exposure should be minimized as much as possible. However, it is prohibitively expensive to protect entire hospitals from TB with HEPA filtration and pressure control. As mentioned previously, even if current antimicrobial techniques were much less expensive, they are still plagued by deficiencies due to malfunctions, etc. Again, a relatively inefficient antimicrobial filter capable of killing only 50 % of viable pathogens would at least be a beneficial addition to the system and could be uniformly applied to an entire facility, protecting HCW in all areas. Of course, such a filter would have to be much more cost efficient than adding HEPA filtration or pressure control to an entire hospital for it to be a viable alternative. Because of the high costs of HEPA filtration and pressure control, the prospect of the development of a less expensive antimicrobial filter is high.

The development of a low-cost antimicrobial solution for incorporation into HVAC air filters would provide an effective way to limit the spread of biological air contaminants, decrease HVAC maintenance costs and improve IAQ. Integran USA has two technologies which may create such an antimicrobial filter solution: 1) the ability to coat low-cost polyurethane open-celled foams with nanocrystalline metal coatings (Nanometal foams), and 2) UFG-Cu, a natural, recyclable metal coating that exhibits excellent antimicrobial activity against all forms of microbes (including spores).

Electrodeposited Ultra Fine-Grained and Nanocrystalline Metals

Integran USA has patented technologies to produce ultra fine-grained metallic coatings on a variety of substrates using electrodeposition. Electrodeposition is the simplest and most cost-effective method of producing ultra fine-grained and nanostructured materials as there is an established industrial (electroplating) infrastructure. For many applications, Integran USA has concentrated on the development of materials with grain sizes in the nanoscale. Nanostructured materials provide a unique combination of hardness with ductility that cannot be obtained in conventional coarse-grained materials. Integran's principals pioneered the earliest systematic studies on the use of electrodeposition to produce nanocrystalline materials in the late 1980's as well as the first large scale structural application for nanostructured materials in 1993 (the Electrosleeve process for nuclear steam generator repair) and own some of the earliest issued US patents in the field of nanotechnology. The general conditions for producing nanocrystalline metals and alloys by electrodeposition are documented in US Patent Nos. 5,352,266 (Oct.4, 1994) and 5,433,797 (July 18, 1995). Recently, the technology has been extended to produce Nanometal foams with relative densities in the range of 1 to 25% of the fully-dense bulk nanostructured material.

As a result of Hall-Petch strengthening, metals with ultra fine and nanocrystalline grain sizes display significant increases in yield strength and hardness relative to their coarser-grained counterparts (Figure 2A). Hardness increases on the order of 200% to 700% are typically observed in nanometals. Furthermore, as grain size decreases, abrasive wear resistance improves considerably as predicted by Archard's law (volume wear loss is inversely proportional to hardness) (Figure 2B). Corrosion studies conducted on electrodeposited nanocrystalline nickel and cobalt alloys have demonstrated that significant improvements in the pitting potential, which is normally associated with localized corrosion resistance (particularly with regard to intergranular corrosion and stress corrosion cracking), are observed in comparison to coarse-grained materials. Similar observations were made for the corrosion behavior of other ultra fine-grained and nanocrystalline alloys, whereby reduced susceptibility to localized corrosion was attributed to fine-grained microstructure.



(A) (B)

Figure 2: (A) Vicker's Microhardness and (B) Taber Wear Index (an inverse measure of surface wear resistance) of electrodeposited nickel as a function of the inverse square-root of grain diameter (d) [31].

These studies show that ultra fine-grained and nanocrystalline materials exhibit enhanced mechanical properties compared to coarser-grained counterparts. Current techniques to deposit coatings on surfaces, such as vapor phase deposition, often require post-treatments to produce stable properties (ie. annealing) which promote grain growth and recrystallization. This annealing step significantly alters and may even diminish the effects of the material's fine grain-sized properties. In contrast, Integran USA's process can deposit ultra fine-grained and nanocrystalline materials in a straight forward single-step process, allowing the material to retain its excellent mechanical properties. Furthermore, Integran USA's process produces fully-dense metal coatings which do not require the use of or produce potentially harmful nanoparticles.

Nanometal Foams

The Nanometal foam concept originated from a previous Integran project with the Office of Naval Research concerning the design of a lightweight structural armor for a new class of vehicles (MEFV). During this program, a platform of nanotechnology solutions was developed, including the first ever nanocrystalline metallic foams. In one approach, conventional open-cell aluminum and carbon foams were reinforced by the electrodeposition of a high-strength nanocrystalline sleeve (Figure 3). Microhardness measurements on the strut cross-sections show that the hardness of the reinforcing Nanometal sleeve is significantly higher than the aluminum or carbon substrate.

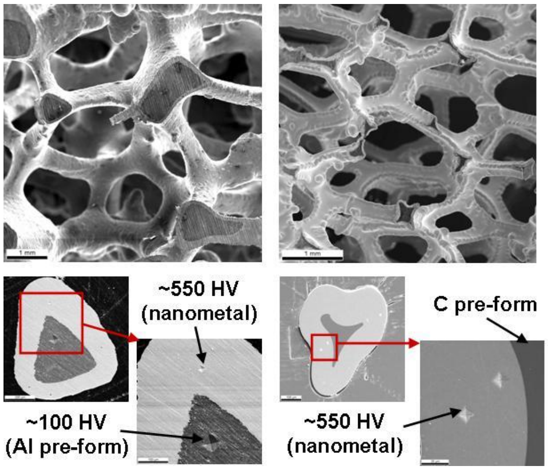
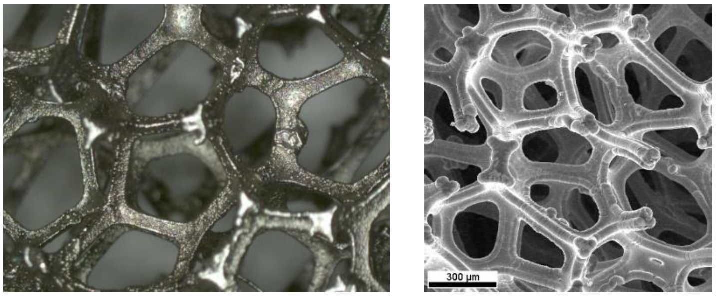


Figure 3: Scanning electron micrographs of Nanometal foams (top) and strut cross-sections (bottom) produced by Integran using Al (left) and carbon (right) pre-forms.

Recent developments in the Nanometal foam technology has enabled Integran USA to fabricate Nanometal foams from a reticulated polymer substrate of any size shape or form (such as polyurethane foam). Figure 4 shows images of Nanometal foams with two different pore densities, 5 pore per inch (ppi) and 90 ppi, respectively.



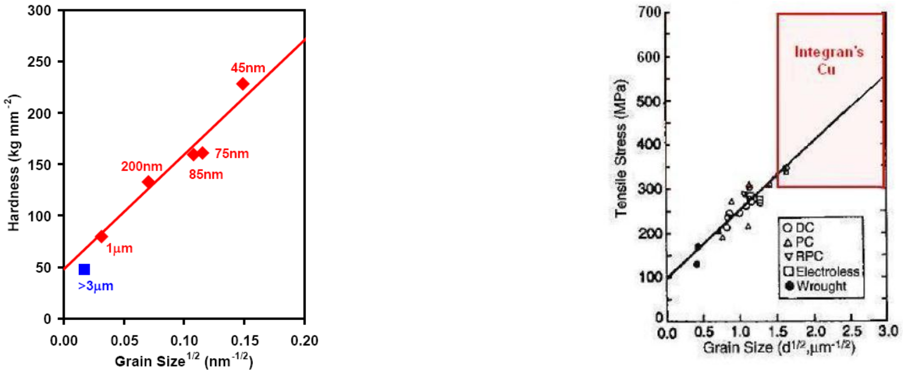
(A) (B)

Figure 4: (A) Digital stereo micrograph of a 5 ppi Nanometal foam, and (B) scanning electron micrograph of a 90 ppi Nanometal foam.

In the proposed Phase I program, Integran USA's UFG-Cu would be used to coat porous polyurethane foams to provide a cost-effective, high-strength, durable foam structure with excellent antimicrobial activity for incorporation into air filters in HVAC units.

