Designing a New Coating Device and Fabrication Process to Develop Ceramic Microtubes

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Abstract

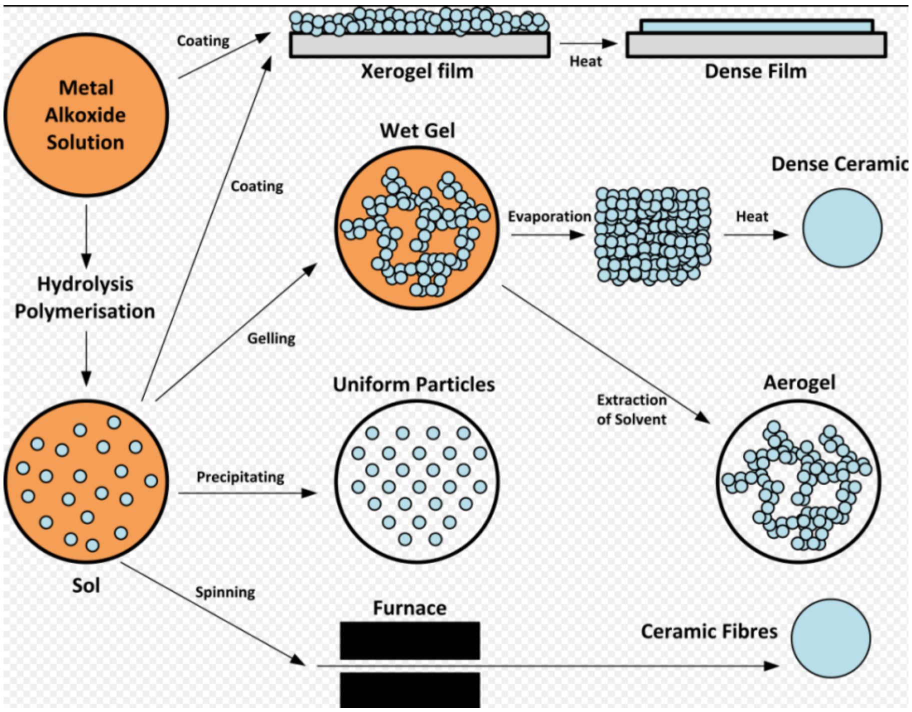
Ceramic microtubes are especially attractive due to their resistance to thermal shock, high temperature, pressure and corrosion, their biological stability and in some cases, thermal or electrical conductivities. A wide variety of applications include liquid and gaseous component separation in chemical, oil/gas, steel, power and electronics, paper and pulp, pharmaceutical, biotechnology, food and beverage, and drinking water. In this research, ceramic microtubes were made using removeable templates covered by layers of ceramic materials using sol-gel technology. A low-cost device was designed and built for coating multiple layers of slurry onto templates efficiently. Tested templates include silk (single and triple strands), cotton thread and angel hair pasta coated with 1, 5, 10, 15, 20 or 25 layers of slurry and fired with a 5-stage heating cycle up to 1100°C/1450°C over a period of 20 hours. Samples were analyzed using a Scanning Electron Microscope (SEM). The 20X and 25X coatings on single silk strand sintered at 1450°C resulted in the strongest and most density-uniform microtubes by decreasing the porosity. The single silk strand with 20X coating under 1450°C firing formed a 25um diameter hole and a 40um outside diameter (OD), while the 20X coating under 1100°C resulted in a 67um OD. The 25X coating resulted in a 50um OD when fired up to 1450°C.

Introduction

With electronic devices, biomedical research and applications sizing to micro and nanoscale dimensions, material scientists and engineers have spent lots of time to research and develop tubes, wires or rods for manipulating nanoobjects with nanotools. Silk microtubes for blood vessel engineering were manufactured using layer-by-layer deposition of concentrated silk fibroin on a stainless-steel rod of defined diameters [10]. Ceramic microtubes are especially attractive due to their thermal shock resistance, high temperature and pressure capability, corrosion resistance, biological stability and in some cases thermal or electricity conductivities compared to polymeric membranes [5]. Initially ceramic membranes were used in waste water technology. Now there are a wider variety of applications where liquid and gaseous components are separated using ceramic technology. Such applications include chemical, oil/gas, steel, power and electronics, paper and pulp, pharmaceutical, biotechnology, drinking water, food and beverage [14].

Microtube (from Micro-filtration to Nano-filtration) has been widely used in virus filtration and bacteria filtration [3][5][13]. Zirconia ceramic microtubes with 1.6 and 1.0 mm outer and inner diameters for bacteria filtration were extruded and sintered at temperatures between 950 °C and 1250 °C after a debinding step [5]. Tubular and microporous ceramic membranes of mullite with average pore size of 0.39 µm were characterized and implemented in separation processes in order to retain the bacteria *Escherichia coli* [13]. High temperature ceramic heat exchange systems have been listed in many applications [6]. Ceramic thermocouple tubes are used to manufacture temperature measurement and control devices and are designed with alumina or silicate ceramics [12].

Traditional extrusion manufacturing process to make tubes has dimensional limitations in micro- and nanoscale tube production. One of the methods, widely applied for preparation of micro tubular ceramic materials, is based on using organic or anorganic fibres, different membranes, ionic liquids etc. as templates. These templates are covered by a layer of ceramic materials by using sol-gel technology, coating of the surfaces by different mixtures of ceramic precursors, chemical vapor deposition (CVD) processes, laser deposition processes, thermal vapor deposition, layer by layer absorption coating, electrophoretic deposition, hydrothermal deposition or some other methods. The tubes are obtained when the template at the core of these structures is removed. This can be done by using burning, melting or dissolving of the template [9].



