Materials by Design

Additive manufacturing techniques deliver three-dimensional microstructures with previously unobtainable material properties.

EVER wonder why on hot days a door sticks in its jamb or a car's fuel gauge registers more gas than is actually in the tank? The answer is thermal expansion. Rises in temperature cause materials, including solids, liquids, and gases, to swell and grow in volume as the heat increases but pressure stays relatively constant. Thermal expansion is one of many properties scientists look for when adapting materials for new applications. Others include fracture toughness, strength, and thermal conductivity.

A material's properties and overall performance are determined by its chemical composition, crystalline state, and underlying microstructure—how the constituent elements within the material are arranged relative to one another. These characteristics force scientists to accept certain trade-offs when choosing a material for a specific application. British materials engineer M. F. Ashby developed charts that provide selection guidance by categorizing materials such as metals, ceramics, polymers, and foams based on their properties in bulk form. An example chart comparing a material's stiffness (Young's modulus) with its density illustrates how the two properties are coupled, or linked, so that typically the denser a material is, the stiffer it is. (See the figure on p. 16.)

Livermore materials scientists and engineers Chris Spadaccini, Joshua Kuntz, and Eric Duoss are designing a class of materials that will open up new spaces on many Ashby material selection charts, such as those for stiffness and density as well as thermal expansion and stiffness. In collaboration with partners at the University of Illinois Urbana-Champaign, the Massachusetts Institute of Technology (MIT), and the University of Wisconsin–Madison, the Livermore team is advancing three additive manufacturing techniques to fabricate three-dimensional (3D) microstructures with micrometer resolutions. Spadaccini, who leads the effort, says, "By controlling the architecture of a microstructure, we can create materials with previously unobtainable properties in the bulk form."

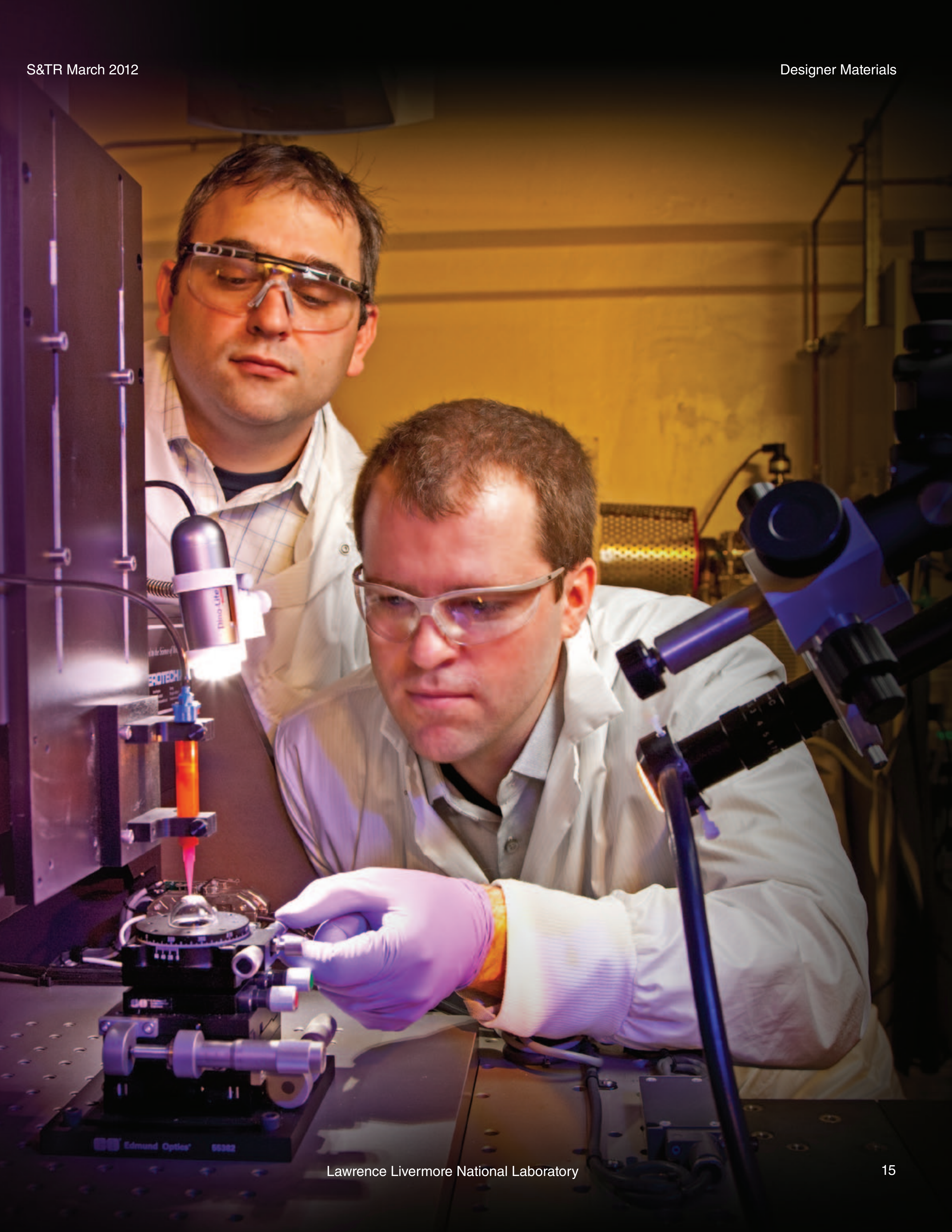
In projects funded by the Laboratory Directed Research and Development Program and the Defense Advanced Research Projects Agency, the collaborators are combining sophisticated computer modeling with projection microstereolithography, direct ink writing, and electrophoretic deposition to design, build, and test designer materials. "Our goal is to use these techniques to effectively alter the chemical composition and crystalline state of materials at their microstructural level so we can control their properties and performance," says Kuntz, who leads the team's work on electrophoretic deposition.

