Author: Douglas Corrigan
Email: douglaspaulcorrigan@gmail.com

PRODUCTION OF MACROSCOPICALLY ORDERED NANOSTRUCTURED MAGNETIC COMPOSITES USING AN INNOVATIVE DRAWING AND BUNDLING TECHNIQUE

I. SUMMARY

Two solutions are presented in this submission that are derived from the same principle. The first solution is based on the thermo-mechanical drawing of a bi-component magnetic rod to reduce its cross section, and then bundling these smaller patterns together and repeating the drawing and re-bundling process many times to produce a macroscopic material with a nano-patterned structure. The second method is to use this same process on glass to construct a glass photo mask, and then applying this mask in a selective laser melting 3D printing process to build up a macroscopic material with features on the nanoscale. Both methods are generalizable across multiple material classes, provide nano features of 5nm in at least 2 dimensions, and produce structurally stable materials with macroscopic sizes in all 3 dimensions.

II. DETAILED DESCRIPTION

A. Basic Theoretical Principle

This solution is based on research conducted at the Naval Research Lab that was presented at the AIp conference in 2007, titled: "Materials Characterization and Nanofabrication Methods—Nanochannel Glass Materials". This paper in its entirety is included in the appendix. The Solver identified this paper and realized that this process can be adapted and modified to produce bulk magnetic materials with nanostructured patterns with resolution on the order of 5 nm.

This process works by first inserting an etchable glass cylindrical rod (core) into an inert glass hexagonal tube (clad). These tubes are of macroscopic dimensions. This tube is then drawn at elevated temperature using the same type of technology used to manufacture optical grade fiber. This drawing process retains the overall shape and configuration of the initial macroscopic cross section, but significantly reduces the cross section to a fraction of its initial value. The fibers are then cut to length, and bundled together in a repeating pattern, and then drawn through the draw tower again. This process is repeated until the final nano-structured material results. Each cycle of this process reduces the feature size by the same factor describing the cross-sectional area reduction.

The figure below demonstrates the basic principles of this process.

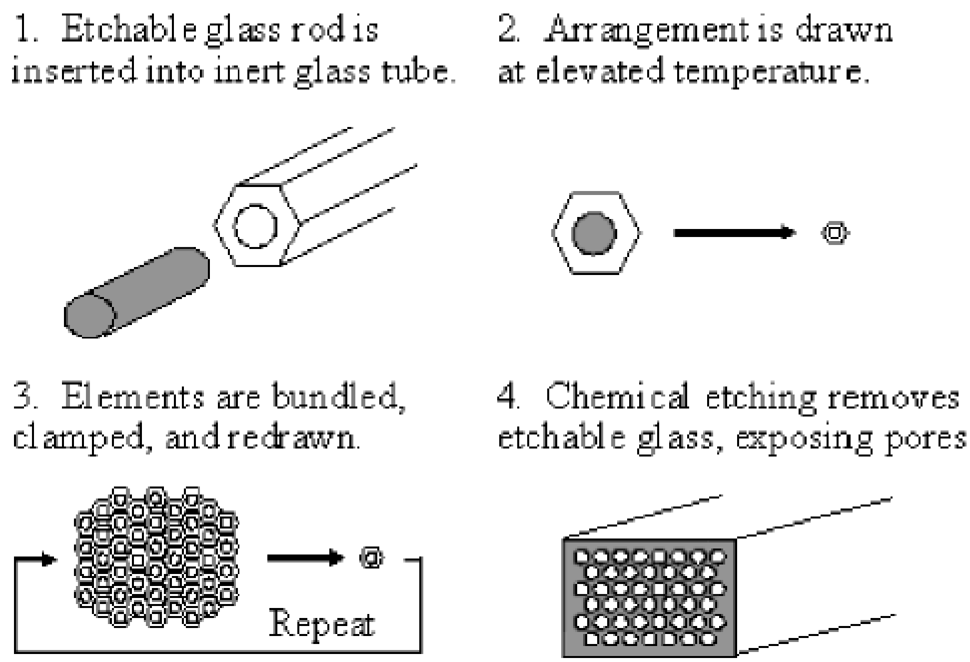

Figure 1 – Principle of Creating a Macroscopic Bi-Phasic Nanopatterned Material Using A Repeated Drawing and Bundling Technique.