The sol–gel process is a method for producing solid materials from small molecules. Sol–gel research grew to be so important that in the 1990s more than 35,000 papers were published worldwide on the process [4]. A facile sol–gel coating procedure has been successfully applied for the ZrO2 coating of eggshell membranes (ESM)[1].

Porous inorganic materials with controlled pore structure and size have attracted much attention because of their wide potential applications in catalysis, sorption, separation, and optics. In addition to synthetic templates, a variety of natural biological templates have been employed for the synthesis of porous materials with sophisticated structural ordering analogous to natural materials. Compared with artificial templates, biological templates are inherently complex and hierarchical; moreover, they are generally cheap, abundant, and environmentally benign. Notably, biological templates, such as organized bacterial threads and wood cellular structures have been used to synthesize hierarchically ordered macroporous materials with bimodal porosity, which combined the good mass transport and accessibility of macroporous networks with the high surface area, selectivity, and catalytic properties of the smaller pore systems. Recently, a novel synthesis of hierarchically ordered macroporous networks composed of TiO2 tubes are reported by using eggshell membranes (ESM) as templates via a sol–gel coating method. However, this ESM templating approach remains to be extended to the synthesis of hierarchically ordered networks of other oxide systems[9].

An example of a tiny tube of lead zirconate titanate that can be formed when dipping vermicelli into a slurry pf PZT [7][8]. A dip-coating process is developed using PZT microtubes fabricated by dip coating of aqueous PZT powder slurry on vermicelli, followed by burnout of the vermicelli and sintering [8]. The structure of hair was replicated via a sol-gel process using human hair as a template to obtain titania microtubes [11]. Mineshige developed a microtube of yttria-stabilized zirconia of ca. 100 um diameter was prepared. The thickness of the zirconia layer was about 3 um [2].

Design Goals of Coating Device

- Create an efficient and reliable design for coating slurry onto different threads
- Machine should coat slurry onto threads consistently
- Machine should not be permanent and should be easily modified or changed for alternative coating processes
- Machine should be simple, low cost, and easy to use

Experimental Questions of Microtube Coating Process

- What is the best structural template for creating strong, consistent density microtubes?
- How many layers of coating is needed to make a density-consistent and strong microtube?
- How does different firing temperatures affect the properties of the microtube?

Experiment Variables

Independent Variables	• **Templates/temporary support structures:** Silk, Cotton thread, Angel Hair Pasta, Stainless steel needle w/ cotton thread wrapped • **Firing Temperatures:** Furnace was set to a 5 stage cycle going up to 1100°C/1450°C over a period of ~20 Hours • **Template Size:** Single strand, triple strands • **Number of Coatings:** 1x, 5x, 10x, 15x, 20x, 25x
Dependent Variables	• Outside diameter of tubes • Diameter of tube holes • Strength of tubes • Porosity and density
Controlled Variables	• Coating process • SEM sample preparation process • Coating material

Materials and Methods

Materials to Build Coating Device	Materials for Microtube Fabrication and Property/Characterization Study
• Wood (panels) • V-grooved ball bearings • Clamp shaft collars • Chains • Sprockets • Chain links • 8mm axles • Drill ○ 8mm drill bit • Bandsaw • Ruler • Pencil • Metal files & sandpaper • Hammer • Table Clamp • Hex-bit screwdriver set • Syringe (5mL) • Cotton balls • Pliers • 90° metal brackets (4)	• Scanning Electron Microscope (SEM) • Prototype coating device • Silk • Cotton Thread • High Temperature Furnace • Stainless Steel Needle • Angel Hair Pasta • Slurry mixture • Vortex Mixer • Gloves • Tweezers • Glass beakers • Plastic beakers • SEM sample plates

Mini Experiment: Developing a Coating Process

1. Used tweezers to directly put a piece of thread into the slurry mixture

Result: Minimal slurry stayed onto and coated the thread

2. Wearing gloves, dipped forefinger and thumb into slurry liquid, then tried running thread between the fingers

Result: Some slurry on thread, but inconsistent coatings (some places had noticeable more coating then others while other places had minimal coating)

3. Dipped tweezer tips into slurry mixture then moved the lock on the tweezer so only a small space is left between the tweezer tips. The slurry connected between the small space due to liquid surface tension (cohesion). Ran the thread through the small gap where the slurry was concentrated in the tips of the tweezers.

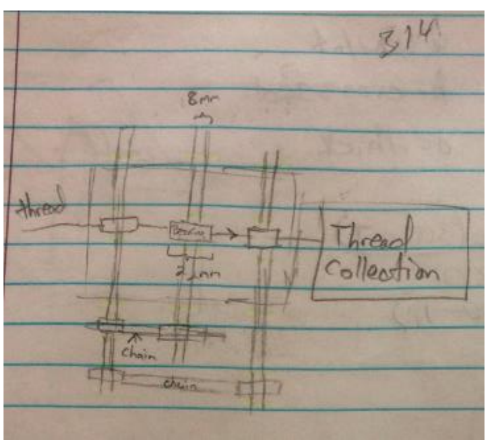
Result: Thread seemed to be coated consistently for only a small amount limited by the amount of slurry that can be put onto the tips of the tweezer. This method will not work because it will be too difficult to maintain the amount of slurry on the tips while constantly coating the thread.

