C100 FINAL REPORT

This report summarizes our work on the Phase I Navy STTR NO4-T034 entitled Clean Gas Reformer - A Compact Fuel Reformer for Undersea Vehicle Fuel Cells. The report details the progress towards obtaining a suitable tri-layer structure to separate hydrogen from reformed diesel fuel at high temperature. Since the glass separation membrane operates at reformer conditions, there are no thermodynamic losses, and therefore the process is more efficient as compared to existing technologies such as palladium separators.

OBJECTIVES

The objectives of this project were to:

- Fabricate the Clean Gas Reformer (CGR) separator elements.
  - Intermediate layer
  - Glass separation layer
- Test the permeance of the separation elements at room temperature.
- Perform thermal cycling tests.
- Join the separation elements.

APPROACH

A slip cast ceramic layer with a 5 micron pore size is formed to support a thin (less than 1 micron) glass separator element. The support layer serves as a transition between a reticulated monolith with a 130 micron pore size to a dense glass layer. The primary goal of this intermediate support layer is that it be flat, smooth, and have a uniform surface pore structure. The layer should have an approximate 40% porosity. The glass must be contiguous (hole free) and allow hydrogen to permeate but block all other gases. The glass and support layer are joined to a reticulated cordierite monolith. The monolith is catalyzed with reformer catalyst. The fuel is reformed and hydrogen separated in one step in the same reactor.

ACCOMPLISHMENTS

The accomplishments are presented in three sections:

- Materials
- Trilayer Structure
- Testing

Materials

Monolith

We obtained a reticulated structure that facilitates the passage of fuel, air and steam, supporting the intermediate separation layer and having a coefficient of thermal expansion similar to the glass separation layer. The cordierite material is manufactured by Vesuvius High Tech Ceramics and has 80 pores per inch.

Intermediate Layer

We slip cast the intermediate layer using 940LE, a ceramic paste adhesive, manufactured by Cotronics Corp. The adhesive composition was successfully modified to produce a smooth, flat, hole-free surface with the target pore size of approximately 5 microns. The approach of starting with the smoothest layer and transitioning to the roughest was suggested by Prof. Ron Goldner of

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Tufts University. This very simple approach was the primary reason for our success in creating a smooth, flat intermediate layer.

We obtained commercial disks from Ceramatec with the target pore size and 35% porosity. We also obtained 3mm diameter tubes from Advanced Materials Inc. with 300 micron wall thickness and a similar porosity and mean pore diameter.

Glass Separation Layer

We obtained glass coated samples from both Tufts University and MER Corporation. Tufts supplied 1 micron glass coatings on both in-house cast samples and the Ceramatec samples using ion bean assisted deposition. MER Corporation provided glass coatings onto Ceramatec substrates using large area filtered arc deposition (LAFAD).

Tri-layer, glass coated structure

An integrated tri-layer structure was successfully formed by placing the monolith into the wet, cast 940LE ceramic, sintering the assembly, depositing glass onto the surface and annealing the glass coated structure. We reduced the number of fabrication steps from nine to five and significantly reduced the fabrication time and cost. A microwave oven was used to sinter the assemblies, thus avoiding the need for a high cost, high temperature furnace. Multiple thermal cycles did not result in surface cracks. Microwave processing also permits ceramic processing at lower temperature thereby minimizing "locked in" thermal stresses.

Testing

Testing results indicate an adequate air flow rate through the in-house cast ceramic of just under 1 liter/min at a differential pressure of 5 psi. The flow is an order of magnitude higher than the flow through the Ceramatec samples. Testing on the glass coated samples showed a small air slip attributed to a non-contiguous glass coating.

CONCLUSIONS

Our work to date shows that the approach is not only technically feasible but potentially durable. We have shown that the glass conformally coats and adheres to the intermediate layer. We have also verified (and it is supported in the literature) that this thin layer survives multiple thermal cycling. The robustness of the layer and ability to withstand reformer temperatures offers a potentially durable design.

Both the IBAD (ion-bean assisted deposition) and LAFAD (large area filtered arc deposition) processes deposit an oxide of silicon. Since the stoichiometry is unknown it is referred to as SiO_x. Post annealing infuses the layer with more oxygen bringing it to theoretical density or SiO_2. In doing so, the layer becomes denser, further reducing the air permeance (flow slip). The effect of silicon oxygen stoichiometry is an area of intense current interest. It appears that a reduced oxygen content in silica affects its stability towards silanol formation in the presence of steam.

The porosity and pore size of the intermediate layer can be tailored to desired properties by adjusting five parameters: viscosity, surface tension, particle interaction, porosity, and particle size.

Although microwave sintering is successful, the rice starch pore former and water should be baked out at moderate temperature (400F) prior to sintering. To complete sintering in 10 minutes with reproducible results the substrates should be dry and free of hydrocarbons. The sample must reach at least 900C to be fully sintered. If not fully sintered the layer is unsuitable for glass deposition using the IBAD process.

Finally, we have shown that the parallel pore model is invalid in the case of our intermediate layer. The model does not account for the varying internal pore size and interconnectedness of the layer. To verify pore size and pore distribution, experimental methods are recommended, such as mercury intrusion porosimetry.

WORK PERFORMED

Intermediate Layer

Figure 1 shows a slip cast intermediate layer. Note the smooth, hole-free, perfectly white surface. The following sections detail the process to fabricate the intermediate layer.

Properties

The quality of the cast ceramic intermediate layer is a direct result of the approach used to form it. Years of development work were spent on previous Analytic contracts trying to impregnate the monolith material with a ceramic filler by putting the filler onto the monolith. This primary filler surface was invariably bumpy and of very poor quality, often with large cracks. Multiple dip coatings using a boehmite sol gel were required to obtain a surface smooth enough to accept the thin glass top layer. Separate cycles of application and drying were needed to prepare the surface. It could take up to 2 days to complete the process and the rejection rate was close to 70%.

Figure 1. Photograph of ceramic intermediate layer.