After drawing, the core glass can be sliced into a wafer, and etched using a chemical etching solution to reveal the nano-patterned structure of the bulk material, as shown in Fig 2 below:

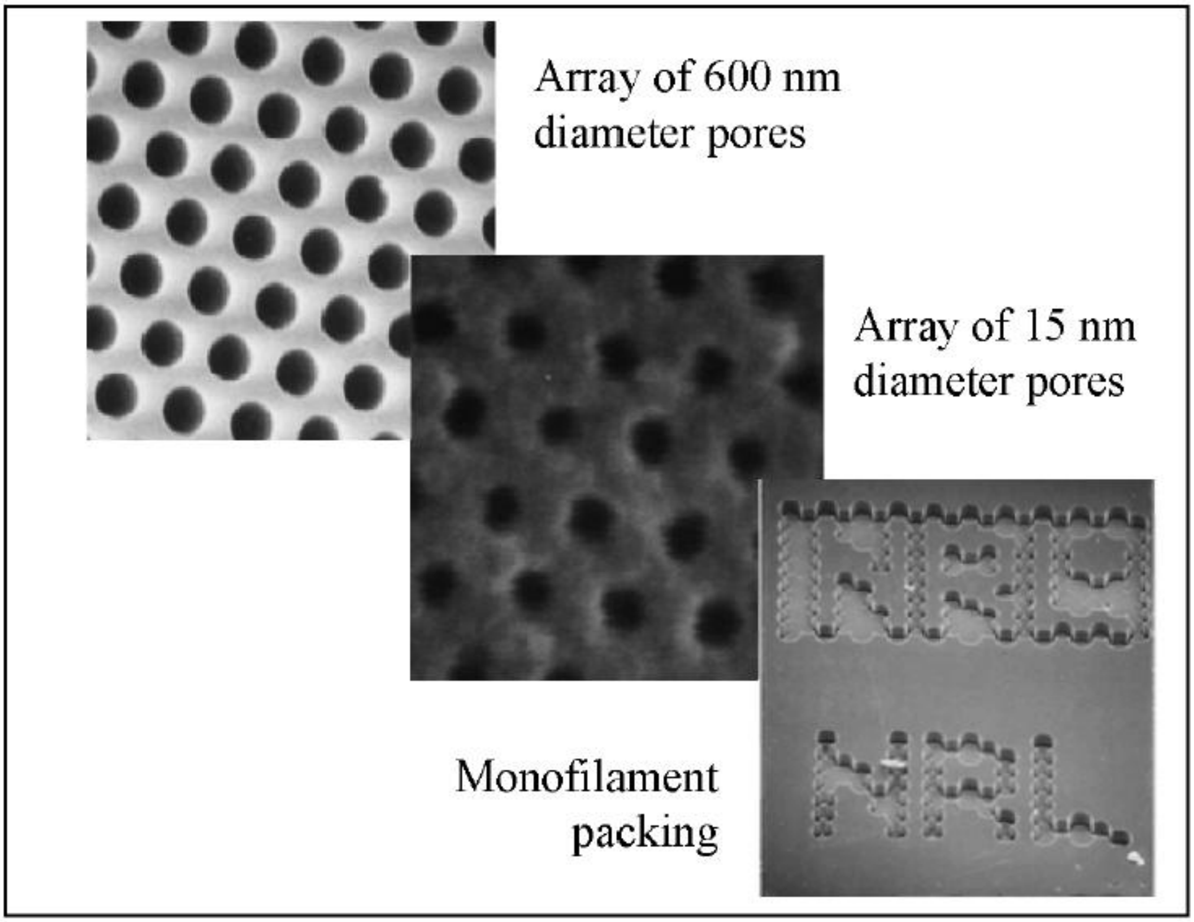

Figure 2– SEM Micrographs of Nano-structured glass after etching.

As can be seen, feature sizes in this report were realized down to 15 nm in size. In this solution, it is predicted that another bundling and drawing cycle would result in features of 5 nm or less.