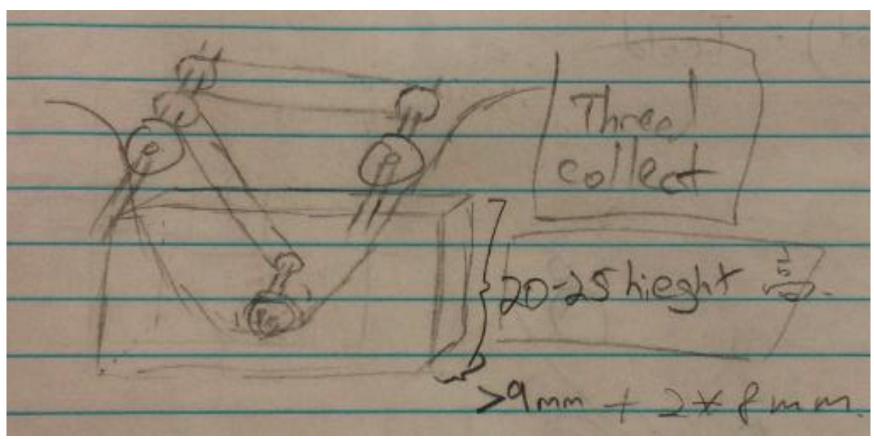
4. Used Syringe to saturate two small balls of cotton with the slurry mixture. Put the 2 pieces together with saturated sides facing each other and ran thread between the cotton balls.

Result: Slurry seemed to have coated the thread very evenly and well throughout to the naked eye. Potential problem that may come up is when the slurry in the cotton runs out, will need to "refill" the cotton using the syringe periodically in the machine.

Slurry does not seem to coat the thread without applied pressure on the slurry and the thread. In both cases that resulted in a consistent slurry coat, pressure was applied by fingers with slurry squeezing on the thread, or pressure applied between the saturated cotton balls.

Design of Coating Device



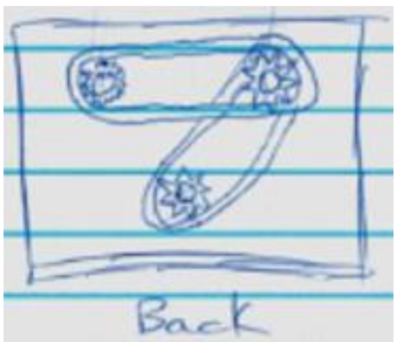


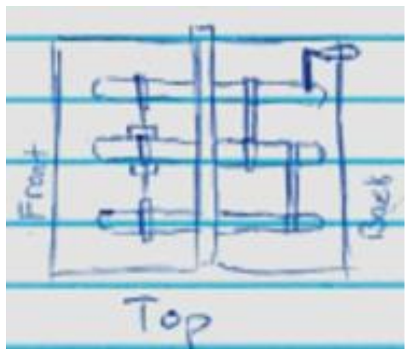
The 3 V-grooved Ball-bearings will be used as wheels to move the thread through the machine. They will be connected to 3 axles that will have a total of 4 sprockets on them with chains linking them together. (This was the original idea,

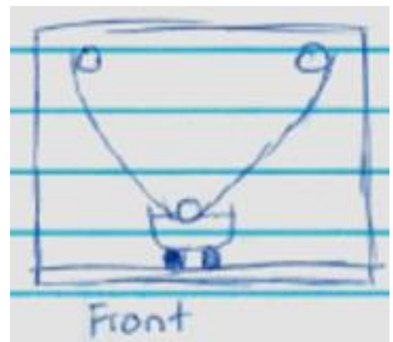
which included using a box and dip the thread into the slurry that was help within the box. Later this was replaced with having the thread slide through 2 saturated balls of cotton.)

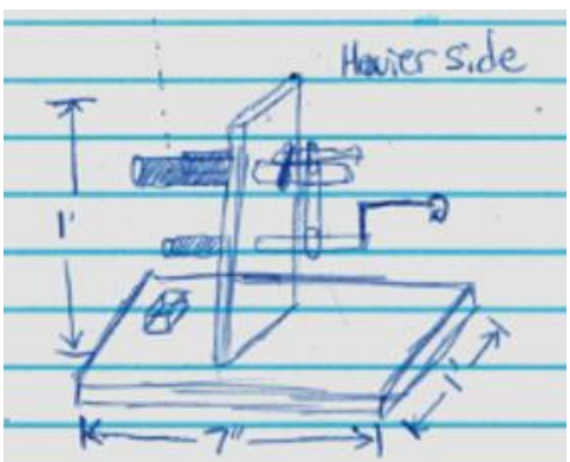
The area where the 2 chains link to the same axle (top left axle in design drawing) will be connected to another stick where the hand can turn the axle. This will allow the machine to be hand-powered and easy to control.

If the machine is to be made fully automatic, the drying section would include an infrared light bulb will be used after the coating to evaporate some of the solvent.