Ultra Fine-Grained Copper (UFG-Cu)

Integran USA has recently developed the capability to produce UFG-Cu. Although UFG-Cu grain sizes are not always in the nanoscale, UFG-Cu exhibits many of enhanced mechanical properties of Integran USA's electrodeposited nanostructured materials. Vicker's microhardness testing of UFG-Cu showed microhardness values ranging from 80 to 210 VHN, inversely proportional to the grain diameter produced (Figure 6A). Tensile strength, a measure of the maximum engineering tension stress that can be sustained by a material without permanent fracture, is also dependent on grain size. Cu samples produce by Integran exhibited significantly higher tensile strengths compared to values documented for wrought Cu and Cu deposited by other electrodeposition techniques (Figure 6B). The enhanced hardness and strength of Integran USA's UFG-Cu are expected to lead to enhanced wear resistance and durability of the coated surface. A summary of UFG-Cu's physical characteristics compared to other conventional coating metals is shown in . Notably, Integran USA's process to produce UFG-Cu does not use or produce potentially harmful nanoparticulates.



(A) (B)

Figure 6: (A) Plot of hardness versus the inverse square-root of grain size for Cu samples produced by Integran (red line). Grain sizes for plotted points are indicated. The hardness of coarse-grained Cu (EG-CRA) is also indicated (blue square). (B) Plot of tensile strength versus the inverse square-root of grain size for Cu deposited by direct current (DC), pulse current (PC), reverse pulse current (RPC) or electroless deposition, and wrought Cu. A range for tensile strengths of Integran's Cu samples is superimposed on the previously documented data (red box)

Table 1: Property comparison of Integran's UFG-Cu and commonly used coating materials.

Metal	Tensile Strength (MPa)	Hardness (VHN)	Antimicrobial Activity
Integran USA's UFG-Cu	570	210	Excellent
Copper (Type C101)	33	50	Very Good
Stainless Steel (Type 304)	215	130	None
Chrome-plating	n/a	>700	Poor
Brass (Type 260, annealed)	75	60	Good
Bronze (Type 314, annealed)	85	70	Good

In addition to its enhanced mechanical properties compared to conventional coarse-grained Cu, Integran USA's UFG-Cu also demonstrates excellent antimicrobial activity due to its ultra fine grain sizes. Reducing material grain size has been previously demonstrated to significantly enhance the efficacy of other known antimicrobial metals. Enhanced antimicrobial properties have been observed in nanocrystalline silver, a well-known antibacterial agent, in the non-structural powder and small cluster forms. Studies of the effect of increased grain size on the efficacy of nanocrystalline silver indicate that the biological activity of the metal remains high at small grain sizes, but reduces rapidly as the crystal size begins to increase. However, because of its high cost and limited structural capabilities, the applications of nanocrystalline silver are quite limited.

Antibacterial testing demonstrated that Integran USA's UFG-Cu killed *Staphylococcus aureus* bacteria at a more rapid rate than even conventional pure Cu (the most potent antimicrobial solid material registered by the EPA) (Figure 7). UFG-Cu was found to reduce the bacterial load by >99.99% in 30 minutes (compared to stainless steel, on which bacteria can grow for many days). Similar results were observed for the food-borne pathogens *Salmonella typhimurium* and *Listeria monocytogenes* (data not shown).

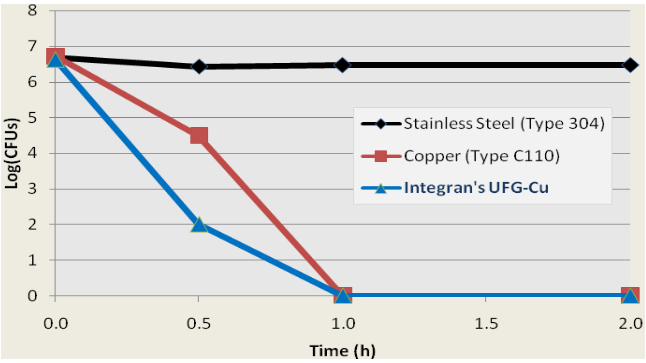


Figure 7: Antimicrobial efficacy of stainless steel, conventional Cu (type C110) and Integran USA's UFG-Cu against *Staphylococcus aureus*. Metal coupons were inoculated with a known quantity of bacteria. At the indicated times after inoculation, the number of surviving bacteria were enumerated (CFUs = viable bacteria).

Integran USA proposes to coat polyurethane reticulate open-celled foam using its Nanometal foam technology with its recently developed UFG-Cu coating. Due to UFG-Cu's enhanced mechanical properties compared to conventional Cu, this excellent antimicrobial material can be utilized in applications that were previously restricted to other materials with less antimicrobial efficacy. It is expected that the proposed Phase I project will produce cost-effective UFG-Cu-coated foams suitable for use in air filters for HVAC systems in healthcare facilities.

Integran USA's Ultra Fine-Grained Copper (UFG-Cu)

The proposed added value of using Integran's metallic approach for filter construction originated from the idea that the there have been previous studies showing the beneficial application of copper in the reduction of air pathogens. While this result is encouraging, from a commercial standpoint it will be necessary and advantageous to provide any filter system at the most competitive cost. For a copper – coated system, this can only be achieve by providing the thinnest possible complete coverage layer of copper on the filter.

From a use perspective, the filer as a whole must be active from the biological point of view, this would imply the need for a large surface area and the necessity for complete coverage. Furthermore, the filer must be rigid enough to resist collapse upon fouling.

We therefore have two competing objectives, to provide a copper surface of high surface area at the minimum weight of copper. To satisfy these objectives, one possibility would be to reduce the filter section size to reduce the amount of copper to be added. This however, weakens the product making the support of the filter necessary in application so that the moving air does not cause collapse of the filter as it fouls and drag is increased. By using Integran's high strength nanocrystalline copper, this potential design change for the filter may be possible.

Integran USA has patented technologies to produce ultra fine-grained metallic coatings on a variety of substrates using electrodeposition. Electrodeposition is the simplest and most cost-effective method of producing ultra fine-grained and nanostructured materials as there is an established industrial (electroplating) infrastructure. For many applications, Integran USA has concentrated on the development of materials with grain sizes in the nanoscale range. Nanostructured materials provide a unique combination of hardness with ductility that cannot be obtained in conventional coarse-grained materials. Recently, the technology has been extended to produce Nanometal foams with relative densities in the range of 1 to 25% of the fully-dense bulk nanostructured material.

For this application, a result of Hall-Petch strengthening, metals with ultra fine and nanocrystalline grain sizes display significant increases in yield strength and hardness relative to their coarser-grained counterparts (Figure 2A). Hardness increases on the order of 200% to 700% are typically observed in nanometals. The nanocrystalline structure also shows improvement in corrosion studies, [particularly in the pitting potential, which is normally associated with localized corrosion resistance (particularly with regard to intergranular corrosion and stress corrosion cracking), when compared to traditional coarse-grained materials.

Copper (Cu) and many of its alloys are known to possess significant antimicrobial properties. As such, the Environmental Protection Agency (EPA) has recently approved the registration of antimicrobial Cu alloys with public health claims for residential, commercial, industrial and institutional non-food contact use. These products are registered under the Federal Insecticide, Fungicide, and Rodenticide Act’s no “unreasonable adverse effects” standard. Such Cu alloy products have been rigorously tested and have demonstrated antimicrobial activity while posing no risks to public health. Therefore, these products could provide a significant benefit to inhibiting the transmission of pathogenic organisms as a supplement to existing infection control measures.

The antimicrobial effects of Cu have been shown to be most effective when the Cu content is at its highest, as in the case of pure Cu. The antibacterial effects were assessed for pure Cu and Cu alloys (brasses, bronzes, Cu-Ni, Cu-Ni-Zn) spanning a range of Cu concentrations (65%-100%) for use in the food processing industry to replace current AISI 304 and 316 stainless steels. Cu, Cu alloy and steel surfaces were seeded with *Escherichia coli* bacteria and incubated at 20^{o}C or 4^{o}C. At both incubation temperatures, nearly all Cu alloys reduced the bacterial content within 6 h, whereas the stainless steels showed no reduction in bacterial content in the same amount of time. Further, there was a trend of increased bactericidal efficacy with alloys containing greater Cu content (Figure 5A). Cu and its alloys have also been shown to effectively kill (MSRA), a serious nosocomial pathogen that is resistant to antibiotics and causes serious and potentially life threatening infections. Cu and Cu alloys (brass, Cu-Ni-Zn) have been shown to be effective in reducing MRSA cell count from 10^7 colony forming units (CFUs)/mL to zero within a few hours when incubated at 20^{o}C, with the most rapid effects being observed with pure Cu surfaces (Figure 5B). In work measuring the effects of Cu concentration on growth inhibition of TB, pure Cu was shown to have the highest growth inhibition index for two clinical strains of *Mycobacterium tuberculosis*, inhibiting growth by 88 % and 98 % when compared to the control surface.