The key difference in the present approach is to place the monolith onto the filler rather than putting the filler onto or into the monolith. To cast the intermediate layer in one application, the finish properties must be achieved in that casting. Since variations in pore size and porosity can be controlled, this becomes a viable option. We were able to alter four of the five desired properties of the glass based adhesive. Particle interaction requires a modification to the surface properties of the ingredients, such as the shape and size of the fugitive pore formers, and was not modified due to time constraints.

A glass based ceramic adhesive was chosen in order to match the CTE of the glass top layer. The contents of the adhesive are proprietary and consist of a dry ceramic powder with glass reinforcing rods and a water based activator with a working time of approximately half an hour.

To alter particle size, a coffee mill was purchased and used to fluff the powder to an overall density of 0.49 gm/ml. This eliminated agglomeration and created additional surface area for liquid ingredients to wet the particles. To improve surface wetting during the casting process, a surfactant was used. Without a surfactant, the surface tension resulted in raised craters (see

Figure 2 below). These are common in glaze finishes in the pottery industry. A soap solution, 0.216 gm Dawn Complete (about 3 drops) in 20 ml of distilled water, works well to eliminate surface bumps and help spread the compound into the shallow mold. We suspect that the active surfactant in this commercial preparation is sodium lauryl sulfate. To reduce viscosity, soap solution is added to the liquids in the amount of 20% by weight of activator. This is done mainly to allow the trapped air to escape. Too little soap solution produces a thick paste which traps the air and too much soap solution results in voids or holes on the surface. Controlling viscosity alone is not enough to eliminate trapped air bubbles. We add a commercial bubble breaker manufactured by Troy Corporation. One of the problems with the Troy Corporation "Troykyd D04" product is that it contains solids. The solids melt at 150F but leave a void during sintering. This is fine if the void is internal to the layer but not fine if it's exposed. We have an alternative compound, Troykyd D472, that may be a better substitute. More parametric tests need to be done to determine the optimum percentage to use.

Starches were used to increase the porosity of the intermediate layer to enhance the flux of hydrogen through the glass. Both corn and rice starches were used. Better results were obtained with the rice starch. One problem with the starch is agglomeration. Since only 2% by weight of dry powder is added, good mixing is required. To enhance mixing and swelling of the starch, it is added to the liquids prior to adding the ceramic powder. Prior recipes without starch produced a smooth mixture. Starches tend to make it more granular. Even the small addition of starch caused tiny holes to reappear on the surface. This was an early problem that was solved using a solution of Photo-flo (product of Kodak) and soap. Photo-flo alters the surface tension of the water. However, it was not strong enough to break the bubble surface tension. Starch additives required a stronger bubble breaker.

The complete recipe and instructions to fabricate the tri-layer structure are contained in the Appendix.

Effect of surfactants

Figure 2 illustrates what can happen when insufficient surfactant is used. This is also the result when using alcohols. Although alcohols sometimes break up the bubbles they cause craters and large holes, and prevent the compound from spreading in the mold. The addition of soap had the best result on surface smoothness.

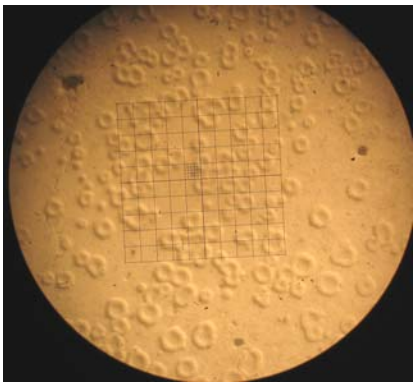

Figure 2 Raised craters on cast ceramic surface

Effect of bubble breaker

Figure 3 shows the effect of using a bubble breaker (Troykyd D04) on casting the intermediate layer. The two samples were broken in half and viewed under the microscope. The top sample fabricated in August was made without any rice starch or bubble breaker. There is a marked difference in the number and size of the trapped air bubbles. The reticle shown is 7 mils on a side. The holes in the upper sample vary between 3-7 mils while the sample below shows holes on the order of 2 mils or less. Note that the bottom part of each coupon is the cast surface which supports the glass coating. The bubbles are rising upwards from that surface. The area close to the cast surface is fairly

dense with very few holes. The bubble breaker eliminates about 90% of the trapped air. During casting there is approx. a 65% success rate. Coupons with holes on the surface are rejected.

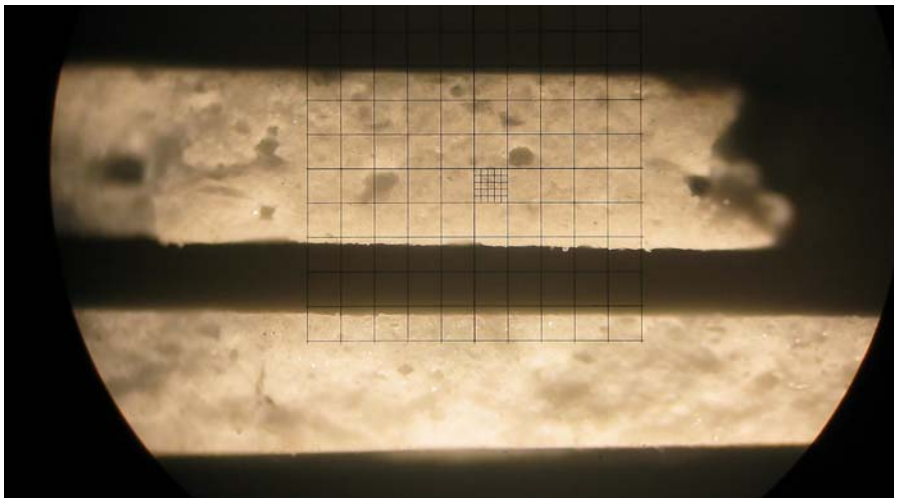

Figure 3 Effect of bubble breaker on intermediate layer (1 square=7 mils)

Starch additive

Rice starch improved the intermediate layer permeance. However, as shown in the comparison below, the improvement was mostly in increasing viscous flow. Figure 4 shows a comparison between samples with (S/N0020) and without (S/N0009) rice starch. The sample without rice starch is mostly linear. The sample with rice starch matches the slope and Y-intercept until 2 atm, then it transitions to a higher parabolic slope. This indicates that the improved permeance is a stronger function of pressure which is viscous flow while the Knudsen flow is independent of pressure. The preferred modification would be the same slope with a higher Y-intercept. The results indicate that the starch is not well distributed. Starch agglomerates might result in larger internal connected pores contributing to higher inertial effects. Mixing might be improved by an ultrasonic blender.