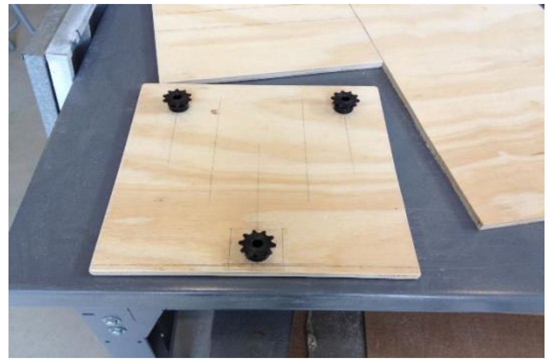


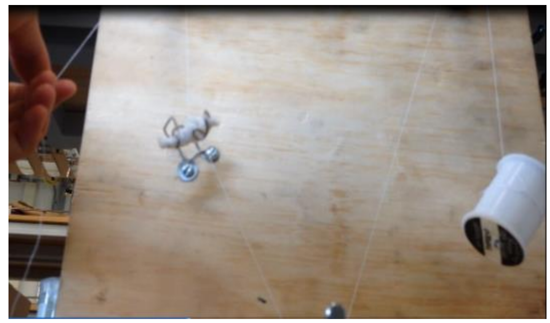




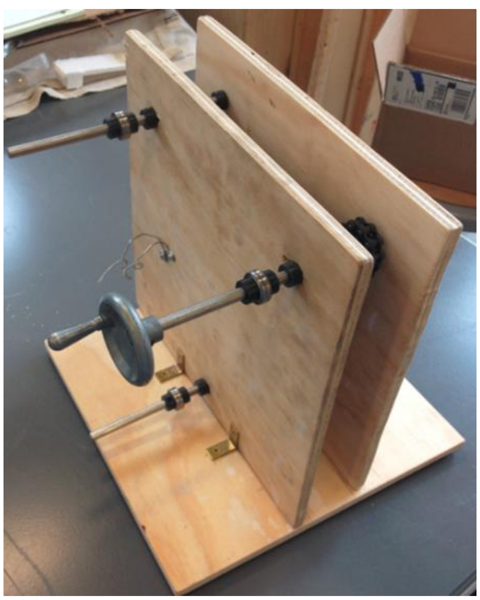


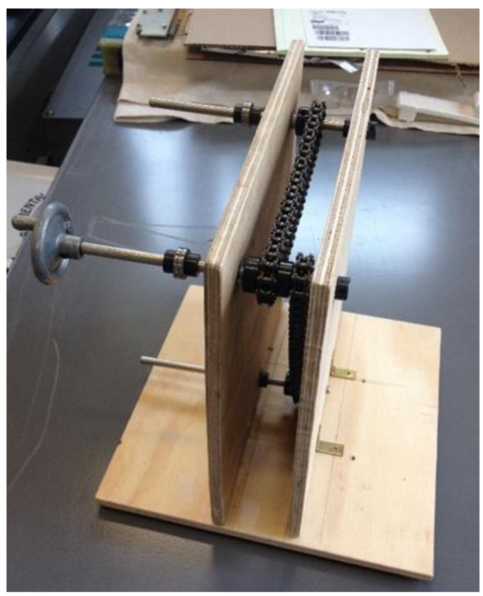
Building the Coating Device





1. Measured and cut wood to proper size. The panel is about 2’ x 2’. Do not need the stand to be that big, only needed 1’ x 1’ sized panels for base and upright stand.
2. Using a band saw from the engineering lab, cut the panel into the two 1’ x 1’ panels.
3. Measure out distances between the axles directly using the sprockets and chains. Drill the 3 axle holes in the panel.
4. File the inside of the bearings and the outside of the axle down so the bearings and axles fit.
5. Use metal 90 degree brackets with screws to hold the panel upright to the base.
6. Add chains to connect the four sprockets
7. Added a cotton ball holder

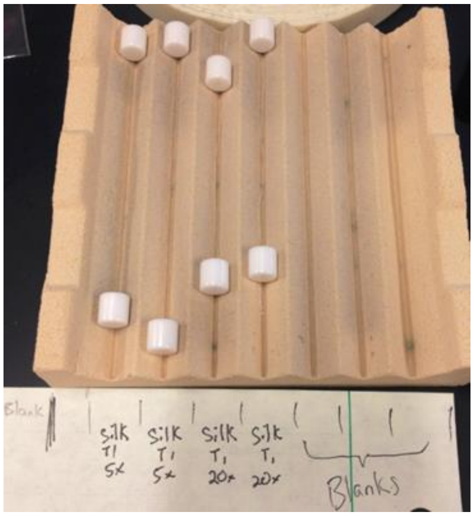


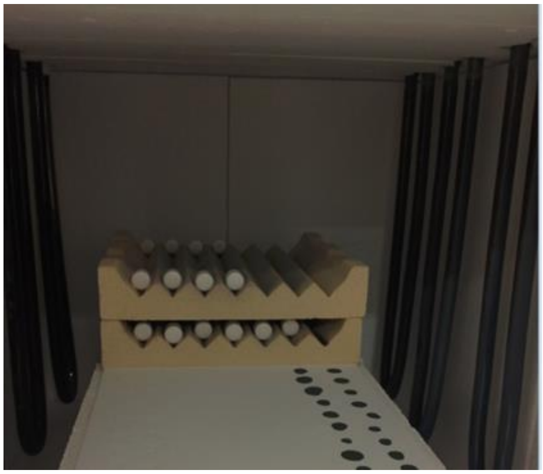


Process of Making Microtubes: Coating Templates, Using a 5-step Firing Cycle Furnace, and Analyzing with SEM

1. Remix slurry to create a homogeneous mixture
2. Put slurry into syringe for saturating cotton balls
3. Saturate cotton balls with slurry
4. Coat the templates with slurry
5. Let coating on template dry
6. Repeat steps 4 and 5 for different numbers of coats
7. Let coating dry completely then store into labeled plastic bags
8. Cut samples into similar sized pieces and put into ceramic heater tray
9. Set furnace to a 5-stage cycle going up to 1100°C/1450°C over a period of ~20 Hours
10. Let samples cool
11. Place samples onto SEM sample plates
12. Coat samples with gold using argon plasma
13. Conduct SEMs of cross sections and surface
14. Analyze SEM pictures