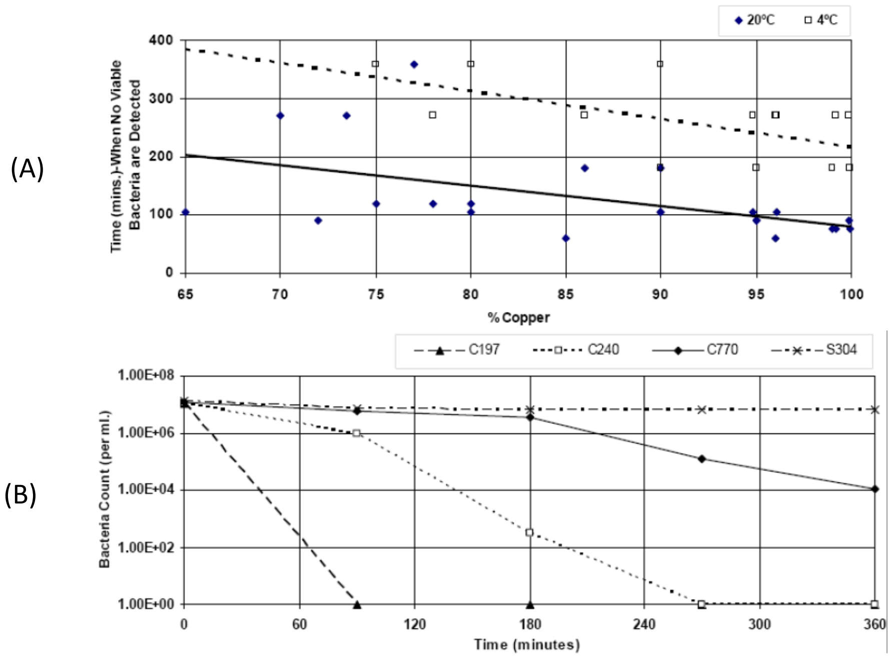


Figure 5: (A) Effects of alloy Cu concentration on the time to completely kill *E. coli* bacteria incubated at two different temperatures (20°C and 4°C). (B) MRSA viability on pure Cu (C197), brass (C240), Cu-Ni-Zn (C770) and stainless steel (S304). Increased bactericidal efficacy was observed with increasing alloy Cu content [44].

In addition to their proven antibacterial effects, Cu-containing metal species have recently been shown to exhibit antiviral effects. Following exposure to polyester fibers doped with Cu, the amounts of West Nile virus and HIV-1 were found to be significantly reduced compared to Cu-free control surfaces. In addition, pure copper has shown to be remarkably effective at controlling Influenza A Virus. In this study, stainless steel and pure Cu substrates were inoculated with Influenza A Virus. After 6 hrs incubation, the amount of infectious viral particles on pure Cu was reduced from 2×10^6 to only 500, while 500,000 virus particles were still active on the stainless steel after 24 hrs. The Copper Development Association Pub 195 provides a nice review of the broad range of bacterial, viral and mold species that copper has shown effective antimicrobial activity against. Recent results also show that Cu exhibits potent sporicidal activity against highly resilient *Clostridium difficile* spores. These studies clearly suggest that Cu and its alloys are very effective in significantly reducing the transmission of infectious organisms. Pure Cu in particular is desired as an antimicrobial coating as it has been shown to be the most effective. Notably, the tarnishing of Cu does not affect its antimicrobial efficacy.

4.2 Phase I – Technical Objectives

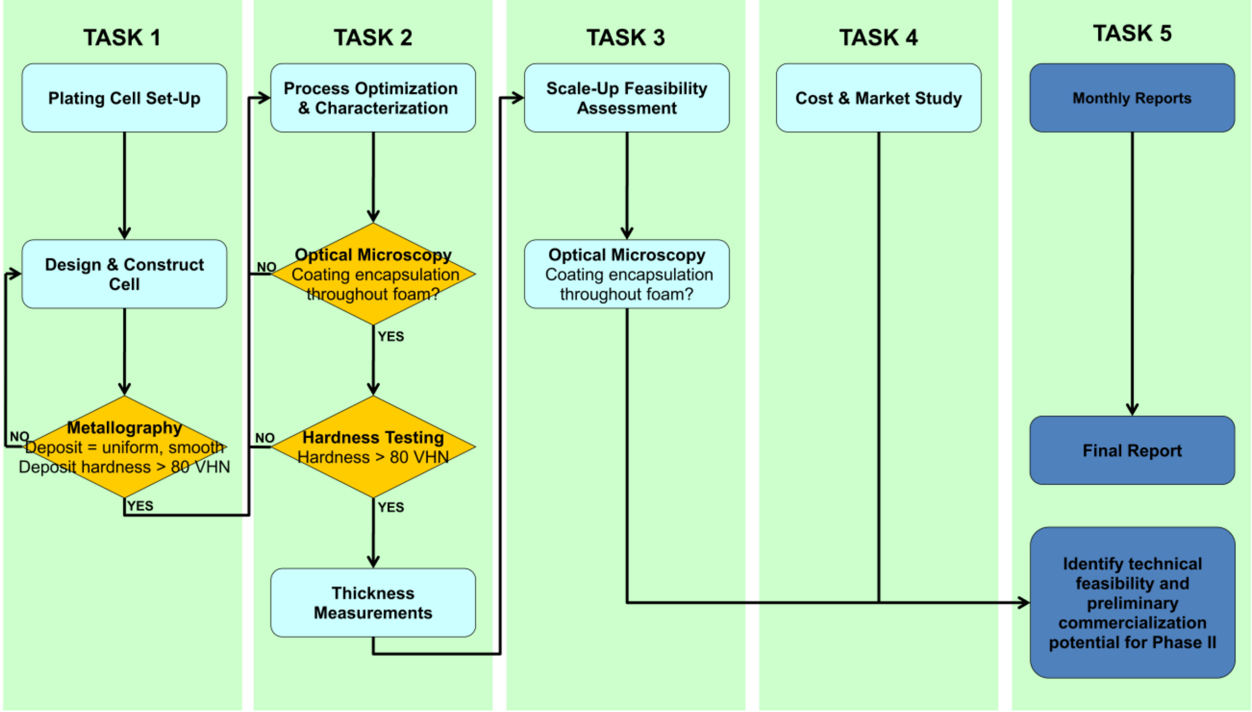
The main objective of this program is to develop the process to coat polyurethane reticulated open-celled foams with Integran USA's UFG-Cu. The specific goals of the project are to:

1. Establish an electroplating system suitable for coating foams with UFG-Cu,
2. Identify the optimal process conditions for coating polyurethane foams with UFG-Cu, including:
    a. Identifying the optimal foam thickness and porosity for coating with UFG-Cu,
    b. Optimizing the electroplating conditions for coating polyurethane foams with UFG-Cu,
3. Determine the feasibility of producing UFG-Cu-coated foam sample sizes applicable for use in air filters,
4. Perform an in-depth cost and market analysis of the potential antimicrobial air filter product.

4.3 Phase I - Work Plan

To meet the Phase I objectives, the proposed project will be divided into the following tasks.

- Task 1 – Plating Cell Set-Up
- Task 2 – Process Optimization and Characterization
- Task 3 – Scale-Up Feasibility Assessment
- Task 4 – Cost and Market Study
- Task 5 – Reporting and Project Management



Task 1 – Plating cell set up

In this task, an electroplating bath for the deposition of UFG-Cu on a variety of foam shapes and sizes will be designed and constructed. Design parameters will be chosen based on the experience of the applicants and are expected to include cell size, rack design and adjustable anode/cathode spacing.