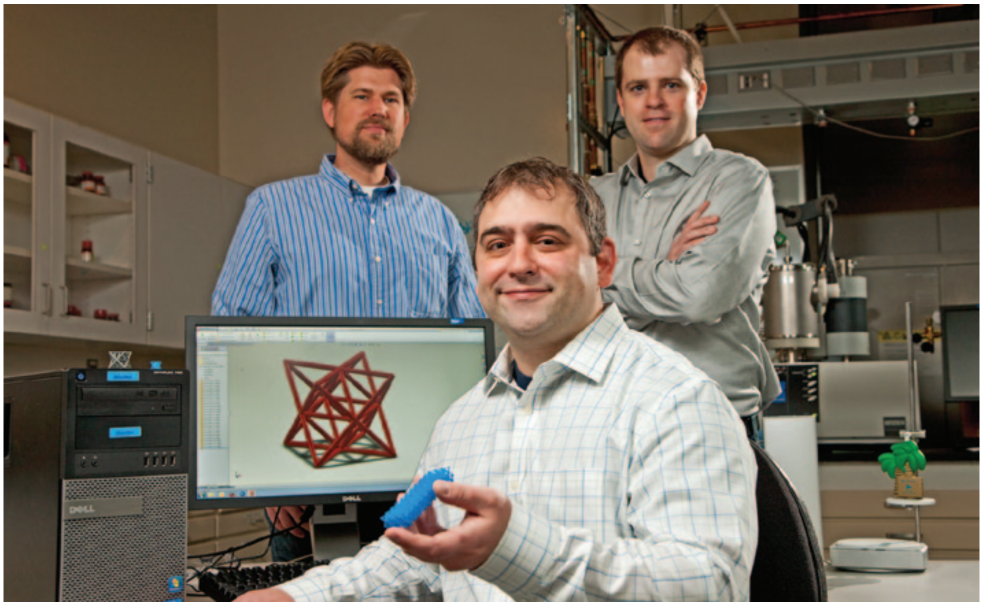
In particular, the researchers will focus on creating materials that exhibit high strength but low density or ultralow thermal expansion or improved energetics. Such materials are important for a wide range of national security applications and in the areas of energy, photonics, microfluidics, and semiconductor manufacturing.