* Repeat testing process for different templates

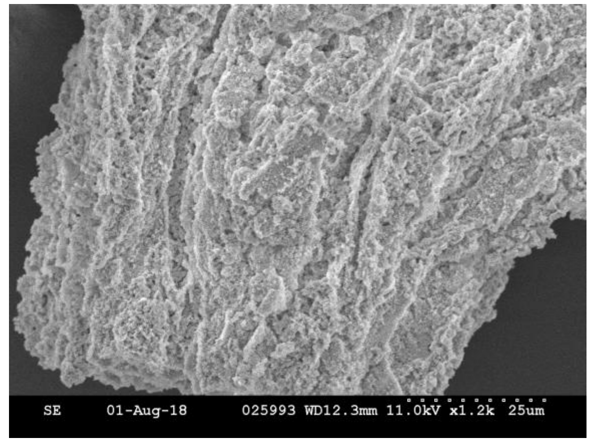




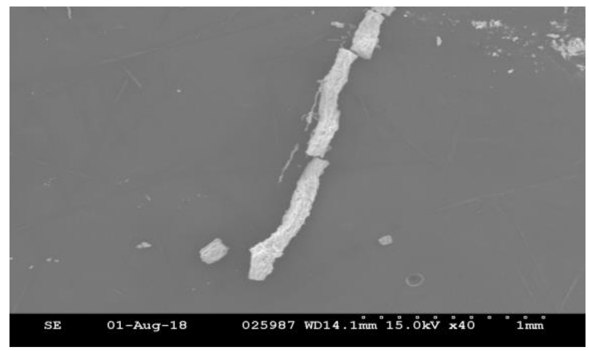
Results

<u>1st batch</u>

Coated Cotton thread (1X coated)— Sample survived the firing at 1100°C with noticeable white ceramic "tube" left.

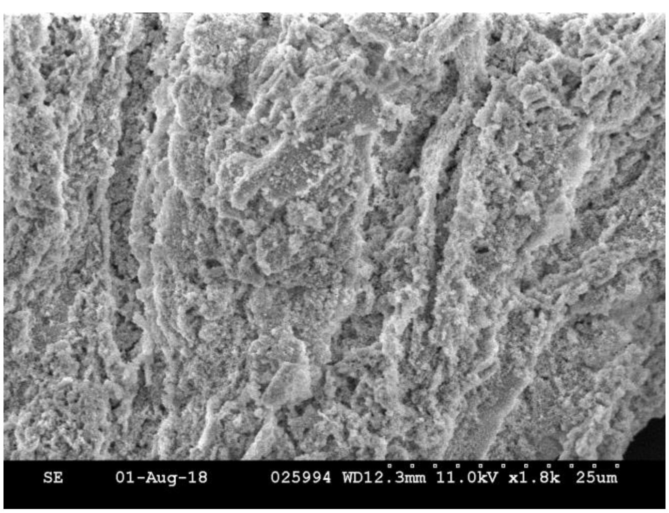


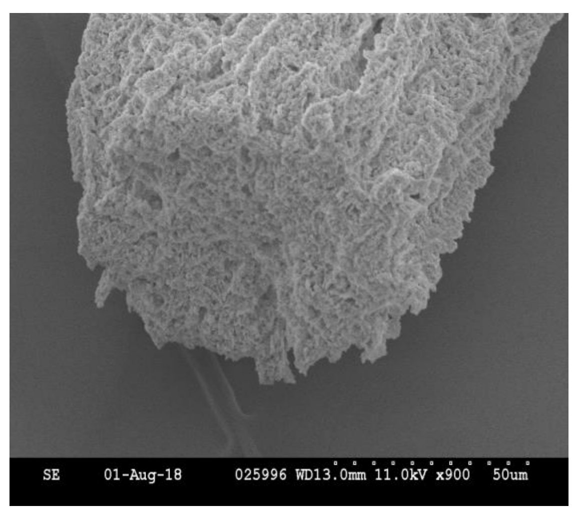
Coated Silk (single strand, 1X coated)—powderized, so <u>no SEMs</u> were conducted on this sample



SEMs of Coated cotton samples:

Surface is very porous with many channels, but the thickness is consistent. After firing, the sample became extremely fragile and easy to break (cannot be picked up using tweezers). Had to setup the samples for SEM by picking samples up with the sticky tape to minimize breakage of sample. Even careful transferring of samples onto the SEM sample stands resulted in lots of breakages in the sample. The sample broke into pieces and powderized when small amounts of pressure was applied. Cross section picture of sample shows no central hole. Either cotton thread was burnt out before the ceramic could sinter together or the cotton absorbed the slurry during the coating process and left minimal spaces after burning out. Another possible reason is due to ceramic shrinking during heating and closing on the hole. The outside diameter of the tube is about **75um.**

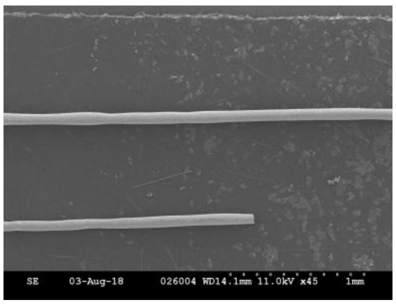




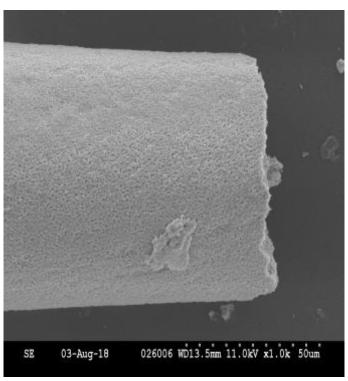
2nd batch

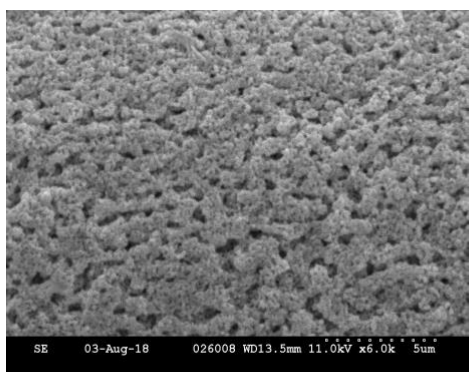
Single strand silk with 20X coating survived the firing at **1100°C**. Sample is set up at SEM.

Samples are straight and are coated very evenly throughout.