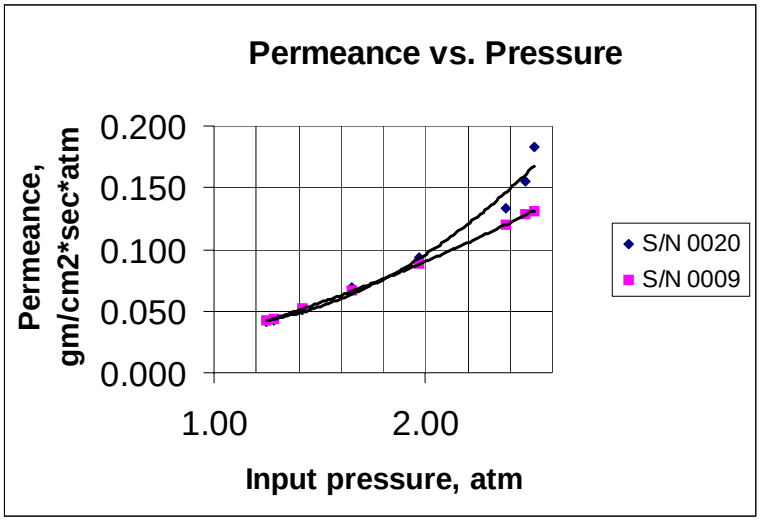

Figure 4 Comparison of samples with and without rice starch. S/N 0020 in upper curve contains rice starch.

Alternative intermediate layers

As an alternative to our in-house cast layers, we received several samples from Ceramatec and Advanced Materials Inc. (AMI). Ceramatec's CERCANAM discs have a 5 micron pore size and

35% porosity. The samples we received were approx. 1 mm thick and 1 inch diameter. The surface is fairly smooth with minor imperfections. The CERCANAM discs can be diamond polished to enhance the surface properties. The body of the disc has a very uniform pore size throughout with only a few trapped air bubbles. The disc has a fairly low uncoated flux so thinner samples would be desirable. Ceramatec can provide samples less than 10 mils thick however, strength of the disc is important when it is not integral or cast with the monolith. To adjoin the CERCANAM disc to the monolith we would use 940LE adhesive to "spot weld" it.

Thin alumina tubes were received from AMI. They are approx. 6 inches long with a 300 micron wall thickness and 3 mm diameter . Since they are tubular, the wall thickness can be minimized without a loss in strength. This is a considerable advantage in gaining higher fluxes. The wall thickness of 300 microns or 12 mils is 3 times thinner than our cast samples which are about 35-40 mils. The AMI tubular permeance, which takes the wall thickness into account, is roughly two times higher. Thus, it is reasonable to assume that the flux through our cast samples is not through large discrete holes.

The final structure of the tubular samples would necessarily be different. The glass coating would be on the exterior so hydrogen would flow into the tube circumferentially and out of the tube axially. The catalyzed reformer monoliths would be on the exterior and would require a separate structure or housing. However, steam, air and fuel distribution might be improved by a radial design rather than the prismatic approach of the CGR.

Intermediate Layer Flux

The following charts show a comparison of all uncoated intermediate layers. The x-axis shows pressure in atmospheres and the y-axis shows permeance in gms/sec-cm^2-atm. Figure 5 shows the permeance through an uncoated cast 940LE layer on an 80 ppi monolith. Figure 6 shows the permeance through an uncoated Ceramatec layer for serial number 17 and Figure 7 shows the permeance through an AMI tube. The fit curves are about 95% or greater. They are all parabolic.