From the Bottom Up

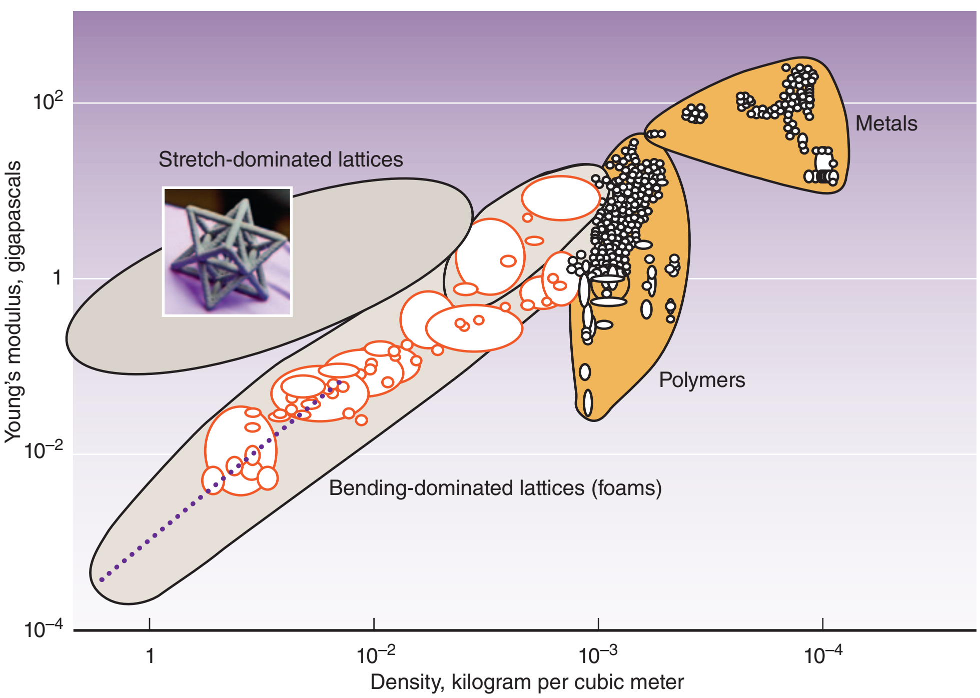
Additive manufacturing is the process of building 3D structures by sequentially layering one material on top of another in a desired pattern. It is a dramatic departure from more conventional fabrication techniques in which material is removed from a bulk piece through processes such as etching or machining. Contrary to what the name might imply, additive

Livermore engineers Chris Spadaccini (left) and Eric Duoss experiment with the direct ink-writing process.


Dino-Lite
Edmund Optics



Livermore scientist Joshua Kuntz (left) is working with Spadaccini and Duoss to develop additive manufacturing techniques for designing materials with improved properties.



Materials designed with new additive manufacturing techniques exhibit high stiffness and low density, occupying a previously unsettled area of the Ashby material selection chart for Young's modulus (stiffness) versus density. The octet truss structure recently fabricated by Livermore researchers is a stretch-dominated lattice.

manufacturing actually requires less material than "subtractive" fabrication methods. It also results in less waste and can reduce manufacturing costs.

Over the last decade, additive manufacturing has become a burgeoning industry, enabling rapid prototyping of components for automotive, medical, and electronic applications. News headlines in recent years have showcased the often-remarkable capabilities of 3D printers that produce macroscale objects, such as a prototype musical instrument. Although specialized technologies are available for developing 3D structures with small, mesoscale (millimeter-length) features—hearing aids, for example—they are limited to a small number of materials as well as component size and shape specifications.

According to Duoss, who leads the team's direct ink-writing effort, commercial additive manufacturing systems can at best fabricate single-material structures at resolutions of about 100 micrometers. "In contrast," he says, "our techniques can incorporate several materials into structures with feature sizes in the micrometer and even submicrometer range."