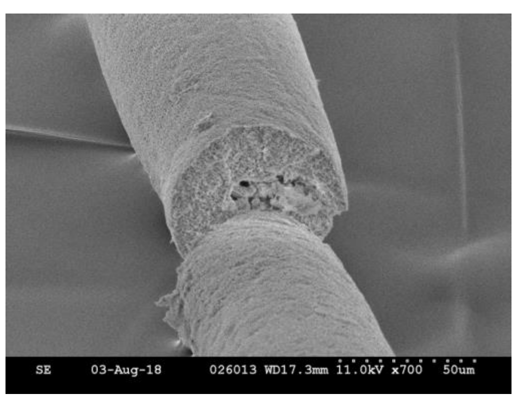


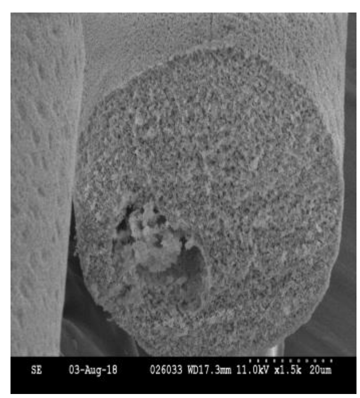
Surface close-up: Surface is consistent in density. Less holes at the surface than first batch; looks like the texture of a sponge.





Cross section: a large central hole can be seen near the center of the tubes where the silk was burnt off. By viewing different cross sections from different locations of the tube, the hole is consistently presented along the whole tube. The outside diameter of the tube is about **67um**, smaller than the single cotton strand sample (first batch) of **75um.**





3_{rd} batch

Single strand silk with 5X, 10X–Powderized (No SEM)

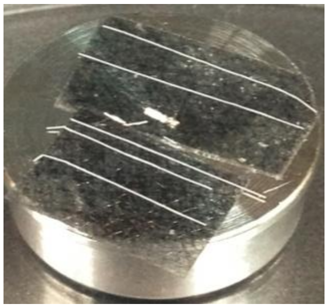
Single strand silk with 15X, 20X, 25X coated

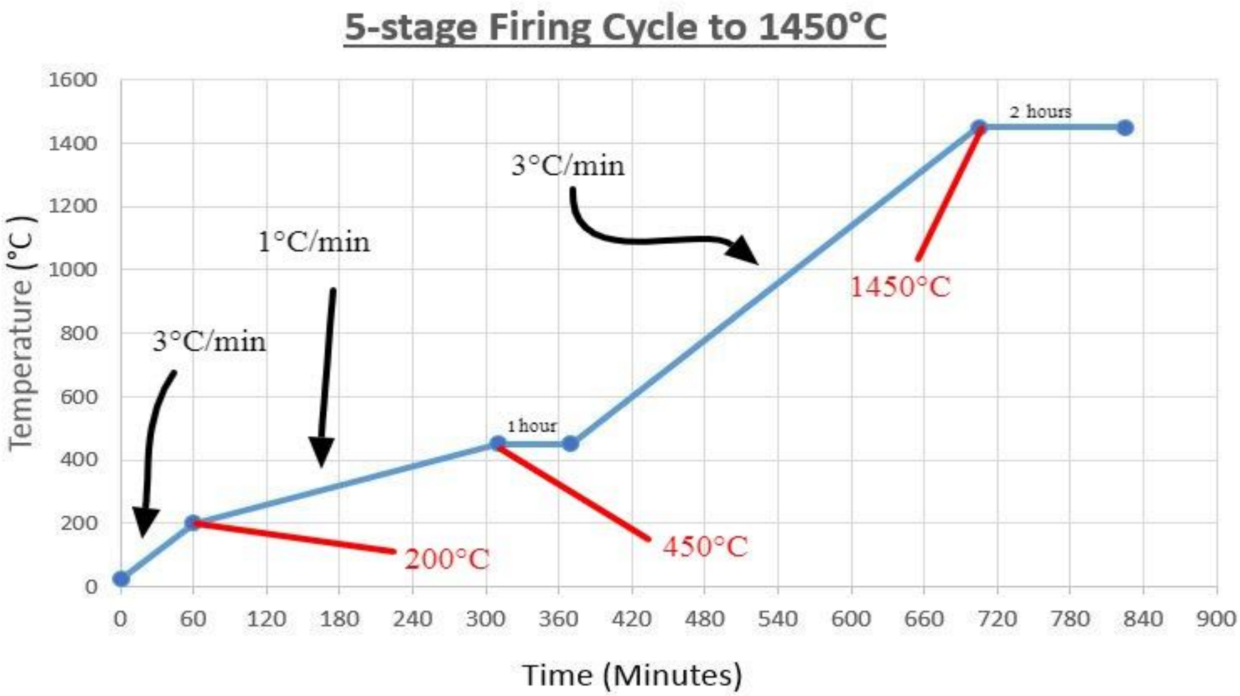
Three strands silk with 20X coated—too weak and fragile to transfer onto sample plate and tape, so no SEM was conducted on this sample.

Stainless steel needle wrapped with cotton thread—powderized

Angel Hair Pasta—not able to coat evenly; next consecutive coatings would wipe off the previous coating, so it was impossible to make multiple coats.