The diameter of the etched channels and center-to-center spacing between the channels are highly regular and exhibit a tolerance of 1%. Different patterns can be produced, depending on the initial Core/Clad geometry, and the pattern of bundling. Also, isolated glass monofilaments can be bundled in a hexagonal array, a rectangular array, or more complicated arrays, as shown in Figure 3 below:

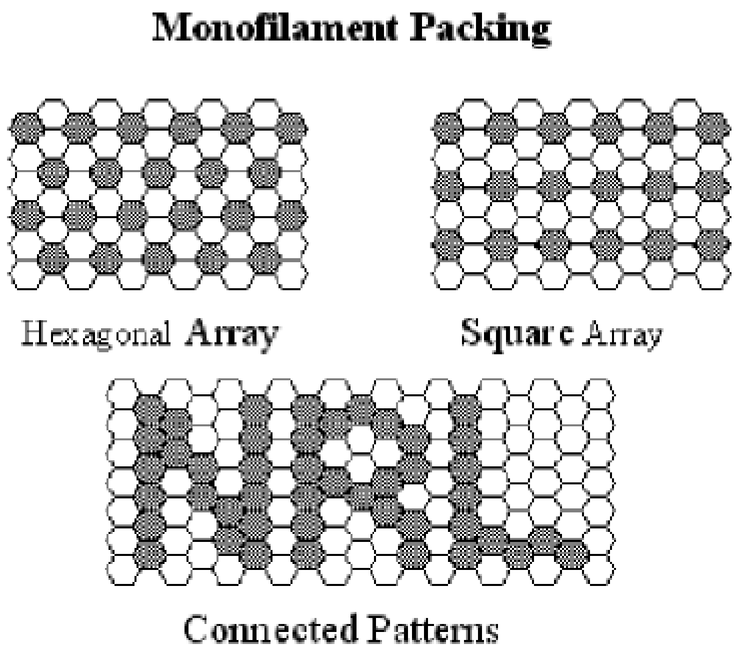

Figure 3– Various Methods for Producing Different Nano Patterns Using Different Monofilament Packing Geometries.

In this report, they were able to achieve macroscopic bulk materials on the order of 2.5 cm on a side, with geometries ranging from 10 nm to 600 nm. Packing densities are reported to be in the neighborhood of 10^{11}/cm^2. There is no indication that any practical or theoretical limits were reached, or that the process was optimized. It is predicted that higher densities and repeat distances of 5 nm or less can be achieved with this process, over a macroscopic scale. Please see the attached report for further detail.

B. Method A

The first solution presented by the Solver is to repeat this process on dual component metallic materials using an analogous procedure. In this method, a rod comprised of magnetic metal A (hard magnetic material) is placed inside magnetic metal B (soft magnetic material), as shown below.

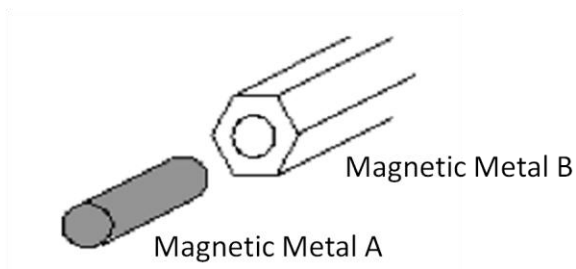

Figure 4 – Hybrid Rod of Soft and Hard Magnetic Materials

Note: The initial shape of the material can be round, hexagonal, rectangular, or square. This will dictate how the bundles most efficiently stack.

This macroscopic hybrid material is then drawn through a die using a thermal drawing process that elevates the temperature of the material to increase its ductility/workability. This drawing process is similar to the methods used in metallurgy to draw rod, tube, or wire. The drawing process reduces the cross-section as depicted below:

Figure 5 – Reduction in Cross Section Area from the Thermal Drawing Process

This drawn wire is then cut into the desired lengths, and then bundled in a repeating pattern. This is then repeated as follows:

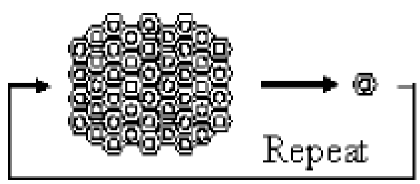

Figure 7 – Bundling Individual Wires/Rods and Re-Drawing

Each cycle of drawing reduces the repeating dimension by the same cross-section reduction factor. Therefore, the space between features is given by the following formula

$$\mathbf{d_f = A^n * d_i}$$

Where, d_f is the final center-to-center spacing of the features, A is the scale of reduction, n is the number of times that the process is repeated, and d_i is the initial center-to-center distance of the first bundle.

