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Challenge Title: ARPA-E Challenge: Macroscopic Composites with Nanoscale Order

Solution Title: Aerial Nucleation of Macroscopic Materials with Nanoscale Order

Challenge Type: Ideation

Challenge ID: 9933436

THE CHALLENGE: The desired end goal of this Challenge is to find a way to make near fully dense macroscopic materials with nanoscale order. Porosity is not desirable and the presence of contaminants (such as surfactants from nanoparticle production or large amounts of binding agents) is also not desirable.

Technical Requirements:

1. *Macroscopic*: Volume of 1 cm^3 or larger, ideally in a cubic form factor. Larger volumes are desirable. No dimension should be smaller than 0.25 cm.

2. *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.
3. *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.
4. *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.
5. *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.
6. *Stability:* After consolidation, materials must be able to maintain nanostructure up to 200 ^{0}C. The ability to withstand processing temperatures of up to 300 ^{0}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.
7. *Orientation/Anisotropy*: Able to control key properties (e.g. crystallinity, magnetization, or thermal conductivity) along a desired axis to induce anisotropy is desirable.

Project Criteria:

1. A detailed description of the materials and process that can meet the technical requirements above. Note: partial solutions will be considered. You may answer one aspect, like what material should be used and why or how to maintain properties during temperature increases, etc. Anything that adds value and meets some requirements is eligible. Preference will be given to those ideas that move the Seeker closer to their goals.
2. Any supporting explanation/rationale or results that explain why the proposed solution will work.
3. Attach any relevant supporting documents.

Aerial Nucleation of Macroscopic Materials with Nanoscale Order

Description:

Hail forms inside of rain clouds high up in the air because small dust particles are taken up into the cloud by air currents flowing upward and water droplets condense on these dust particles, then, whenever the temperature is low enough, these drops of water harden into ice. More and more droplets condense on this nucleating dust particle and solidify into more layers of ice increasing the size of the hail. Eventually, the hail gets so big that the upward air currents are not strong enough to maintain the hail airborne so the hail falls out of the cloud and comes down to the ground. In order to make macroscopic materials with nanoscale ordering, a similar concept to hail formation in the clouds should be applied. We call this process *Aerial Nucleation* (AN).

The AN process combines two or more charged gas streams with each charged gas stream carrying one of the nanosized components, i.e. carrying nanoparticles. At least one of the gas streams is charged positively (+), and at least one of the gas streams is charged negatively (-). Since nanoparticles are so small they are easily taken up by the flowing gas. Because of the contact interaction of the nanoparticles with the charged gas molecules due to any turbulence during the flow, the positive (+) or negative (-) charge in the carrier gas gets transferred from the gas onto the nanoparticle. For example, the carrier gas stream can be made of ionized helium (He) molecules or the carrier gas stream can be made of ionized argon (Ar) molecules. Helium and argon make good choices as carrier gases because they are stable noble gases that will not react chemically with any of the nanoparticles. By using a commercially available plasma gun, it

is very easy to ionize these gases because there are many available plasma gun devices sold commercially that can make either positive or negative plasmas (where the term plasma is the name given to a charged gas).

Next, after the nanoparticles are taken up into the charged carrier gas (remember that one gas stream is positive while the other gas stream is negative) and sufficient mixing of the nanoparticles with the charged carrier gas is provided to allow for efficient charge transfer from the carrier gas to the nanoparticles, the two charged gas streams are combined together in a nucleation column at a controllable mixing rate and a controllable dilution or concentration rate (whichever matches the best conditions in order to obtain the required composition pattern of the macromaterial with nanoscale ordering that is being produced). For example, if a checkerboard pattern is required then equal amounts of the two components are introduced whereas if an imbedded sphere pattern is required then the carrier gas containing the imbedded component will be significantly less in concentration compared to the other carrier gases so that this embedded component gets trapped into the crystal structure as an inclusion in the macroscopic material.