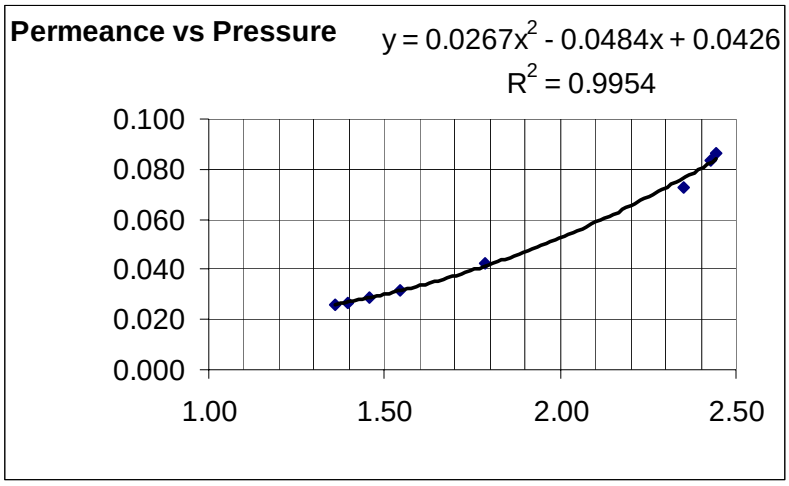

Figure 5. S/N0019 Cast 940LE on 80 ppi monolith

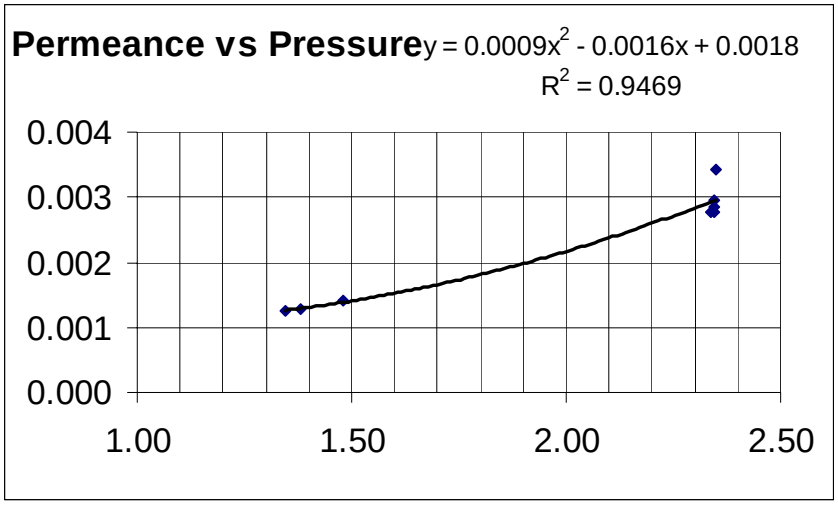

Figure 6. S/N0017 Ceramatec C-16

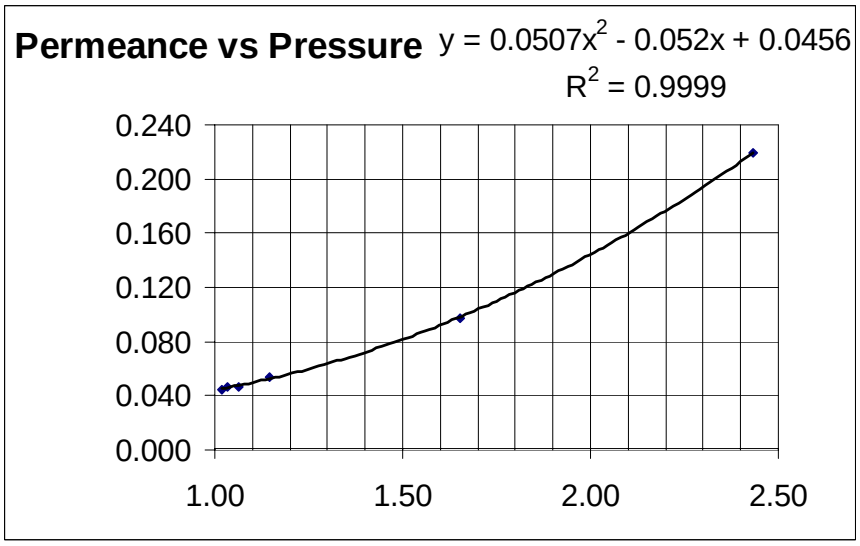

Figure 7. AMI tubular sample

Process change

The proposed fabrication method consisted of 9 separate steps to produce the "tri-layer" assembly. The glass was to be deposited onto a separate plastic substrate and later transferred and bonded to the ceramic intermediate layer. This required a ceramic layer that was smooth, perfectly flat and hole free. Since the dense glass layer is ~ 100 nm, a porous glass layer is needed to support it. The proposed method co-deposited aluminum with the glass. The aluminum is later leached out. This would make the layer substantial enough to survive being transferred in tact. The plastic substrate would then have to be chemically and/or thermally removed, a messy and difficult step. The remainder of the process separately prepared the monolith with a ceramic topcoat capable of supporting the thin glass assembly. The final challenge was permanently

joining the components using anodic bonding. Although many references cite this process, no information could be found on how to go about doing it.

The current method consists of the following 5 steps.

Ceramic casting

Several step changes were made to greatly simplify this process. The first major accomplishment was slip casting the ceramic onto a smooth plastic polycarbonate sheet. Polycarbonate was used for its flatness, smoothness and the fact that it is shipped with a protective paper shield preventing scratches. It is also inexpensive and easily cut to size with shears. It is also transparent which allows the sample surface to be inspected prior to removal. A simple mold is created using silicone rubber cut to the shape desired. The silicone rubber is bonded to the polycarbonate with a spray adhesive. This allows the silicone rubber to be easily removed and thus facilitating removal of the coupon without bending or cracking it. The $1/16^{th}$ inch thick polycarbonate is slightly flexible allowing the ceramic to be picked off the surface by the edge. The ceramic mixture takes approx. 5-10 minutes to make. It is poured into the mold and the underside is tapped firmly to eliminate trapped air. The mixing process should be changed to improve repeatability. The success rate is approximately 65%. Ultrasonic mixing may yield more consistent results improving particle distribution and complete elimination of trapped air. Currently the coupons are checked for surface bubbles prior to completing the process.

Adjoining monolith

While the ceramic is still wet, the cordierite reticulated monoliths are dipped in distilled water and placed on top of the wet ceramic. The monolith absorbs water instantly since it has a fine capillary network. Excess water is blown out using an air gun. If the monolith is not pre-moistened it absorbs the liquids in the wet ceramic leaving raised craters and holes. Wetting the monolith has several other functions: it lengthens the drying time and allows diffusion to occur. There are interesting differences between the coupons with and without a monolith attached. The ceramic recipe contains unknown activator ingredients and known organics from the addition of soap and bubble breaker. A cast coupon will often dry with translucent spots on the surface that are not holes (see Figure 8). These are not glass particles either but are likely the organics in the mixture. They are unaffected by treating in a standard oven. However, during microwaving, the spots will turn a dark black and will sometimes leave voids or pits (see Figure 9). When a monolith is placed into the mixture, the spots do not appear on the coupon surface. Thus we theorize that the organics are diffusing away from the surface and possibly into the monolith capillary structure due to a concentration gradient. If the monolith is dipped into a soap solution rather than just distilled water, spots appear on the surface.