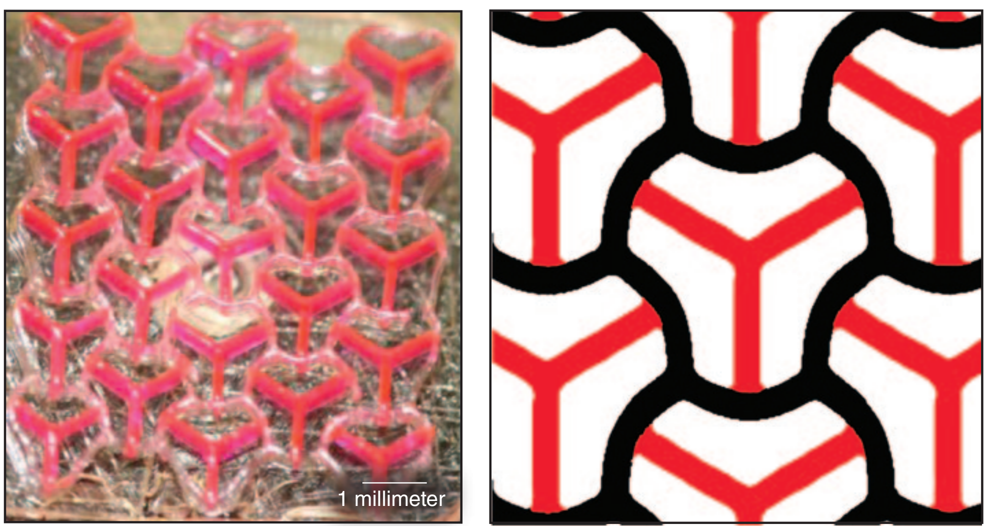
To date, no single technology that fabricates 3D mesoscale objects with micrometer-size architectures and submicrometer precision is compatible with the wide range of materials available. The Livermore-led project is integrating projection microstereolithography, direct ink writing, and electrophoretic deposition into a process that can manufacture materials with these characteristics in high volumes at low cost. In doing so, the team will significantly improve additive manufacturing capabilities and advance material design. "The broad diversity of potentially relevant materials, length scales, and architectures underscores the need for these flexible additive micromanufacturing techniques," says Duoss. "We believe our new patterning methods and design approaches will drive scientific and technological advances in materials science, chemistry, physics, and biology."

Building Complex Structures

Projection microstereolithography, direct ink writing, and electrophoretic deposition offer a unique combination of advantages for fabricating microscale structures from multiple materials. "These three technologies complement each other," says Kuntz. "Where one is weaker in a certain capability, the others are strong."

Projection microstereolithography, for example, can reliably create structures in three dimensions, but for now, it is compatible with only a few materials. Direct ink writing and electrophoretic deposition, on the other hand, work well with more materials but do not offer the same 3D capability as projection microstereolithography. Electrophoretic deposition would have to burn out excess, or fugitive, material within a fabricated component to create void space, but direct ink writing and projection microstereolithography can build these spaces where needed during component fabrication. Says Kuntz, "By combining the techniques, we can create more complex structures than we can produce using one method alone."

With each fabrication approach, the team first applies a computer-aided design program to section an image of the desired structure into 2D slices in the horizontal plane. In a project with MIT professor Nicholas Fang and his colleague Howon Lee, the team used projection microstereolithography to display 2D images on a digital photomask made from a micromirror or liquid crystal on a silicon chip. An ultraviolet light-emitting diode illuminates the miniature display, which reflects light and an image of the component to be fabricated through a series of reduction optics onto a photopolymer liquid resin. As the resin cures, it hardens into the shape of the image. The substrate holding the resin is then lowered using a motion-controlled stage, and the next 2D slice is processed.



The Livermore team fabricated this heterogeneous polymer structure (left) using projection microstereolithography and integrated microfluidics. The schematic (right) delineates the two materials incorporated into the final structure: (red) polyethylene glycol with rhodamine B dye and (black) hexanediol diacrylate. (Courtesy of Nicholas Fang, Massachusetts Institute of Technology.)

Projection microstereolithography is a high-speed parallel process that can fabricate structures at both micro- and macroscales within minutes. "Using projection microstereolithography, we can rapidly generate materials with complex 3D microscale geometries," says Spadaccini, the principal investigator for the technique.