Once the cell is constructed, flat test coupons will be generated and analyzed by conventional metallography to confirm proper bath function. This data will form the basis for Go/No-Go decisions with regard to further use of the cell. Criteria for a Go determination are:

- Deposit = uniform, smooth,
- Deposit hardness > 80 VHN.

Failure to meet these criteria will result in modification to the cell design

Task 2 – Process Optimization and Characterization

In this task, 2”x2” polyurethane reticulated open-celled foam samples will be coated with Integran USA’s UFG-Cu coating using the electroplating cell designed in Task 1. The process specifications will be determined for optimal foam coating conditions. Parameters to be analyzed will be chosen based on the experience of the applicants and are expected to include foam porosity and thickness, bath current, and anode/cathode spacing. Foams will consist of samples with 5-25 ppi (these foams have sufficient porosity to ensure initial air flow resistance characteristics meeting the requirements of standard ASTM F1040 (“Standard Specification for Filter Units, Air Conditioning: Viscous-Impingement and Dry Types, Replacable”)) and thicknesses of ½” to 1”. The expected experimental matrix for these investigations is outlined. This matrix may be modified throughout the Task based on on-going results from the plating runs to ensure efficient and thorough optimization activities.

The successful coating of foam samples with UFG-Cu will be analyzed by optical microscopy. Coated foam samples will be cross-sectioned and analyzed throughout the sample (sides and middle). Coatings that show full encapsulation throughout the foam sample will be analyzed for hardness using nano-indentation. These data will form the basis for Go/No-Go decisions with regard to further use of plating and sample conditions. Criteria for a Go determination are:

- Coating encapsulates all strands throughout foam sample,
- Coating hardness > 80 VHN.

The thickness of the UFG-Cu coatings will also be measured by optical microscopy. This data will not form the basis for Go/No-Go decisions but rather will provide a quantifiable center-to-edge ratio in coating thickness to further characterize the sample and process conditions.

This task is expected to determine the foam sample thickness and porosity that can be effectively plated using the plating cell designed in Task 1. As well, this task will provide a fundamental understanding of the plating conditions required for optimal coating coverage of foam samples.

Task 3 – Scale-Up Feasibility Assessment

This task will consist of applying the sample and process specifications identified in Task 2 to 12”x12” foam samples to determine the feasibility of the system to produce samples applicable for use in air filters. Some process optimization may be required to ensure complete coating coverage throughout the larger foam samples. The coating of these foam samples with UFG-Cu will be analyzed by optical microscopy for full encapsulation throughout the foam sample as in Task 2. This data will provide a feasibility assessment of the production of large UFG-Cu-coated foam samples suitable for use in air filters.

Task 4 – Cost and Market Study

This task will consist of an in-depth study of the market potential and production costs for residential, commercial and institutional HVAC air filters containing UFG-Cu-enabled foams. Topics to be considered include: how the foams would be incorporated into air filters, estimated production costs, the cost benefit of an improved antimicrobial system compared to existing antimicrobial HVAC systems, the market potential for such a product, the air filter competition landscape, supply chain analysis, and an overall assessment of the commercialization potential for UFG-Cu-enabled foams in HVAC air filters.

Task 5 – Reporting and Project Management

Reporting deliverables and project management activities for the proposed Phase I project are:

1) Kick-off meeting within one month of award notification,
2) Final report documenting all experimental findings, including a critical analysis of the feasibility for further research in Phase II.

The total duration of Phase I activity is expected to be 6 months. The estimated schedule is provided in the following Gantt chart.

		Month					
	TASK	**1**	**2**	**3**	**4**	**5**	**6**
1	**Plating Cell Set-Up**	■	■				
2	**Process Optimization & Characterization**			■	■	■	
3	**Scale-Up Feasibility Assessment**						■
4	**Cost & Market Study**					■	■
5	**Reporting & Project Management**	■	■	■	■	■	■
	Kickoff meeting	*					
	Final report						*

4.4 Phase I Results

Task 1 – Plating cell set up

Task 1 for this project has been executed and successfully completed. Polymeric foam substrates were successfully activated and electro deposition plating cell designed and constructed. Two flat test coupons were generated on titanium substrates and hardness was verified to be 91 VHN and 115VHN

- An activation line was constructed and built in order to activate polymeric foam substrate (Figure 8).

Figure 8 - Photographs of the activation process line.

A Plating cell for the electrodeposition of UFG-Cu was constructed and flat test coupons were produced. UFG-Cu coupons (2” x 2”) were produced by electrodeposition on titanium substrates and peeled off. Samples were tested for hardness and showed an indicated Vicker’s hardness of: 91 VHN for 15mA and 115VHN for 30mA, suggesting ultra fine grain morphology. Deposits were also smooth and uniform over the entire surface area. Decisions were made to continue using the plating cell set up with the following criteria met:

- Deposit = uniform, smooth
- Deposit hardness > 80VHN

Task 2 – Process Optimization and Characterization

In order to efficiently optimize the activation and metallization process, 2” x 2” polyurethane reticulated open celled foam samples were coated with Integran USA’s UFG-Cu coating using the electroplacting cell designed in Task 1. The parameters to be analyzed were:

- Anode spacing
- Electroplating current density
- Thickness of foam samples
- Foam porosity

Anode spacings were to be at 2” or 8”, chosen based on experience of closest recommended for even distribution of coating and the furthest distance that the set up cell would offer. Current densities stay at the upper and lower limit of our known process that would create UFG-Cu with deposit hardness above 80VHN.

Samples were examined under scanning electron microscope to verify fully encapsulation of the foam as well as a uniform deposit. Below (Figure 9) are SEM images of cross sections of the plated foam.

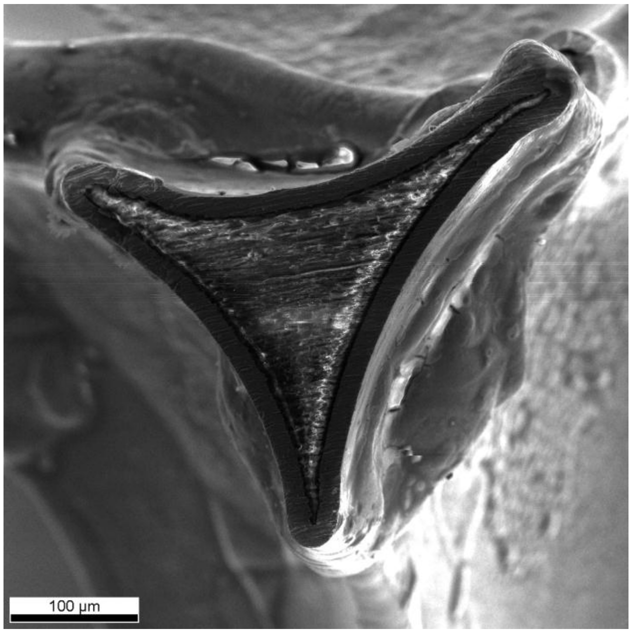


Figure 9. Scanning electron microscope image of a cross section of the Integran USA plated foam at a magnification of 130X . Plating conditions were 6ppi, 15mA/cm^2, 8 inch anode spacings. Image shows complete encapsulation of foam strand without pits, pores, or crack

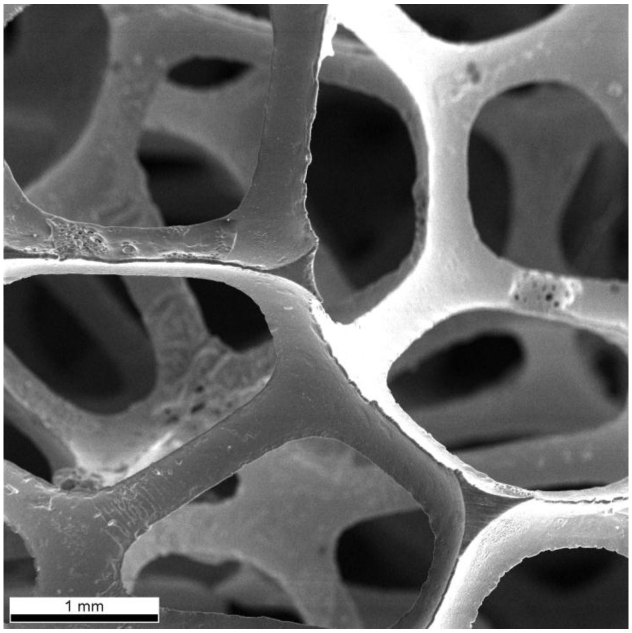


Figure 10. Scanning electron microscope image of a cross section of the Integran USA plated foam at a magnification of 15X . Plating conditions were 6ppi, 15mA/cm^2, 8 inch anode spacings. Image shows uniform and smooth deposite and complete encapsulation on foam substrate.