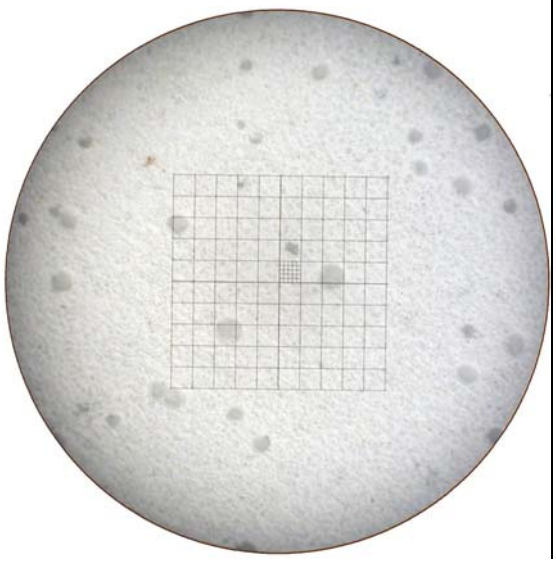

Figure 8 spots on surface before microwaving

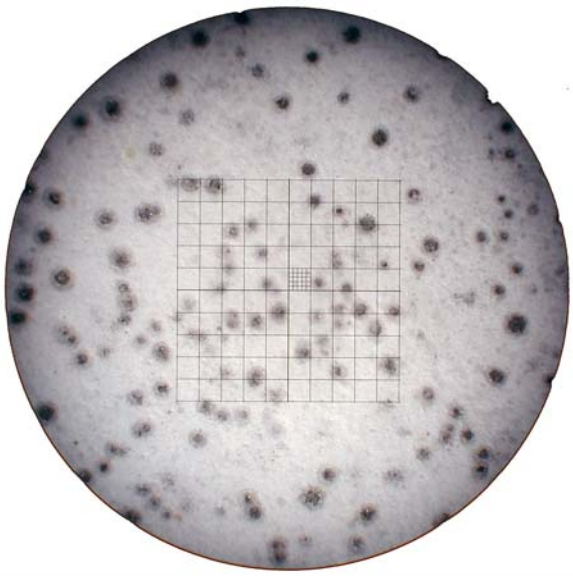

Figure 9 spots on surface after microwaving

Drying and sintering

The assembly is allowed to air dry. Drying time varies but the coupon can usually be removed within 6 hours. The dried assembly is placed in a cool oven and heated to about 400 degrees to bake off the starch and drive off the water vapor. It is better to do this in a conventional oven. Burning off the starch in the microwave can cause some smoking and affects the sintering process. Sintering is accomplished by microwaving at 90% power for approx. 10-15 minutes depending on the size of the sample. The temperature reached is the important factor. Currently we do not have a temperature control, only a power level control. So the temperature varies from part to part. The sample is left in the microwave with the door shut until it reaches less than 100C. Removing it too early can cause cracking.

Glass deposition

The next step is glass deposition. Depositing directly onto the substrate represents a great simplification. By depositing onto the intermediate layer directly we no longer require a flat surface. However, we do require a hole-free surface. Ideally, all pores should be within 5-10 microns. Depending on the quality of the surface the final glass layer can be thinner than with a separately deposited layer since it does not have to survive being transferred to a new surface. It is also stronger since it conformally coats the surface pore interiors. It is less prone to cracking (as shown by Gavalas and Tsapatsis, reference 1) and it is automatically bonded with the assembly. A further simplification eliminates removal of the plastic substrate from the glass surface. As originally planned, methylene chloride (paint stripper) would be used to remove the plastic layer. Methylene chloride is hazardous (carcinogenic) and requires multiple applications to remove a $1/16^{th}$ inch thickness. In addition, remnants of plastic on the surface would char and smoke in the microwave.

Glass annealing

The final step is the annealing process. This is identical to the sintering process.

Microwave processing

Sintering can be performed in a microwave oven as opposed to a standard furnace. High temperature electric furnaces must reach temperatures above 1000C to fully sinter the ceramics for our application. To avoid thermal stresses and cracking the substrate, the standard furnace ramp rate is limited to 2-4 degrees C per minute on both the up ramp and down ramp or cooling. The process usually requires over 24 hours to complete. This time limit makes experimentation difficult. If the sample has cracked on the up ramp, we still do not know until we've waited the full cooling cycle. Thus the motivation is there to circumvent the standard thermal cycle.

The microwave cycle time is a tiny fraction of the above process (Reference 2). It takes only 10-15 minutes to complete. Cool down prior to handling is within 1-2 hours. An additional advantage of the microwave is that sintering can be accomplished at a lower temperature, about 900C. This places less stresses on the material during cool down which is the likely period for cracks to appear. Sintering changes the lattice structure of the material while its expanded so that during cool down the stresses are locked in.

To utilize the microwave, the materials being sintered must either absorb microwave radiation (MW susceptors) or be surrounded by a material that does. The absorbent material must also not be shielded from the microwave source. In our case, the ceramic and cordierite monolith are non-susceptors so a crucible was used. The crucible was fashioned from castable silicon carbide. The wall thickness was held to a minimum to reduce thermal mass and thus increase response time without cracking. Uniform wall thickness is also important to avoid uneven heating and crack formation. This was an early problem and several crucibles were built and discarded.

In addition, location within the microwave and a rotating carousel are both important. The klystron in a microwave targets a specific spot which apparently varies with each oven. This is the reason most microwaves have a rotating dish. If the crucible is not located in the line of the klystron then the crucible does not effectively absorb the microwave resulting in uneven or limited heating. The crucible is placed in the center of the rotating dish to allow insertion of a stationary thermocouple wire through the top lid. The height of the crucible is adjusted using an alumina block and an insulating pad to protect the glass plate, standard with most microwave ovens. The alumina block is a non-susceptor and can handle the 900C temperature of the crucible placed atop it. However, over time the alumina block will heat up by conduction from the crucible. When this happens the alumina block will start absorbing the microwave radiation and can overheat the oven. For this reason, it is important to allow the contents of the microwave to fully cool between processing samples or to have additional sets of insulators to facilitate the process.

It is interesting to note that a thin metal thermocouple wire, properly placed, will not cause arcing within the oven if it is thin enough. It must be less than the microwave radiation wave length. Unfortunately, it is not foolproof so the process should be monitored at all times. An arced wire will leave a carbon residue. Since carbon is a susceptor it must be cleaned off before the microwave can be used.