For example, if the initial distance is 0.5 cm, the process is repeated 6 times, and the reduction factor is 1/10 (0.01), the final spacing dimension will be 5 nm.

This method will be able to produce bulk 3D Macroscopic materials in x, y, and z directions. The rods will exhibit a feature spacing of the desired magnitude in the x and y directions (cross section of the material), while the rods will extend macroscopically in the z direction. The volume of the material is a function of the final die opening (which controls the x and y geometry), and the length of the draw. The final nanocomposite material can be cut to length (z –direction). This is shown below:

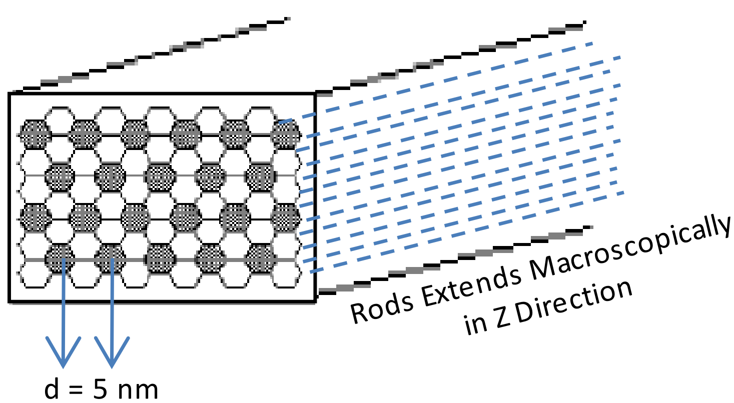

Figure 8 – Macroscopic Representation of Hybrid Nanocomposite Magnetic Material

Magnetization anisotropy can be controlled by thermally drawing the material under the influence of a high strength magnetic field which points in the desired direction, and allowing the material to cool in the presence of this magnetic field.

C. Method B

This method uses a 3D Printing technique used in metals referred to as Selective Laser Melting (SLM). In this process a thin layer of powder is deposited onto a substrate. A high power laser (usually a high power ND;YAG laser) scans the surface of the powder and creates a small melt pool. After first layer is fully formed by the raster scan, the table drops the part by a few microns and then deposits another layer of powder to be melted by the laser. Figure 10 shows a schematic of this process.