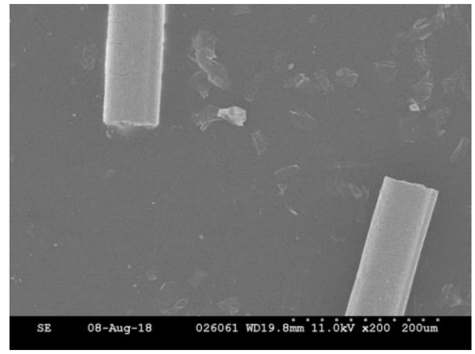
Furnace was set to a 5-stage cycle going up to 1450°C over a period of ~20 Hours



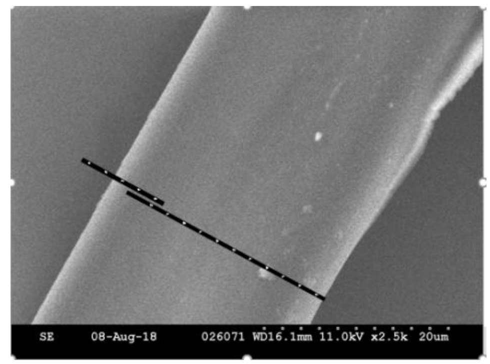


SEM Results Of 3rd Batch

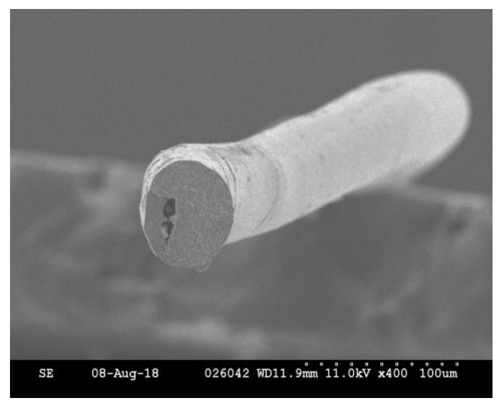
- Top view shows that the 25X samples are straight, and the cross-section edges were cut smoothly into flat edges.



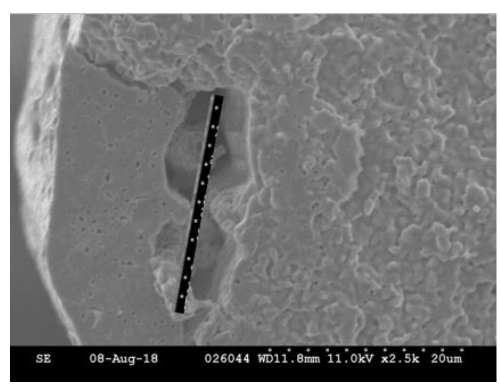
- Using the scale at the bottom of the SEM picture, the diameter of a single thread of silk is about 12.5 white boxes. Distance between each white box is 2um. This means the diameter of the silk is about 25um.



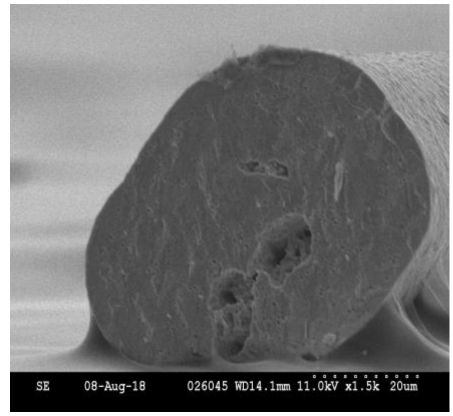
- Cross-section pictures of 25X show what looks like "two holes". This is because after the silk is burnt and the temperature increases, the sample shrinks and the hole "collapses" a little.
- The density of the **25X** coated from batch 3 is much higher and with less pores than 2nd batch. Also, the holes are connected. The outside diameter of the **25X** is about **50um.**



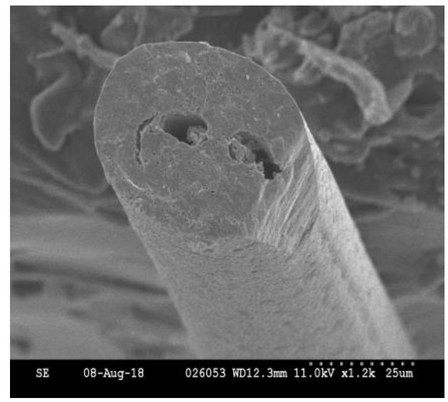
- The hole is about **25um** diameter matching the diameter of silk that we found before (**~25um**).



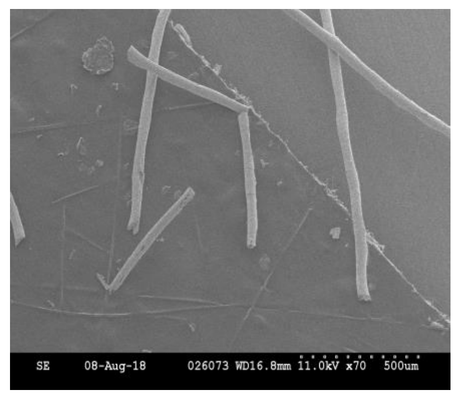
- Noticeable difference in the porosity and density of this sample of 25X coated compared to the lower firing temperature samples. The batches 1 and 2 were fired up to 1100°C while batch 3 was fired up to 1450°C. The increase in temperature led to more shrinkage of the material, and more sintering, increasing the density of the tube and removing the “network” of spaces in the material.

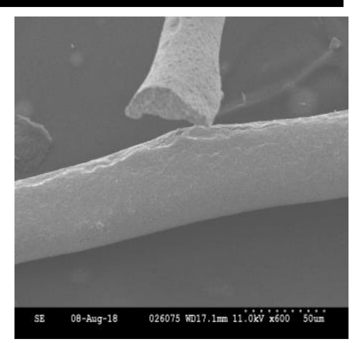


- The 20X has a diameter of ~40um. Previously, the diameter was measured at 67um with 20X when fired at 1100°C. This proves that there was an increase in shrinkage that resulted in a thinner OD despite the same number of coats applied.