The microwave is sensitive to sample mass. Thus it takes longer to process thicker samples. Since there is an over-temperature sensor which shuts off the microwave before it can sustain

damage, insulating the crucible would likely produce more consistent results. This will allow larger samples to be processed for a longer time before the safety cutoff is reached. In all cases, the sample must reach approximately 900 C to be completely sintered. If the sample is not fully sintered, the resultant layer has a soft core with a thin outer hard shell. During glass deposition, this shell can be compromised. The result is large divots in the surface which prevent a contiguous glass coating.

Glass layer

IBAD and LAFAD processes require a high vacuum. Thus it is a lengthy process to pump the system down before deposition occurs. Although the process can be optimized in the future by maximizing the number of samples per batch, the current IBAD time frame is 2 days (one day is taken up reaching vacuum).

The IBAD process is directional and targets a silicon sample with an ion beam creating a plasma. The samples are tightly held in a moving fixture so they cannot shift during the process. The samples move in a planetary action to produce a more uniform coating thickness and overcome the directional problem. To produce a silicon oxide coating an oxygen ion gun is used. Currently, there is no method of controlling the stoichiometry of the coating. The deposition rate is adjusted to allow more or less oxygen to co-deposit with the silicon. Based on the literature findings, a sub stoichiometric level of oxygen is desired.

The LAFAD process can produce a superior coating of more uniform grain size. This is because the particles are filtered so they are more uniform in size. The beam is accelerated and bent so that the larger particles impinge on a target and the smaller particles will turn with the beam and deposit onto the samples.

Many samples have been coated in the Tufts IBAD hardware including Ceramatec coupons and Analytic cast ceramic monoliths. Although the samples have some minor pits and divots beforehand, the resulting coating appears to have larger holes and some surface dust or debris. One theory is that the cast ceramic monoliths were not completely sintered. The plasma is kicking up dust and the particles are being deposited onto the surface along with the glass. There is evidence of glass deposited on the walls of the divots but it is incomplete at the base allowing leakage.

Annealing the glass is also done in the microwave and creates a more dense layer by infusing the silicon oxide with more oxygen forming silicon dioxide. There is a change in the color of the layer as well. Silicon is dark gray whereas oxygen deficient silicon oxide is light gold. Further annealing turns the coating a pinkish tone then clear with red spots.

Thermal cycling

Thermal cycling tests were performed on the Ceramatec substrates and in-house substrates coated with 1 micron glass by Tufts University. The maximum temperature reached during processing was between 900-1000C for all samples cycled. The thermal cycling (or glass annealing) procedure is identical to the sintering step performed prior to glass application. The layers did not show evidence of cracks. In fact, the coatings become denser. Thermal cycling on a Ceramatec C-16 substrate reduced the permeance by half from 0.004 to 0.002 gm/sec-cm2-atm. The air flow appears to be uniform over the surface indicating that the coating is porous and the

flow is not from an isolated hole. Tests done after thermal cycling show a significant reduction in the permeance, although the glass coated layer should have zero air permeance.

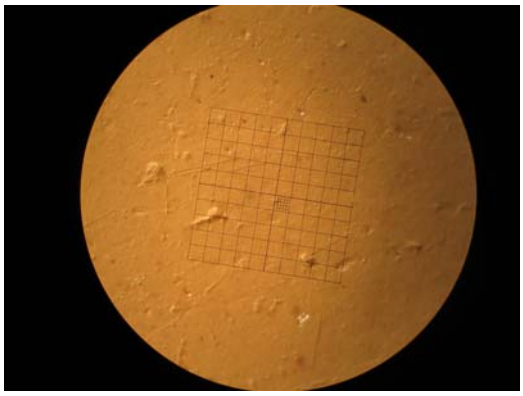

Figure 10 Glass coated CERCANAM disc

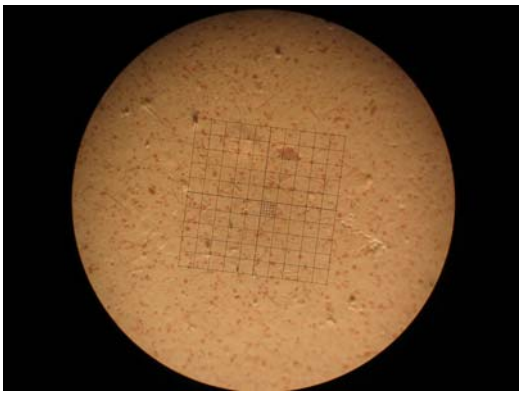

Figure 11 Disc in Fig. 6 after thermal cycling

The photos above show a CERCANAM sample with a 1 micron glass coating before treatment (Figure 10) and after 2 thermal cycles (Figure 11). Sintering the layer in an oxygen atmosphere infuses the SiO_x with more oxygen to create a SiO_2 coating. Repeated thermal cycles change the color of the coating from a light gold/beige to a pink and then to a clear with distinct red spots. The color change occurs on both Ceramatec substrates as well as cast ceramic layers. So the properties are isolated in the glass layer. The red spots are most likely photoluminescence caused by nanometer sized silicon clusters in the SiO_2 matrix. There is an increase in the optical gap into the visible range up to an annealing temperature of 500-650C after which the gap decreases (Reference 3).

Complete Tri-layer Structure

Figure 12 is a graphic representation of the structure as originally envisioned. Figure 13 is a photograph of the completed tri-layer assembly.