However, the method does have its limitations. "The quality of a component depends on the uniformity of light at the image or polymerization plane and both the lateral and depth resolution of the system," he says. "Resolution is restricted both by the optical resolution and the physical–chemical characteristics of the exposed monomer solution."

Expanding the technique's capabilities requires a thorough understanding of the physics involved in the fabrication process. The team is developing process models based on differential equations to assess physics parameters, such as light-scattering effects, chemical composition, and fluid dynamics. Through these computational methods, parameters can be altered to determine the best ones for achieving a desired resolution and geometry.

Microfluidic systems can also be incorporated with projection microstereolithography to create heterogeneous structures that integrate multiple materials into one component. "After we fabricate structures from one material, we can flow the remaining uncured resin out of the fabrication zone and flow a new resin in," says Spadaccini. "By simply shining light in a new pattern, we can fabricate a second structure with the new material on the same device layer." With the combined process, researchers can develop a two-material composite with void space, the same structures that form the building blocks for designer bulk materials.

Inking a Material

The direct ink-writing process can also create micro- to macroscale structures with extreme precision. With this technique, a print head mounted to a computer-controlled translation stage deposits inks into programmed designs on various substrates. The process works layer by layer, adding a continuous filament to a substrate. The patterns it generates range from simple, one-dimensional wires to complex, 3D structures.

Inks are administered through one or more nozzles, and filament diameter is determined by nozzle size, print speed, and rates of ink flow and solidification. The time required to build a final part is determined by the distance from the nozzle to the substrate and by print speed. The finest feature size obtained with this technology is approximately 200 nanometers—smaller than the features produced with projection microstereolithography. Recently, the team constructed two direct ink-writing platforms that can travel 30 centimeters at up to 10 centimeters per second while maintaining micrometer and submicrometer resolution.

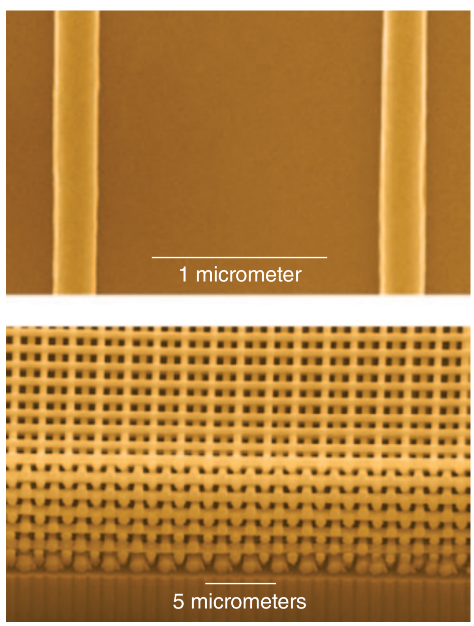
Direct ink writing can rapidly pattern different materials into multiscale, multidimensional structures for an array of applications. However, process improvements, including more sophisticated inks, are needed to achieve the arbitrary, complex 3D structures required for designer materials. To date, the researchers have designed particle- and nonparticle-based inks derived from metals, ceramics, and polymers.

"We carefully tailor the fluid properties and solidification behavior to obtain inks that readily flow through micronozzles without clogging," says Duoss. "We also want the inks to set rapidly so they will maintain their shape with minimal shrinkage."

In addition, the team is working on a direct ink-writing process specifically designed for building 3D geometries. Adds Duoss, "Through improved ink chemistries, better material characterization, modeling of ink dynamics during deposition, and improved robotic and ink delivery systems, we can create a 3D printing process with ever greater spatial and compositional control."

Electrifying Attraction

Although typically used for creating protective or performance-enhancing coatings, electrophoretic deposition has great potential for building 3D designer materials. Among its advantages are the ability to incorporate multiple materials into one structure, extreme precision, and potential for large-scale production. In the electrophoretic deposition process, an electric field is applied to a liquid medium that contains suspended colloidal nanoparticles. "Within these suspensions, the particles exhibit an induced surface charge," says Kuntz. "By altering that charge, we can use electric fields to control the particles."



Scanning electron micrographs of titanium dioxide structures show the fine-scale features and precision that can be achieved with direct ink writing. (Courtesy of Jennifer Lewis, University of Illinois Urbana-Champaign.)