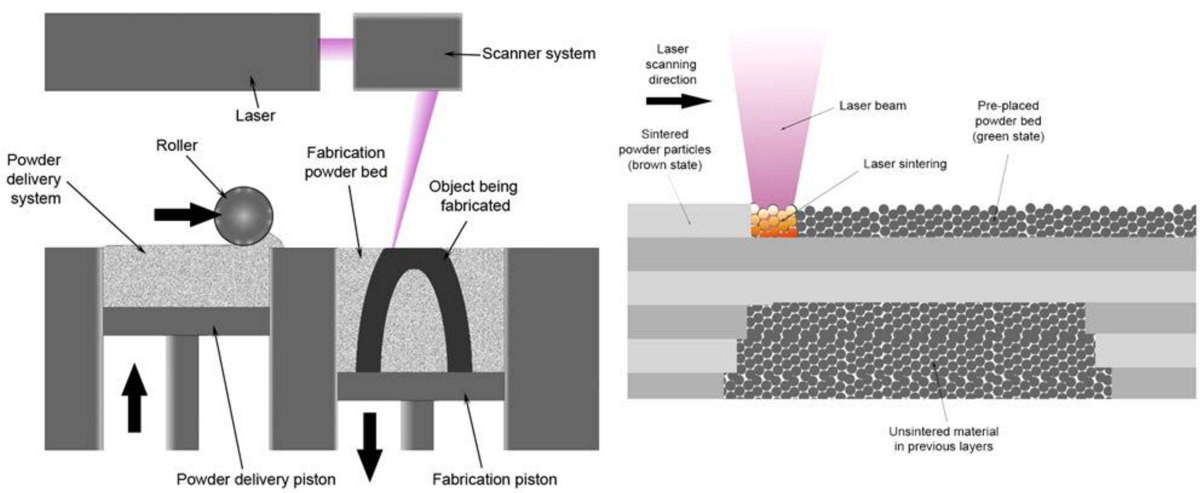

Figure 10 – Depiction of Selective Laser Melting 3D Printing Process

The resolution of this method defines the minimal feature size that can be printed with this technology. This is dictated by the optics and the pulse shape of the laser. Current state of the art can produce resolutions on the order of microns, not nanometers.

To overcome this resolution limitation, this solution recommends the use of a nano patterned photo-mask constructed from two phases of glass that are doped to be optically transparent to specific wavelengths of laser light. This nanopatterned mask can be created to a resolution of 5 nm using the same glass drawing/bundling technique discussed above. However, instead of using an etching glass as the second glass, two different optical glasses are used –each of them being doped for optical transparency to different laser wavelengths. Figure 11 depicts the geometry of the final glass mask.

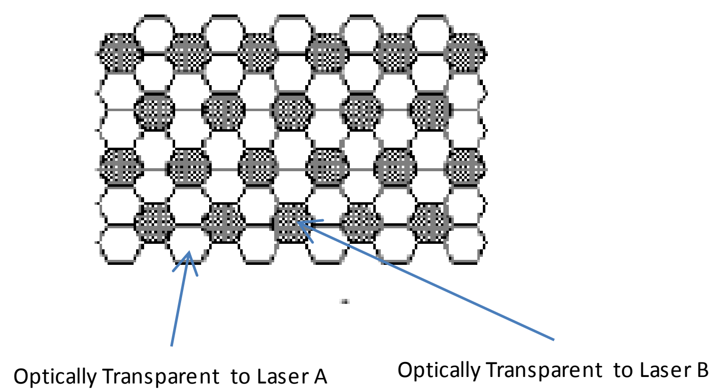

Figure 11 – Nano-patterned Glass Constructed from NRL Drawing Technique.

This mask is then placed directly above the powder bed (as close as practically possible without disturbing the powder). First, a nanopowder layer of magnetic metal A is deposited on the fabrication substrate. Laser A is then raster scanned across the entire surface of the nanopatterned glass mask. The laser light is filtered from the areas of the mask that are opaque to Laser A, and transmitted through the regions transparent to Laser A. After these areas are melted directly beneath the pattern, the unfused powder is removed with a magnet. Then, a nanopowder composed of magnetic metal B is deposited on the substrate in a thin layer. To fuse this powder in the locations intervening metal A, Laser B is rastered across the surface of the mask. The laser light is filtered from the areas of the mask that are opaque to Laser B, and transmitted through the regions transparent to Laser B. After this first layer is built, the build surface drops, and the process is repeated to build the next layer.

The rationale behind using one mask with two different optically tuned glasses is because of the difficulties in "registering" the position of two different masks with a spatial resolution of 5 nm across a macroscopic distance. By combining the mask for material A and material B into one mask, positioning is not a challenge.

For this process to work, a nanopowder of the metal is required with an average diameter less than the spatial resolution of the final part. The nanoparticles should have an average diameter of 1nm to be effective in this process. Magnetic nanoparticles can be synthesized using many different techniques, including co-precipitation, inert-gas condensation, DC plasma jet, DC arc plasma, RF Induction Plasma, microemulsion, flame spray, and thermal decomposition.

Magnetiziation anisotropy can be created in situ during the laser melting process via the application of a strong DC magnetic field pointing in the desired direction during the printing process.

Current state of the art in SLM technology will produce a macroscopic material with nanoscale features in 2 dimensions. The ability to create materials with nanoscale features in the 3rd dimension (the build direction) is limited by the control of the vertical build table. Currently, this Z-layer resolution is in the micrometers.

III. TECHNICAL REQUIREMENTS

A. Macroscopic: Volume of 1 cm3 or larger, ideally in a cubic form factor. Larger volumes are desirable. No dimension should be smaller than 0.25 cm.