The following matrix (Table 2) shows the combination of samples that were coated for the Task 2 of this project

Table 2. Matrix of plating conditions for 2" x 2" foam samples.

Plating conditions for 2” x 2” samples				
Porosity (ppi)	**Thickness (in)**	**Current Density (mA)**	**Anode Spacing (in)**	**Sample Size (in^2)**
5	1/2	15	2	2X2
5	1/2	30	2	2X2
5	1	15	2	2X2
5	1	30	2	2X2
10	1/2	15	2	2X2
10	1/2	30	2	2X2
10	1	15	2	2X2
10	1	30	2	2X2
25	1/2	15	2	2X2
25	1/2	30	2	2X2
25	1	15	2	2X2
25	1	30	2	2X2
5	1/2	15	8	2X2
5	1/2	30	8	2X2
5	1	15	8	2X2
5	1	30	8	2X2
10	1/2	15	8	2X2
10	1/2	30	8	2X2
10	1	15	8	2X2
10	1	30	8	2X2
25	1/2	15	8	2X2
25	1/2	30	8	2X2
25	1	15	8	2X2
25	1	30	8	2X2

Three samples were coated under each condition, giving the total of 72 samples for 24 conditions. Samples were plated under each condition for 2 hours. Stainless steel pins were inserted at the center of each sample before plating for thickness characterization. Foam substrate samples were plated along with the pins at each plating condition. Pins were cross-sectioned and UFG-Cu thickness is recorded along the length of the pins in 1/8” intervals. The ratio of the coating thickness at the center to the thickness at the edge is used to evaluate the distribution of plated copper (Figure 11). The higher the ratio, the more uniform the copper distribution is.

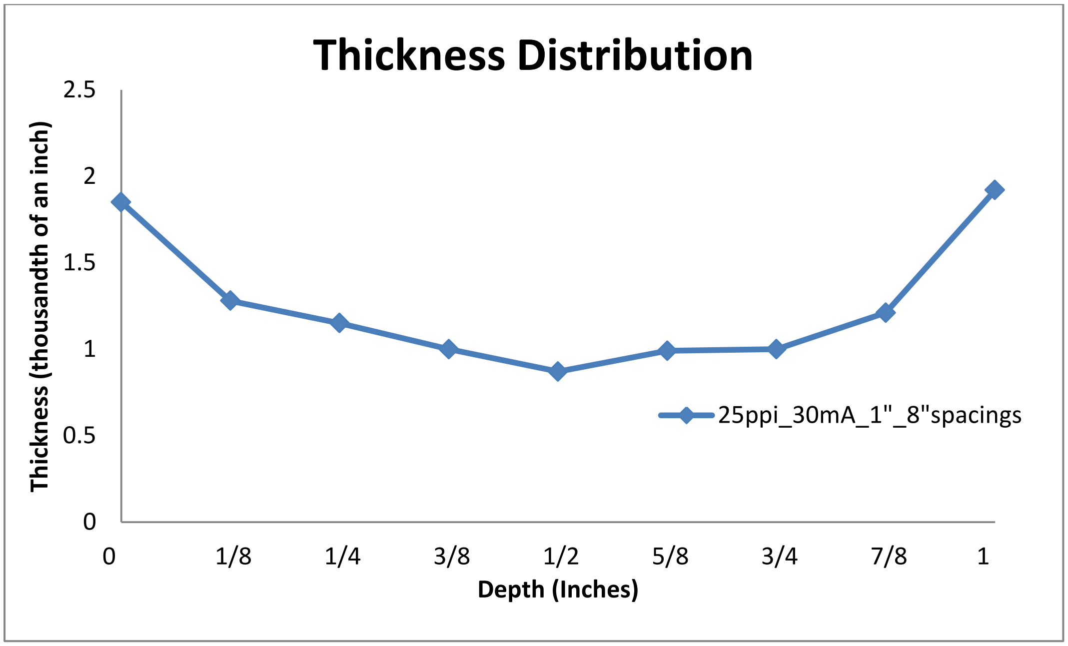


Figure 11. Example of thickness distribution of copper foam plated at 25ppi, 30mA/cm^2, 1" thick, and anode spacing at 8"

From the thickness distribution measurement, center to edge thickness ratio is calculated and used to characterized uniformity of coating. This ratio is compared between different plating conditions. Figure 12 shows a chart summarizing the results.

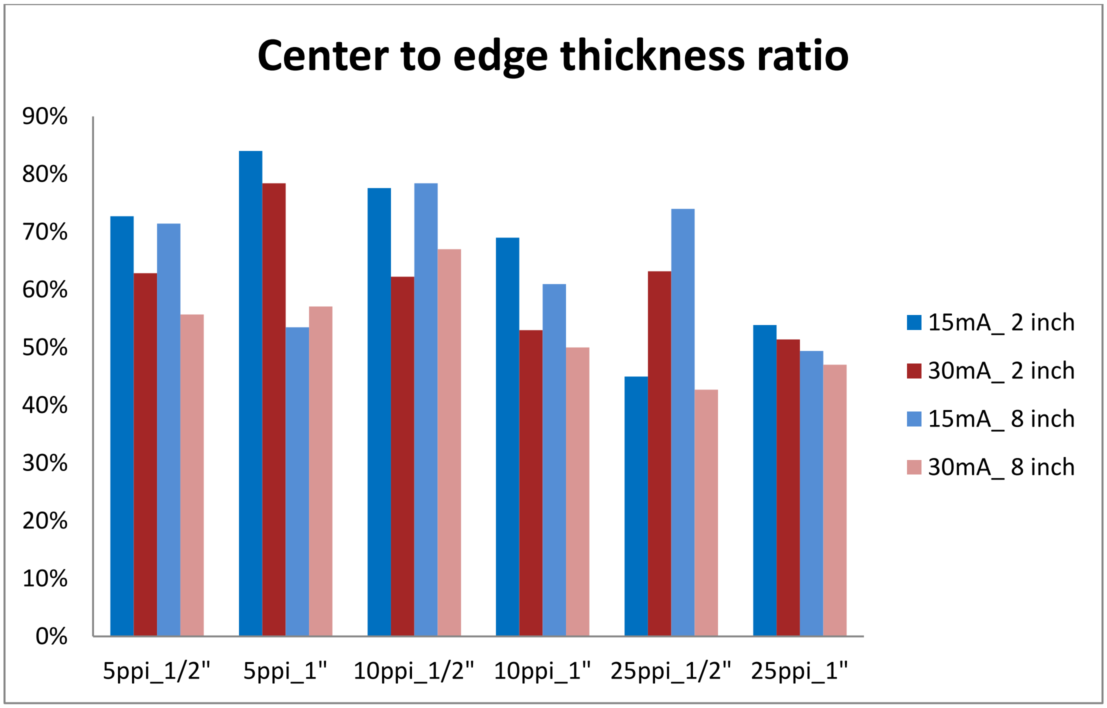


Figure 12. Center to edge thickness ratio of different plating conditions

From the results of the process optimization, it can be seen that:

- Plating at current density of 15mA consistently provides a more uniform coating thickness, except for the case of 5ppi, 1” thick, and 8” anode spacing, and 25ppi, ½” thick, and 2” anode spacing.
- Anode spacing does not affect coating uniformity
- Thinner samples (1/2”) will have better coating uniformity compared to thicker samples (1”)
- Higher ppi samples (pores per inch) will have worst coating uniformity compared to lower ppi samples
- 5 ppi samples do not seem affected drastically by thickness of sample, current density, or anode spacing.

Task 3 – Scale-up feasibility assessments

According to the results of Task 2, all plating conditions were successfully finished according to the objective set in Task 1. 12”x 12” samples were plated according to Table 3. Anode spacing is now limited to 2” due to the consistency of thickness uniformity between 2” and 8” of anode spacing.