As the (two or more) carrier gases mix together, the charged nanoparticles *find* their oppositely charged partner and bind together due to the static charge attraction forces between the positively (+) charged nanoparticles and the negatively (-) charged nanoparticles. As more charged nanoparticles are brought into the nucleation column by the charged carrier gases flowing in, the size of the nucleated nanocomposite material begins to grow bigger and bigger by aggregating more and more nanoparticles. Eventually, this nanocomposite material reaches a size that is too big (or too heavy) to keep it suspended in mid-air by the pressure of the upward flowing carrier gases so it drops out of the carrier gas flow onto a conveyor belt for collection

and further processing. Therefore, increasing the flow rates of the carrier gases increases the size of the macromaterial with nanoscale ordering that gets grown inside the nucleation column.

Finally, once the macroscopic nano-composite materials fall out of the nucleation column onto a conveyor belt. The conveyor belt carries off the macroscopic nanordered materials for collection, verification testing, and packaging.

Alternatively, if the seeker does not like using a nucleation column as described here because they desire a higher level of control of the AN process, then the nucleation column can incorporate a series of baffle nucleation plates facing the charged carrier gas stream which function as a template for growing the macroscopic nanocomposite material. Each of these nucleation plates can be cut into whatever size or shape (for example circles, rectangles, or squares measuring 1 cm^2) is deemed most appropriate or most suitable for the desired application of the macroscopic nanocomposite material. In this case, instead of collecting the macroscopic nanocomposite materials using a conveyer belt, the materials are harvested by directly scraping it off from the nucleation plates.

Beneficial Qualities of the AN Process:

The AN process uses pure carrier gas streams such that foreign impurities are prevented from nucleating with the macroscopic nanocomposites, i.e. no impurity inclusions are allowed into the material. Because the AN process uses only the nanoparticles themselves, the macroscopic nanocomposite material can obtain the maximum theoretical density without the inclusion of voids or spaces in the material.

The AN process is applicable to any nanosized metal materials because it uses universally applicable static electrical (physical) forces without evoking any specific chemical properties of the nanoparticles involved.

By changing the ratio and speed of each charged carrier gas, it is possible to achieve the macroscopic formation of checkerboard and sphere embedded patterns described by the seeker.

Finally, when surrounding the nucleation column with either a constant or a pulsating magnetic field it also becomes possible to align the nanoparticles such that they form the parallel planes pattern described by the seeker.

Furthermore, using a magnetic field in the nucleation column can prove to be a very efficient means to orient the nanoparticles so that they agglomerate together in a suitable orientation giving the best desired anisotropic properties to the macroscale nano-composite material.

The AN process is the best means of combining hard and soft nanomagnetic materials into a macroscopic nanordered material because the magnetic attraction between the hard and soft magnetic materials becomes an additional the binding force of the macroscopic nanocomposite material.

Why It Works:

The reason the AN process works is because it follows the same guiding physical principles of crystallization from a liquid solution. All crystals are made of positive and negative ions. The ionic (positive and negative) forces is what binds crystals together. In the beginning, the charged particles are freely moving around in the liquid solution but eventually, they begin to partner up according to their complementary positive (+) and negative (-) charges. When enough particles agglomerate together, they become large enough and heavy enough that they fall out of solution as a seed crystal. The seed crystal then provides the scaffolding necessary to continue to crystallization process and more ionic particles build up on top of the seed crystal making it bigger and bigger. As long as there is a steady supply of ionic (i.e. charged) particles entering the

solution, the crystal will continue to grow bigger and bigger. The AN works in the same way. The difference is that it uses gas as the medium to bring the charged particles in contact with each other instead of using liquid as the medium of bringing the particles in contact with each other.

An illusive fact that links the nature of gases and liquids together helps to elucidate the physical principles that make the AN process feasible. Both gases and liquids are fluids. One is a compressible fluid (i.e. gases) and the other is considered a near, non-compressible fluid (i.e. liquids). However, both are fluids and the key property exploited by the AN process here is the ability to bring a steady, controllable flow of two or more oppositely charged nanoparticles in contact with each other so that they can electronically bind together through their complementary (positive and negative) static charges into a macroscopic nanordered material.