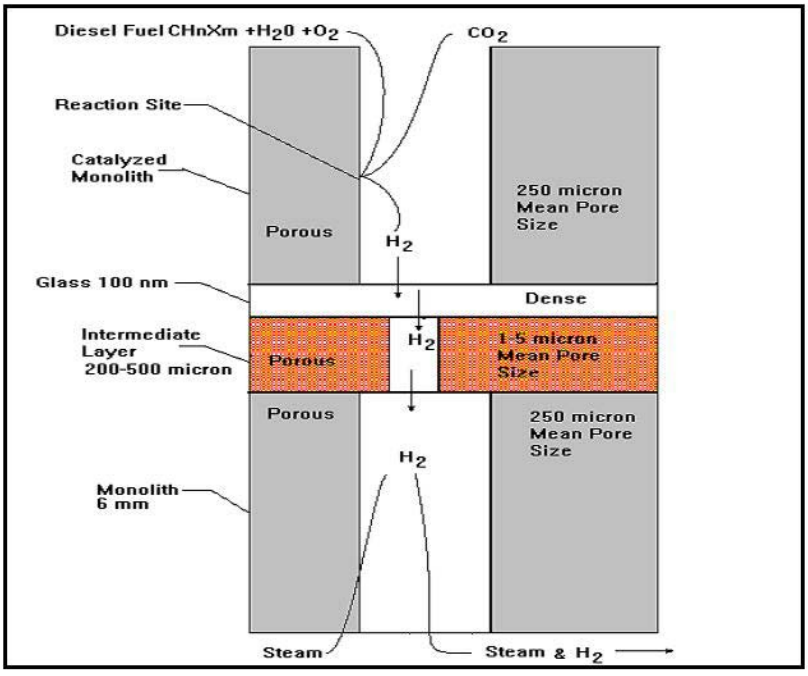

Figure 12 Schematic of tri-layer structure.

Figure 13. Photograph of tri-layer structure showing monolith, intermediate layer, and annealed glass coating.

Permeance Reduction

Figure 14 shows the permeance reduction achieved with an annealed glass coating. The data is based on a Ceramatec CERCANAM C-16 disc. S/N0018 is an uncoated disc. S/N0027 was coated with 1 micron glass by Tufts University. The glass was then annealed twice. At 2.5 atm, the permeance is reduced by a factor of four. As shown, the coating is not yet completely dense. This is attributed to the surface debris and pitting that occurred during the glass deposition process.

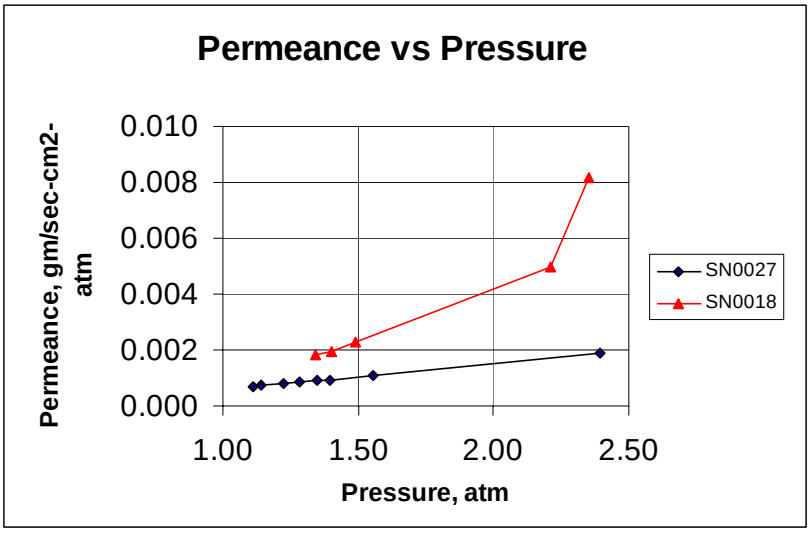

Figure 14 Comparison of S/N0027 (annealed glass) to S/N0018 uncoated

Analysis

Our original approach was based on the assumption that the permeance was a linear function of the pressure. All curve fitting was assumed to be linear and the fit curve crossed the Y-axis at a point less than zero. This was perplexing since the Y-intercept supposedly indicates the Knudsen flow because it is independent of pressure. Since we know that Knudsen flow cannot be negative we suspected that the approach (based on the parallel pore model) was incorrect.

The parallel pore model is a simplistic representation of the real properties of a cast ceramic structure. It does not account for any change in cross sectional area or interconnectedness of the pores. Interconnected pores will contain varying cross sectional areas which cause the flow to contract and expand.

The Blick model produces a theoretical expression for both the viscous and inertial resistance coefficient. Normally, the very low Reynolds numbers encountered would indicate that inertial forces are negligible. However, the more recent models show that the onset of turbulence in porous media, can occur at Reynolds numbers several orders of magnitude less than one experiences in conventional pipe flow. The former produces head loss along the tube while the latter produces local losses proportional to the velocity squared (Reference 4). The permeance is expressed in terms of mass flow (in our case) but if it is converted to volumetric flow per atm per area then it varies as a function of the velocity. The Blick model equation shows that the curve is parabolic not linear. When plotting a fit of the data using a polynomial fit the curve intersects the Y-axis at a positive value. This is verified in most of our test cases with the exception of the glass coated samples. Unfortunately this model does not provide an estimate of the mean pore size of the samples. Experimental methods are required to determine whether the flow slip we are measuring is uniformly dispersed or traveling through a discrete hole in the surface.

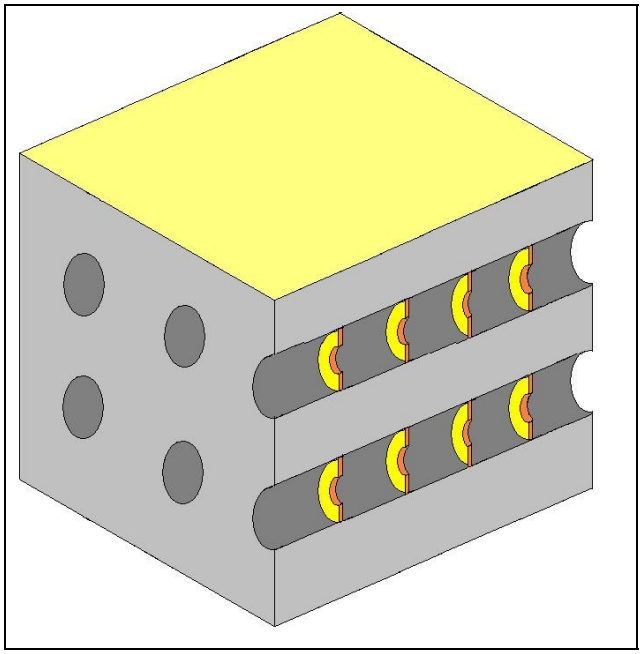

Figure 15 Schematic of Blick's Model

List of References:

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2. “Synthesis of Inorganic Solids Using Microwaves”, K.J. Rao et al, Amer. Chem. Soc., Vol 11, No. 4, 1999.
3. “Structure and Optical Properties of Amorphous SiOx thin films preparted by co-evaporation of Si and SiO”, Rinnert, H., Vergnet, M., Marchal, G., Materials Science and Engineering B69-70, 2000.
4. “Dynamics of fluids in porous media”, Jacob Bear, pg. 180, Dover, 1972.