Table 3. Matrix of plating conditions for scale up assessments of 12"x 12" foam samples

Plating conditions for 12” x 12” samples			
Porosity (ppi)	**Thickness (in)**	**Current Density (mA)**	**Sample Size (in^2)**
5	1/2	15	12x12
5	1/2	30	12x12
5	1	15	12x12
5	1	30	12x12
10	1/2	15	12x12
10	1/2	30	12x12
10	1	15	12x12
10	1	30	12x12
25	1/2	15	12x12
25	1/2	30	12x12
25	1	15	12x12
25	1	30	12x12

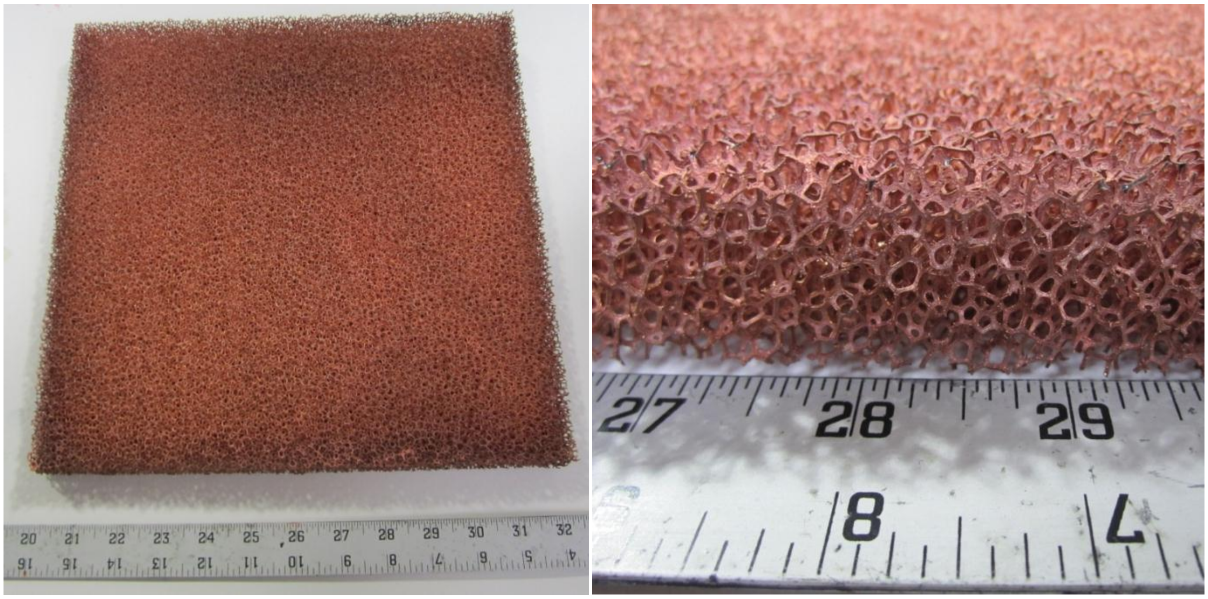


Figure 13. 12" x 12" plated foam sample at 5ppi and 1" thick

Figure 14. 12"x12" plated foam sample at 30ppi and 1" thick

Nine (9) stainless steel pins were inserted into samples to be plated and characterized for thickness distribution. Their locations are marked by the red Xs on Figure 15. Three rows of three pins were inserted: the top row at 2” from the top edge of the sample, middle row half way between the top and bottom edge, and bottom row at 2” from the bottom edge of the sample. The left column of pins was inserted 2” from the left edge of the sample, and right column 2” from right edge of the sample. Pins were cross-sectioned and UFG-Cu thickness is recorded along the length of the pins at the edge of the sample and in the center of the sample.

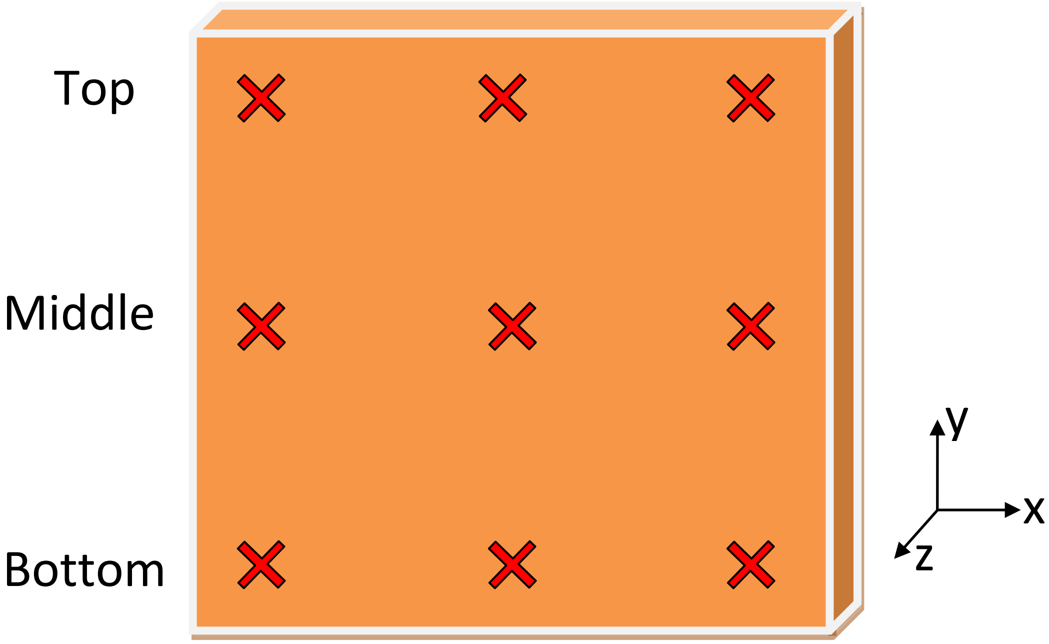


Figure 15. Locations of pins inserted along the Z axis of the foam are marked by red "X"s

Figure 16 shows the surface plating thickness distribution and center plating thickness distribution for 30ppi_1"_30mA sample.

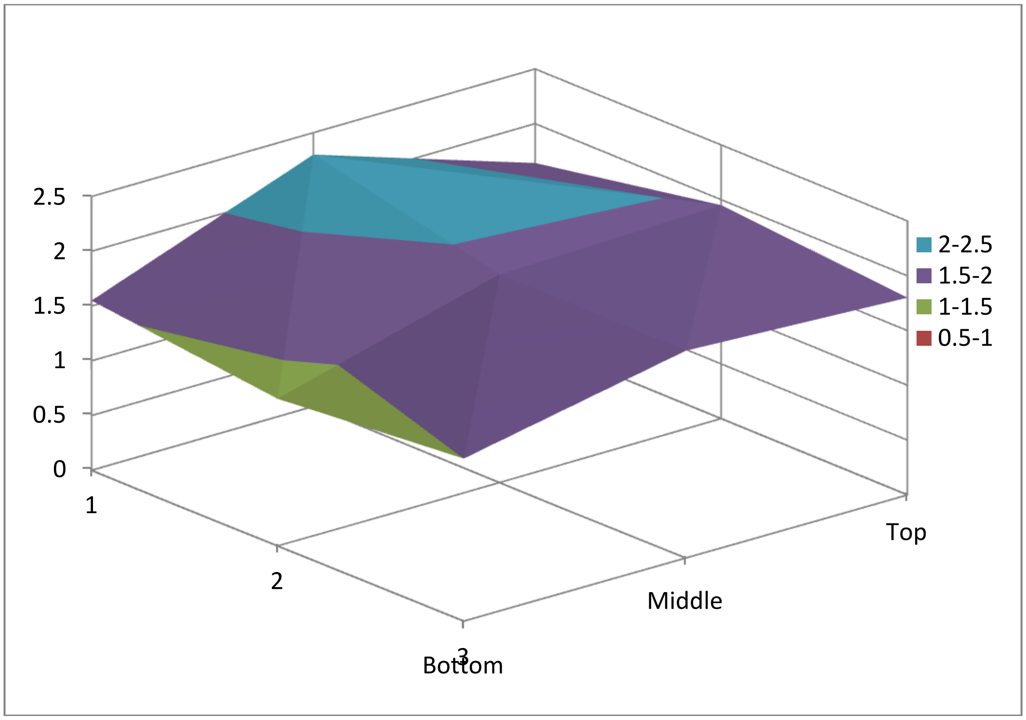


Figure 16. Plating thickness distribution of 30ppi_1"_30mA sample on the surface of the copper foam

Distribution of plating thickness on the surface of the foam along the Z direction (Figure 16) is similar to what is expected, coating thickness is slightly higher at the edge and corner of the sample. Thickness ranges between 1.35 mils and 2.3 mils.