Both methods will enable the production of macroscopic parts with no dimension being smaller than 2 cm. In fact, there is no theoretical limit to either of these methods – it is only limited by the available equipment. In the drawing technique, the size of the drawing die is the limiting factor. Current 3d printing machines can print in all 3 dimensions over 25 cm.

B. Nanoscale: Having features in at least one dimension of approximately 5 nm. Figure 1 shows examples of desired nanoscale order. Other ordered schemes (such as hexagonal packing) are also permitted.

Both methods provide nanoscale features with 5nm resolution in two dimensions with repeat tolerances less than 1% over macroscopic distances. Various geometries (hexagonal, square, rectangular) are possible depending on the initial rod shapes and the bundling geometry.

C. Composition: Macroscopic materials with nanoscale order must be composed of two or more distinct components. The final macroscopic material should contain a minimum of 5% by volume of each component. Macroscopic materials with approximately equal volumes of each component are most desirable. Materials with more than two components are permitted but not required.

Both of these techniques enable a wide range of relative compositional variations. The composition ratio can be controlled by the relative sizes of the "clad" and "core": when initiating the first draw. In the NRL paper, it appeared that ratio was on the order of 50% A and 50% B. However, other compositions are possible.

D. Materials-agnostic: Techniques that require sophisticated linker chemistries or are only applicable to single materials are not desirable. The approach should be generalizable within families of materials (e.g. alloys, ceramics), or across different material families.

This technique will work with all ductile materials that can be "drawn". Therefore, this method is generalizable across both glasses and metals.

Near fully dense: Density should be >90% of the theoretical maximum. Porosity, voids, surfactants, or binding agents should be avoided as much as possible. Any materials added to the mixture to aid the formation, ordering, or alignment of the nanostructure should be removed as much as possible without leaving gaps or contaminants in the final product.

There are no binding agents or surfactants used. Porosity is minimal. Bulk density can be well above 95% with these techniques.

E. Stability: After consolidation, materials must be able to maintain nanostructure up to 200 C. The ability to withstand processing temperatures of up to 300 C or higher is preferred. Materials should also have the ability to maintain structure, order, and magnetic properties in extreme conditions, such as high magnetic fields or thermal gradients.

These materials are bulk solids that are fused together by high temperatures, drawing, and laser melting. Each phase is in a mechanically solid connection at surface boundaries due to melting and/or surface diffusion that causes alloying and chemical bonding at the interfaces. Therefore, these materials are predicted to be mechanically, thermally, and magnetically stable over a wide range of conditions.

Orientation/Anisotropy: Able to control key properties (e.g. crystallinity, magnetization, or thermal conductivity) along a desired axis to induce anisotropy is desirable.

These techniques are amenable to producing magnetization anisotropy in the final material. The introduction of a high strength magnetic field during the drawing or printing process will orient the magnetization vector in the desired direction as the material goes through heating and cooling in the presence of the magnetic field.

IV. REFERENCES

Materials Characterization and Nanofabrication Methods—Nanochannel Glass Materials
Ronald J. Tonucci[a] and Graham K. Hubler[a]
AIP Conf. Proc. 959, 59 (2007);
(included in submission as attachment)

Nanochannel Glass Replica Membranes," *Science*, 270 (1996), 68-70.

Nanochannel Glass Arrays," *Science*, 258 (1992), 783-785.

Kruth, Jean-Pierre, et al. "Selective laser melting of iron-based powder." *Journal of Materials Processing Technology* 149.1 (2004): 616-622.

Rombouts, Marleen, et al. "Fundamentals of selective laser melting of alloyed steel powders." *CIRP Annals-Manufacturing Technology* 55.1 (2006): 187-192.

Abe, F., et al. "The manufacturing of hard tools from metallic powders by selective laser melting." *Journal of materials processing technology* 111.1 (2001): 210-213.

Bremen, Sebastian, Wilhelm Meiners, and Andrei Diatlov. "Selective Laser Melting." *Laser Technik Journal* 9.2 (2012): 33-38.

Osakada, Kozo, and Masanori Shiomi. "Flexible manufacturing of metallic products by selective laser melting of powder." *International Journal of Machine Tools and Manufacture* 46.11 (2006): 1188-1193.