APPENDIX

SLIP CASTING PROCEDURE FOR CERAMIC COATED MONOLITHS

Fluff the powder

- Place a large quantity of 940LE ceramic adhesive powder in the coffee mill
- Place the mill in a glove box
- Fluff the powder using the following times:
  - On for 10 seconds
  - Off for 5 seconds
  - Repeat this 4 times
- Tap the excess powder off the lid
- Don a respirator
- Open the coffee mill lid
- Open the glove box and dump the contents into a dish
- Let dust settle and then remove respirator

Mix the Soap solution

- Weigh out 0.216 grams of liquid dish soap such as Dawn Complete (orange color).
- Add 20 ml of the distilled water to the weigh dish. Stir.
- Pour this into a glass beaker
- Stir in a beaker using a magnetic stir bar until soap droplets are completely dissolved. Do not allow the soap to form bubbly froth.

Prepare the substrates

- Cut small pieces of film covered polycarbonate (PC) approx. 2" x 2"
- Cut 1-1/8 inch diameter circles in small 2" x 2" pieces of silicone rubber 1/32nd inch thick
- Spray the back side of the silicone rubber with 3M-75 spray adhesive
- Remove polycarbonate protective film coating and stick on the silicone rubber circle template
- Let set for 5 minutes to ensure proper adhesion.
- Clean the circle with an IPA soaked Q-tip
- Let dry or dab with a lint free tissue (kimwipe) to make sure PC is dry

Mix the ingredients

- Mix the 940LE adhesive using 100 parts powder to 45 parts liquid activator
- Each puck uses approx. 1 gram powder
- To make 2 pucks for example use the following recipe
  - 2 grams fluffed powder
  - 0.9 gram activator
  - 0.07 gram Troykyd D04 (Troy Corporation) defoamer
  - 0.18 gram soap solution (about 20% of the activator weight)
  - 0.04 gram Rice Starch
- Weigh out the powder in a plastic weigh dish
- Weigh out the activator in a separate plastic weigh dish – discard pipette

- Add the Troykyd D04 defoamer (about 3-4 drops) – discard pipette
- Add the soap solution into the activator. This will spread the liquid. – Reuse pipette.
- Add the rice starch to the liquids.
- Manually stir the starch until completely distributed.
- Add the dry ingredients to the liquid incorporating slowly and stirring until dissolved. Make sure there are no lumps. Spread in the dish.
- When most of the large bubbles are gone, place in a vacuum jar
- Evacuate the bell jar.
- Leave under vacuum for 5 minutes
- Remove the dish

Prepare the monoliths

- Rinse the monoliths in water to eliminate dust or residue
- Dry thoroughly in the oven
- Weigh the monolith dry(this is to determine the final weight of the ceramic layer)
- Place monolith in dish of distilled water so its not fully submerged
- Ensure the surface is moist

Slip casting procedure

- Pour a small amount (1.5 gram) of ceramic adhesive into center of circle template – approx. ½ the diameter of the circle
- Tap the underside of the polycarbonate coupon firmly to spread the compound until it fully fills the circle. Tilt if necessary.
- Using the handle end of the metal stirring tool, tap the underside of the polycarbonate vigorously to raise the bubbles to the surface and mechanically break them.
- Hold the polycarbonate firmly to transmit the maximum force to the mixture
- Continue tapping until the surface does not appear dimpled. If bubbles rise to surface but do not burst then poke with a probe and continue tapping to smooth surface.
- Do not to let the compound spill out of the template
- Take moistened monolith (prepared above) and blow out excess water (filling large pores) with air .
- Carefully place the monolith on top of the circle of adhesive. Make sure that the monolith embeds just slightly in the adhesive but DO NOT PRESS. Pressing the monolith into the paste causes bubbles to be pressed onto the polycarbonate surface leaving holes. Twist just slightly to ensure monolith is firmly embedded.
- Let monolith set for several hours until the cast intermediate layer surface is white
- Lift off silicone rubber and gently remove puck from surface.
- To fully cure adhesive and bake out rice starch place assembly in cold oven and heat to 400 deg F for about 1 - 1-½ hours.
- Do not touch the cast adhesive surface of the assembly because it may be dusty from excess water present in monolith
- The surface of the cast adhesive should be slightly brown. Rice starch will show up as miniscule brown dots well dispersed on surface.

Sintering in microwave

- If there are any large gray/translucent spots on the surface these are most likely organics from the soap solution. When sintered these will char and turn black leaving a slight divot or hole. They must be eliminated before sintering in the microwave.
- Place the puck in a silicon carbide crucible so it is level
- Center in the microwave and place a thermocouple through the lid
- Turn on the microwave at 0 power and check that the crucible is centered
- Adjust crucible location as necessary to center it.
- Set the program to 90% power for about 15 minutes. Microwave may overheat and shutoff after 10 minutes.
- Cooling down slowly is not necessary to prevent cracks with the powdery white layers. However, layers with many blotches/spots often crack.
- Allow assembly to cool inside closed microwave until its temperature is <100C.
- Remove and make sure surface is no longer powdery
- Check surface for cracks or pits.

Figure 16 Silicon carbide crucible set-up in microwave oven.

Place puck into PVC holder and perform flow testing.