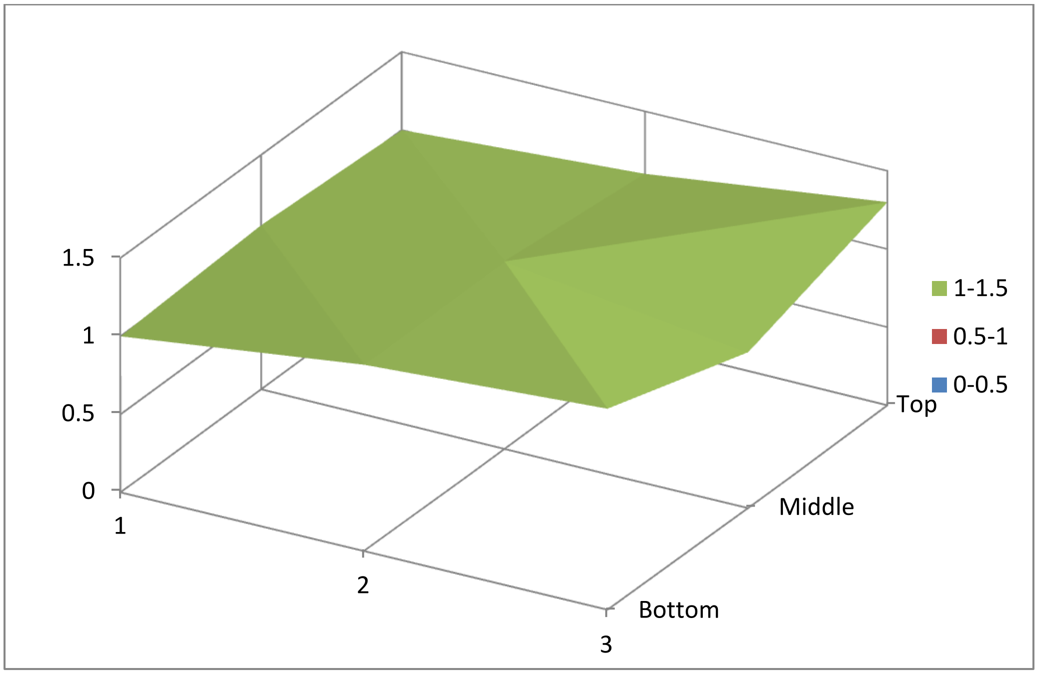


Figure 17. Plating thickness distribution of 30ppi_1"_30mA sample in the center of the copper foam

Distribution of plating thickness in the center of the foam in the Z direction (Figure 17) is similar to what is expected, coating thickness is slightly higher at the edge and corner of the sample. Coating uniformity is excellent, thickness ranges between 1 mils and 1.3 mils. This distribution trend is expected for all 12" x 12" samples.

Thickness distribution was also recorded for surface and center (along the Z direction) at the Top edge, Middle center, and Bottom edge position (along the X-Y plane) The ratio of center to edge thickness is calculated at each position Top1, Middle2, and Bottom1, is recorded. The average of those numbers are then calculated for each plating condition. Below (Figure 18) is a chart summarizing the result

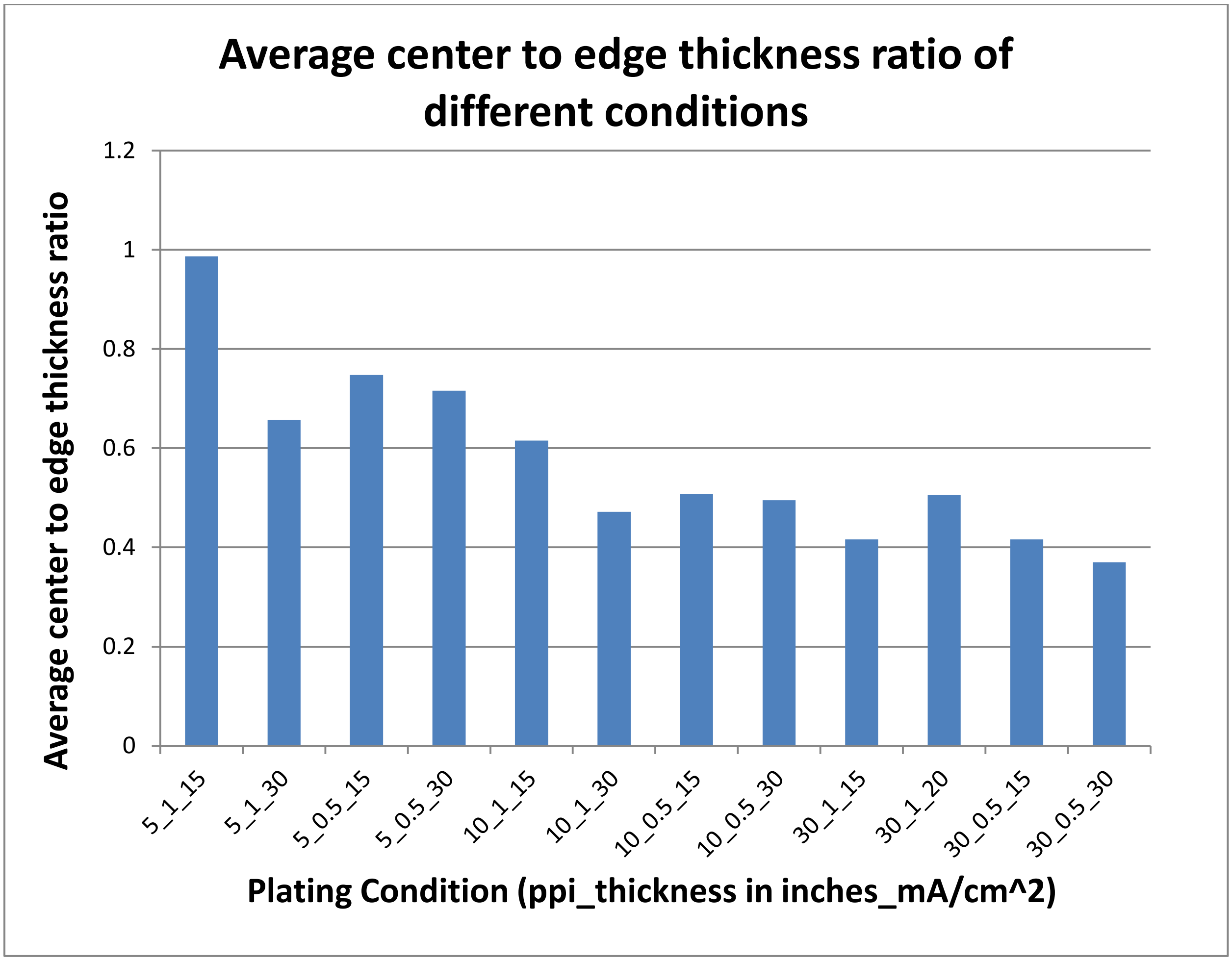


Figure 18. Average center to edge thickness ratio for each plating condition

As expected, the results show a better distribution throughout the foam substrate for a lower pore density samples. 5ppi samples exhibit better plating distributions than 10 ppi samples, which exhibit better distributions than 30ppi samples. There seems to be little variation in thickness distribution regarding sample thickness and plating current density. These findings are similar to the results of the 2" x 2" samples obtained in Task 2. However, the scale up results seem to be much less affected by sample thickness and plating current density.