Typically, the suspension is flowed into a deposition cell that has opposing electrodes. Once an electric field is applied to the deposition cell, the induced surface charge causes the particles within the liquid to travel parallel to the electric field, attracting the suspended particles to the substrate electrode. With this process, the team has built 2D structures with resolutions smaller than 7 micrometers and horizontal gradients of about 1 micrometer.

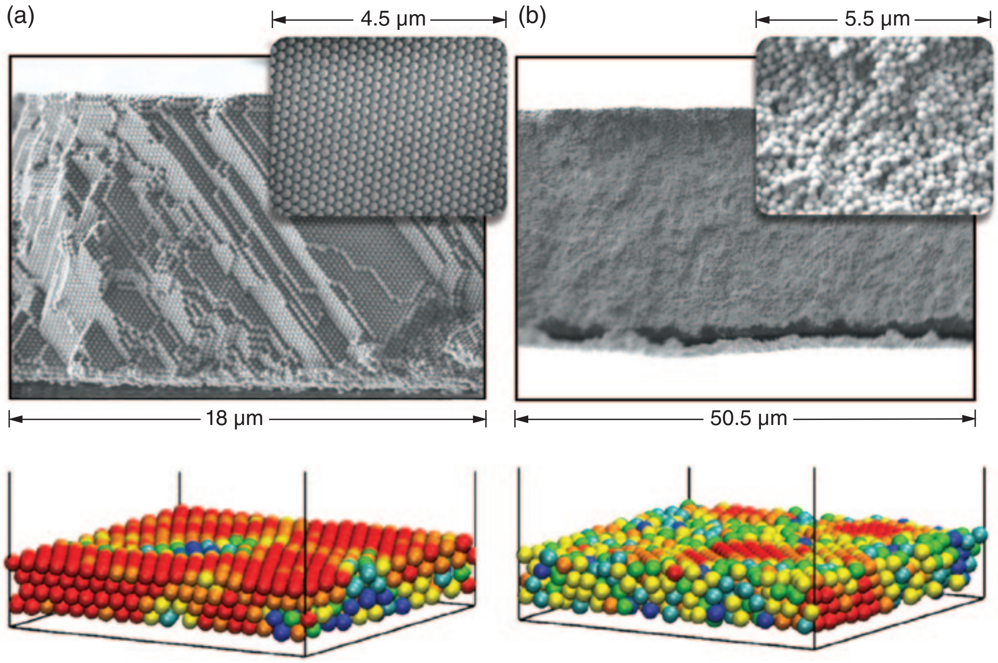
Achieving 3D geometries with electrophoretic deposition is a novel concept, one the team is validating through an innovative electrode scheme. As with projection microstereolithography, an optical system projects a pattern onto a transparent photoconductive layer attached to a dynamic electrode. The electric field emanates only from the illuminated area of the electrode and can be varied throughout the deposition process. Because the image is also adjustable, the team can alter the 2D pattern on the deposition plane during an experiment to build complex 3D structures.

The team is again turning to process models to speed experimental redesign of the electrophoretic deposition technique. "These models save us time," says Kuntz. "They allow us to effectively sculpt the electric field for producing a specific deposited geometry. In this way, we can narrow deposition parameters and the electric field profile to those that are the most successful prior to actually conducting experiments." Armed with a better understanding of processes such as particle motion, electrophoresis, and hydrodynamic interactions, the team has already identified ways to change the electrode design for improving its fidelity and subsequently the surface topography of the fabricated components.

Things that Go Boom

The Livermore researchers are applying the three techniques to improve the performance of thermites—pyrotechnic compositions that combine a metal oxide, such as copper oxide, with a metal powder, such as aluminum. Thermites are designed to produce an exothermic reaction through a process of oxidation and reduction. Such materials typically have a slow burn rate, limited by the irregular placement of the fuels and oxidizers. "Improved performance in energetic materials is contingent upon achieving microstructural control that is not currently available," says Spadaccini. "If we can adjust the thermite microstructure, we can control its burn rate."