- The 15X sample was very easy to break and difficult to put onto the tape. The 10X sample didn’t survive the firing process.
- The ends of 15X were broken and not flat. There were also a lot of cracks that formed along the whole sample. This shows that the minimal number of coatings for a decently strong tube would be 20X.





- The 20X sample with three silk threads had a large hole which made the tube very weak. No SEMs were conducted on this sample because of the difficulty of transferring samples onto the SEM plate and tape.

Discussion and Conclusions

- The single strand of silk with **20X** or **25X** coating under the 5-stage firing cycle up to **1450°C** over a period of ~20 hours resulted in **the best strength/uniformity, most consistent density and least porosity.** The coating device has met all the design goals.
- **Single silk strand** is the only template that meets the goals. Cotton thread, 3 strands of silk, stainless steel needle wrapped with cotton thread and angel hair pasta did not meet the goals because they either did not coat uniformly, lacked the central hole or powderized from the firing.
- Maximum firing temperatures are well correlated to the tube's strength, porosity and diameter. Samples of the 3rd batch with a firing temperature of **1450°C** achieved the strongest tubes with the highest density and the least porosity. It resulted in a smaller outside diameter of **40um** for the **20X,** compared to **67um** with a temperature of **1100°C**.
- Multiple treads of silk as the template resulted in a very weak tube.
- A durable microtube requires a minimum of **20** coats.
- The slightly off-centered hole can be tolerated under certain applications such as collecting high temperature liquid/molten samples using capillary action for analysis. The tubes can even be fired into different shapes such as spirals to easily transport hot liquids. Because of the high surface area to volume ratio, the tubes can also be used for high efficiency heat transfer.
- The prototype machine and fabrication process can be developed into a more precise coating device and be scaled up to coat several threads simultaneously, while also maintaining a centered hole for other specific applications.

References

1. Dong Yang, Limin Qi, and Jiming Ma, Hierarchically ordered networks comprising crystalline ZrO2 tubes through sol‑gel mineralization of eggshell membranes, Journal of Materials Chemistry, 2003, 13, 1119‑1123, https://pdfs.semanticscholar.org/dd9f/26e9e105b8bbd4bd7baf606fa131f1f23c7e.pdf
2. Mineshige, Atsushi; Inaba, Minoru; Ogumi, Zempachi; Takahashi, Tadayoshi; Kawagoe, Tomoo; Tasaka, Akimasa; Kikuchi, Kenji, Preparation of yttria-stabilized zirconia microtube by electrochemical vapor deposition, Journal of the American Ceramic Society; Journal Volume: 78; Journal Issue: 11; https://www.osti.gov/biblio/136523
3. THOMAS EDUARDT HAFEMANN, Porous ceramic microtubes with tailored functionalization for virus filtration, https://www.researchgate.net/profile/Thomas_Hafemann/publication/276277192_Porous_ceramic_microtubes_with_tailored_functionalization_for_virus_filtration/links/5554eaae08ae6fd2d821ba02/Porous-ceramic-microtubes-with-tailored-functionalization-for-virus-filtration
4. Claudionico, Sol-gel Science: The Physics and Chemistry of Sol-gel Processing
5. Stephen Kroll, Laura Treccani, Kurosch Rezwan, Georg Grathwohl, Development and characterisation of functionalised ceramic microtubes for bacteria filtration, Journal of Membrane Science, Volume 365, Issues 1‑2, 1 December 2010, Pages 447-455, https://www.sciencedirect.com/science/article/pii/S0376738810007568
6. Bengt Sunden, “High Temrature heat Exchangers (HTHE)”, Proceedings of the Fifth International Conference on Enhanced, Compact and Ultra-Compact Heat Exchanges: Science, Engineering and Technology, Hoboken, NJ, USA, Sept 2005. http://dc.engconfintl.org/cgi/viewcontent.cgi?article=1024&context=heatexchangerfall2005
7. pwray@ceramics.org, Pasta and PZT microtube preparation, The American Ceramic Society, June 8th, 2010. http://ceramics.org/ceramic-tech-today/pasta-and-pzt-microtube-preparation
8. Kuttan Prabhakaran, Moses Jayasingh, Sooraj Raghunath, Suresh Chandra Sharma, A Dip‑Coating Process for the Preparation of PZT Microtubes, Journal of the American Ceramic Society 90(3), https://www.researchgate.net/publication/230139989_A_Dip-Coating_Process_for_the_Preparation_of_PZT_Microtubes
9. University of Tartu, A method of preparing metal oxide microtubes, https://patents.justia.com/patent/20140186623
10. Michael Lovett, Christopher Cannizzaro, Laurence Daheron, Brady Messmer, Gordana Vunjak-Novakovic, David L. Kaplan, Silk fibroin microtubes for blood vessel engineering, Biomaterials, 28 (2007), http://www.academia.edu/27686630/Silk_fibroin_microtubes_for_blood_vessel_engineering
11. Shuxia Liu, Junehui He, Facile Fabrication of Porous Titania Microtube Arrays by Replication of Human Hair, Journal of the American Ceramic Society 88(12):3513 - 3514 · August 2005, https://www.researchgate.net/publication/229445577_Facile_Fabrication_of_Porous_Titania_Microtube_Arrays_by_Replication_of_Human_Hair
12. CeramTec products, https://www.ceramtec.com/competence/tubes/
13. Dionisio da Silva Biron, Jordana Bortoluz, Mara Zeni, C. P. Bergmann, Venina dos Santos, Characterization of Mullite Ceramic Membranes and their Application in the Removal Escherichia Coli, Materials Research. vol.19 no.3, http://www.scielo.br/scielo.php?script=sci_arttext&pid=S1516-14392016000300513
14. Phillips technical data, https://www.philips.com/c-dam/corporate/ceramics/global/pdf/Philips_folder_Membranes_V3.pdf