Task 4 – Cost and Market Study

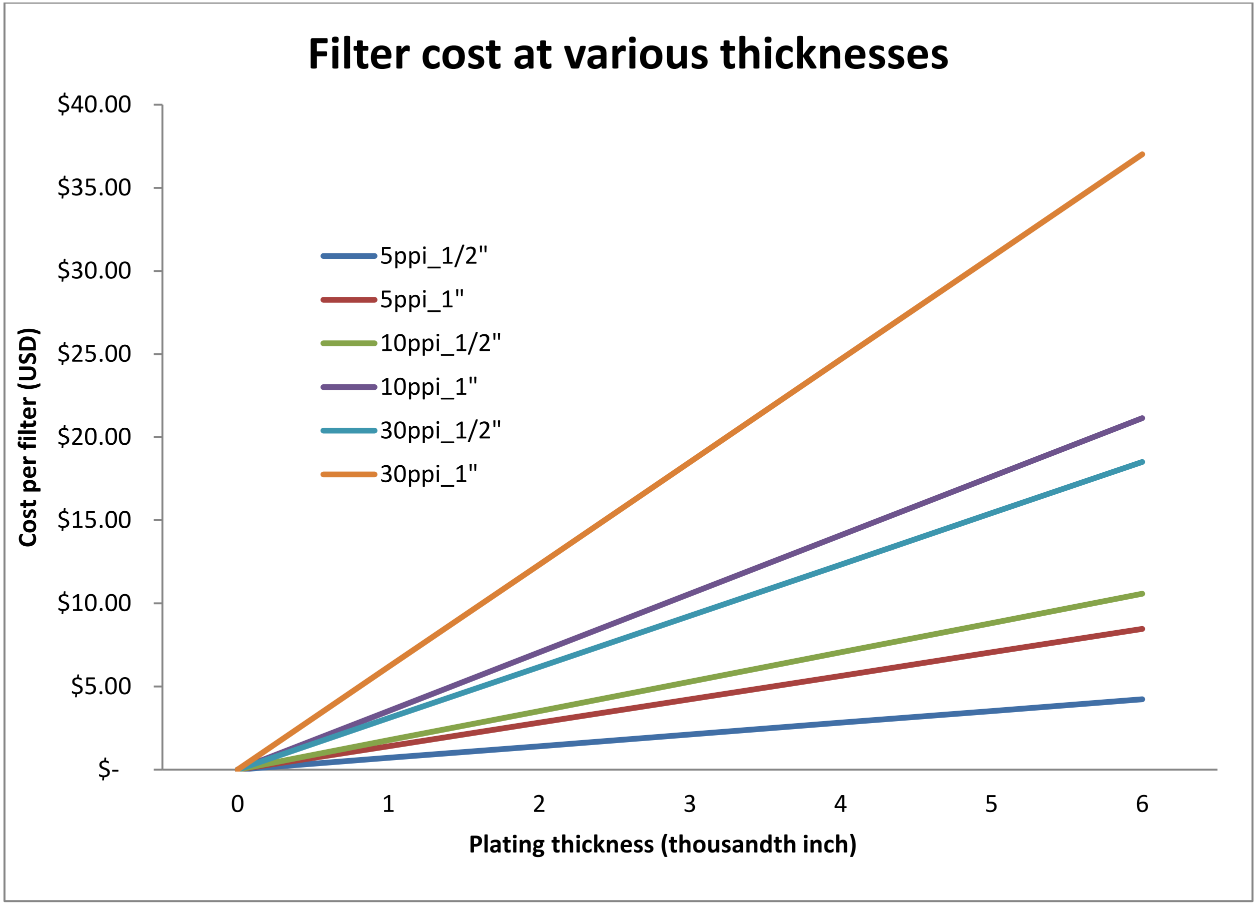


Figure 19. Cost of UFG-Cu enabled antimicrobial filter at various substrate thicknesses, ppi, and plating thicknesses.

Compared at the cost of $25/filter for an antimicrobial filter at 12" x 12" x 1", Integran USA's UFG-Cu enabled filter presents an extremely attractive option for the replacement of conventional antimicrobial filter. For our A minimum thickness of 1 mil (1/1000 inch) is recommended for handling and structural integrity purpose. That puts our start price at below $5 for the 30ppi 12"x12"x1" filter (Figure 19). At the upper end of $25, we can produce everything except for the 30ppi 12" x 12" x 1" at plating thickness above 4 mils. At 1 mil, Integran USA's filters can be recleaned and reused at up to 100 times, and at plating thickness of 4 mils, filters can be reused up to 400 times, giving the equivalent value of $10000 in purchasing conventional antimicrobial filters.

4.5 Summary and Conclusions

Phase I of this SBIR initiative has been successfully completed, and with promising results. Previous studies have shown the improvement in antimicrobial properties of UFG-Cu compared to traditional Copper. Phase I proposes to utilize Integran USA's electrodeposited ultrafine grain Copper to develop reusable antimicrobial air filters for health care worker protection. For this phase, the following has been completed:

From the results of Task 1, plating cell set up:

- Polymeric foam substrates were selected for the electrodeposition process
- Successfully activated polymeric foam substrates for electrodeposition and promotes adhesion
- Polymeric foam substrates were completely encapsulated without any cracks, pits, or pores.
- Surface charactericss were smooth and uniform, with Vickers Hardness above 80VHN (91 VHN at current density of 15mA/cm^2, and 115 VHN at current density of 30mA/cm^2)

From the results of Task 2, deposit thickness of 2" x 2" samples shows:

- Plating at current density of 15mA consistently provides a more uniform coating thickness, except for the case of 5ppi, 1” thick, and 8” anode spacing, and 25ppi, ½” thick, and 2” anode spacing.
- Anode spacing does not affect coating uniformity
- Thinner samples (1/2”) will have better coating uniformity compared to thicker samples (1”)
- Higher ppi samples (pores per inch) will have worst coating uniformity compared to lower ppi samples
- 5 ppi samples do not seem affected drastically by thickness of sample, current density, or anode spacing.

From the results of Task 3, deposit thickness of 12" x 12" samples shows:

- Plating thickness uniformity is better at lower ppi
- Substrate thickness does not affect plating uniformity compared to small scale experiments
- Sample thickness does not affect plating uniformity compared to small scale experiments

Market studies show that matching the cost of production of Integran USA's UFG-Cu to the price of commercially available antimicrobial treated paper filters, Integran USA's filters present a much better value due to better performance of antimicrobial properties of UFG-Cu, as well as the ability to be recleaned and reused. Cost to produce filters at the recommended plating conditions ranges from $1.41 to $24.68, and represents a 400 times value compared to a disposable commercial product, a saving of about $10,000 over the lifetime of the filter

Integran USA strongly recommends that this program be continued in a Phase II initiative. Phase I has been successfully carried out with complete success. All proposed deliverables were achieved and results optimistic. Integran USA will continue developing a large scale production of UFG-Cu enabled foam as well as conduct further investigation to validate the effectiveness of UFG-Cu in an antimicrobial application.

4.6 Appendix A

Itemized Man-Hours and Costs

The total cost incurred in this Phase I program was $94,433.12. A summary of the itemized man hours and costs is provided below in Table 4. 100% of the total budget for this program has been utilized, with the remaining amount of $0.

Table 4. Itemized man hours and costs for Phase I

Senior/Key Person		**Phase I Spending**	
Individual	**Rate/hr**	**Actual Hr**	**Actual Spent**
PI Andrew Brutlag	95.31	386	$36,789.66
Technician - Derek Bollig	50.81	533	$27,081.73
Total Key/Senior Person			**$63,871.39**
Other Personnel			
Advisor - Robert Heard			$7,200.00
Total Other Personnel			$7,200.00
Total Salary, Wages and Fringe Benefits			**$71,071.39**
DIRECT MATERIAL COSTS:			
Foams and Metal Plates			$-
Plating Cell			$2,249.02
Chemicals and Consumables			$2,800.05
Misc.			$1,411.88
Total Direct Materials Costs (TDM):			**$6,460.95**
OTHER DIRECT COSTS:			Phase 1:
Travel			$4,975.80
Total Direct Materials Costs (TDM):			**$4,975.80**
TOTAL DIRECT COSTS (A-F)			$82,508.14
TOTAL DIRECT AND INDIRECT INSTITUTIONAL COSTS (G+H)			$82,508.14
G&A	14%		$11,924.98
FEE	0%		$-
TOTAL ESTIMATED COST:			**$94,433.12**

5 Report Preparer(s)

This report has been prepared by: Andrew Brutlag