Using electrophoretic deposition, the team strategically arranged an oxidizing agent and a fuel to produce a highly ordered, optimized thermite. "With this placement, we can potentially alter the directionality of the thermite reaction as it propagates through the material," says Kuntz. The team's first heterogeneous thermite structure had a power density approximately two times greater than that achieved with more conventional thermite compositions, with half the burn time and twice the burn velocity.



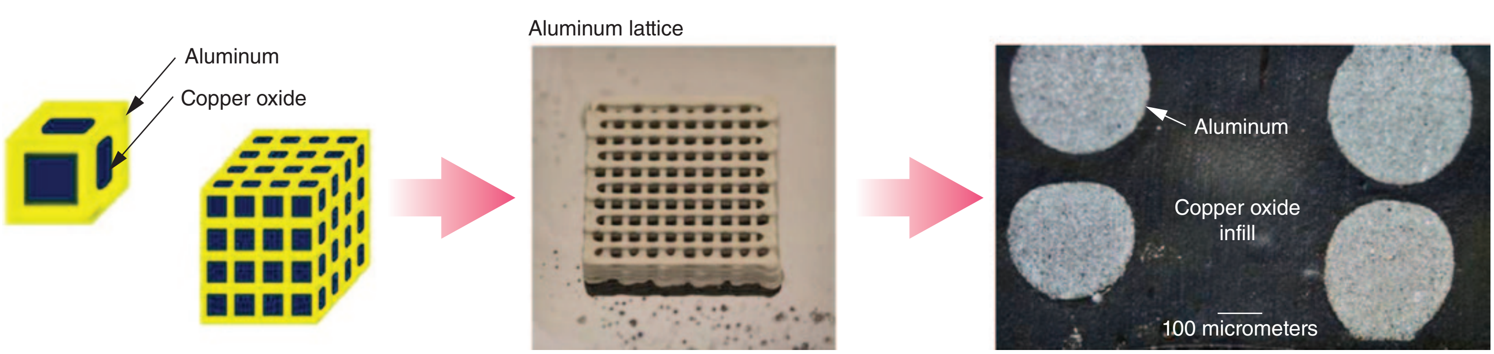
Electrophoretic deposition can be used to fabricate (a) highly ordered and (b) disordered structures. The computational models shown in the bottom row match the experimental results in the top row, where µm = micrometers.

Thermite performance could be improved further by combining the fabrication techniques. A recent experiment showed that direct ink writing and electrophoretic deposition could create a novel 3D microstructure made from multiple materials. In this experiment, the scientists used direct ink writing to build an initial lattice structure complete with void space. They then applied a new material to the void with electrophoretic deposition.

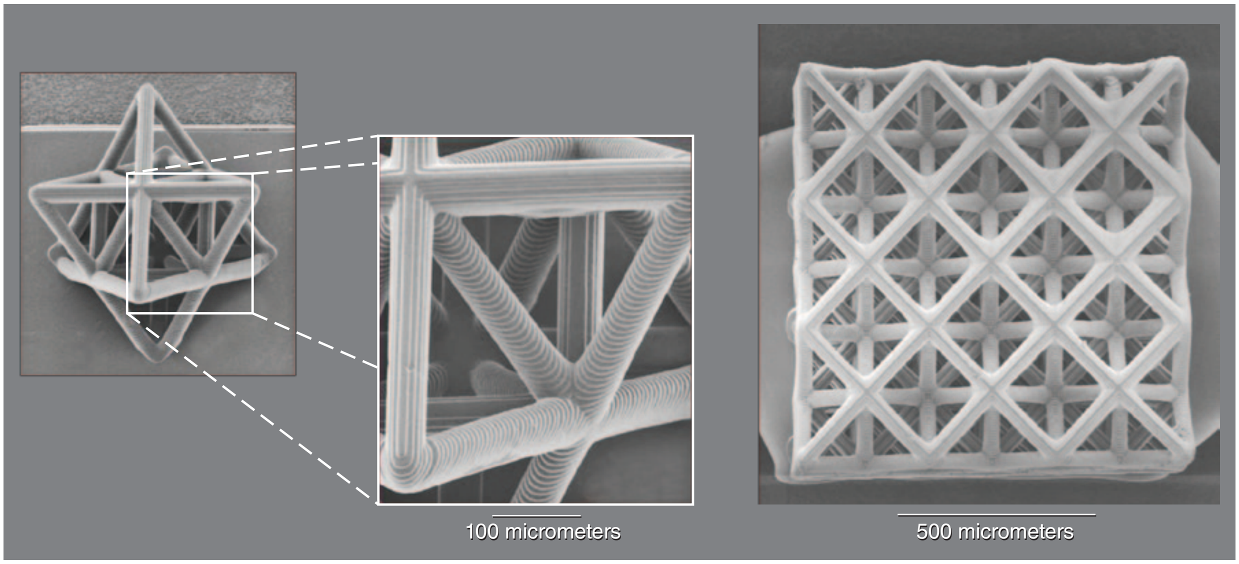
"Working with Jennifer Lewis and her team at the University of Illinois, we've developed copper oxide and aluminum inks and are trying to better understand the fundamental reaction mechanisms of the materials," says Duoss. "We will print both inks in 2D and 3D configurations to study the effects of stoichiometry and structure on properties such as propagation velocity and energy density."

"Uncharted" Territory

Using projection microstereolithography, the team fabricated a 3D microstructure with high stiffness and low weight in the form of a very small octet truss. This geometric configuration is the stiffest and



In a recent experiment, Livermore researchers fabricated a highly ordered thermite structure by combining two additive manufacturing techniques. They applied direct ink writing to build an aluminum lattice structure complete with void space. They then filled the void with copper oxide using electrophoretic deposition.



Scanning electron micrographs compare (left and middle) a single unit-cell octet truss and (right) a 3 × 3 × 3 array fabricated with projection microstereolithography.

lowest weight architectural arrangement for a mechanical structure. The single-material truss can be bound with other identical unit cells to create a bulk material with a precisely arranged lattice structure. Such materials occupy a new realm on Ashby material selection charts for stiffness and density.

In another project, the team developed lattice structures from two materials, arranging the void space such that the composite offered zero or graded thermal expansion but remained structurally sound. "By designing a structure with both high and low expansion materials, we can strategically place void spaces or small amounts of bending or twisting in a local structural member to accommodate growth or shrinkage from temperature changes," says Spadaccini.

Materials that maintain their relative shape under extreme temperatures offer a variety of potential applications, for example, in weapons systems, thermal-imaging diagnostics, energy technologies, and medical devices. Three-dimensional mesoscale structures with microscale features and restricted thermal behavior may also be beneficial in fusion energy experiments, such as those conducted at Livermore's National Ignition Facility, and in developing lightweight, high-strength materials for aerospace components.

A Boon for Manufacturing

Although the researchers are working on the three techniques in parallel, their goal is to integrate the strengths of each process into one technology that does it all. A streamlined fabrication method for producing 3D microstructured materials would benefit academia, scientific research, and the manufacturing industry. "With the ideal technology, users could upload a computer model of a component with an arbitrary shape and size and merely press a button," says Kuntz. "The machine would then build the part to precise specifications with no additional assembly required."

According to Spadaccini, a lower cost, highly efficient fabrication process could also improve the status of the U.S. manufacturing industry in the global market. As opposed to the standard assembly-line process in which several workers build components piece by piece, this tool would require only one skilled technician and one or two designers to develop the computer models. Spadaccini adds, "One way we can help make U.S. manufacturing competitive again is through more advanced fabrication methods."

By pushing the limits of additive manufacturing and material design, the team is demonstrating Livermore's scientific prowess. Says Spadaccini, "As a result of this effort, the Laboratory and our collaborators are becoming scientific and technological leaders in 3D fabrication and micromanufacturing of engineered materials." In providing a boon for the manufacturing industry and enabling previously unobtainable material properties, it is no wonder that these tiny 3D microstructures have such big possibilities.

—Caryn Meissner

Key Words: additive manufacturing, designer material, direct ink writing, electrophoretic deposition, microstructure, projection microstereolithography.

For further information contact Chris Spadaccini (925) 423-3185 (spadaccini2@llnl.gov).