Additive Micro-Manufacturing of Designer Materials

Eric Duoss[1,*], Cheng Zhu[1], Kyle Sullivan[1], John Vericella[1], Jonathan Hopkins[1], Rayne Zheng[1], Andrew Pascall[1], Todd Weisgraber[1], Joshua Deotte[1], James Frank[1], Howon Lee[3], David Kolesky[2], Jennifer Lewis[2], Daniel Tortorelli[2], David Saintillan[2], Nicholas Fang[3], Joshua Kuntz[1], and Christopher Spadaccini[1,*]

[1] *Lawrence Livermore National Laboratory, Livermore, CA, 94551, USA*
[2] *University of Illinois at Urbana-Champaign, Urbana, IL, 61801, USA*
[3] *Massachusetts Institute of Technology, Cambridge, MA, 02139, USA*

Abstract

Material properties are governed by the chemical composition and spatial arrangement of constituent elements at multiple length scales. This fundamentally limits material properties with respect to each other creating trade-offs when selecting materials for a specific application. For example, strength and density are inherently linked so that, in general, the more dense the material, the stronger it is in bulk form. Other coupled material properties include thermal expansion and thermal conductivity, hardness and fracture toughness, strength and thermal expansion, etc. We are combining advanced microstructural design, using flexure and screw theory as well as topology optimization, with new additive micro- and nano-manufacturing techniques to create new material systems with previously unachievable property combinations. Our manufacturing techniques include Projection Microstereolithography (PμSL), Direct Ink Writing (DIW), and Electrophoretic Deposition (EPD). These processes are capable of reliably producing designed architectures that are highly three-dimensional, multi-scale, and often composed of multiple constituent materials.

Keywords: *Additive manufacturing; designer materials; advanced materials.*

1. Introduction

Design of any new hardware component, regardless of the application, is constrained by both the available material set and the geometry that can be fabricated using existing manufacturing processes. Both of these limitations could be overcome through bottom-up fabrication processes if they were capable of achieving

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arbitrary three-dimensional mesoscale structures with microscale architectures and sub-micron precision. These processes would have a broad impact on manufacturing if they were also compatible with a wide range of materials (e.g., metals, ceramics, and polymers), allowed for rapid translation from computer model to fabricated component, and were scalable to large numbers of components or bulk material billets. This paper describes the creation of designer materials on demand with three bottom-up micro-manufacturing processes that can meet these metrics.

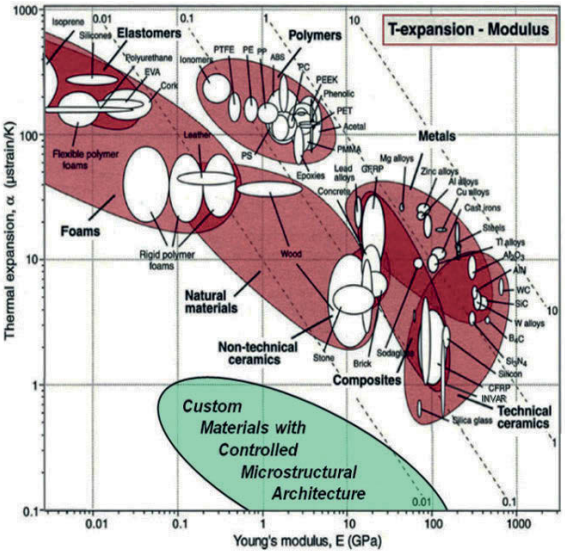

Figure 1. *Ashby chart of thermal expansion coefficient versus Young's Modulus with possible "designer materials" space indicated in green[1].*

Material properties are governed by the chemical composition and spatial arrangement of constituent elements at multiple length scales. This fundamentally limits material properties with respect to each other creating trade-offs when selecting materials for a specific application. For example, strength and density are inherently linked so that, in general, the more dense the material, the stronger it is in bulk form. Other coupled material properties include thermal expansion and thermal conductivity, hardness and fracture toughness, strength and thermal expansion, etc. This coupling can be visualized in the material selection charts such as that shown in Figure 1 for thermal expansion versus Young's modulus [1]. Such plots are also known as "Ashby" charts, being named for their originator, Prof. M.F. Ashby. The coupling between these properties creates significant unpopulated, yet potentially desirable design spaces that cannot be attained using standard manufacturing methods such as mixing and alloying.

However, structural and functional properties of materials may be decoupled via control of the micro- and nanostructure. Recently, Launey et al. demonstrated that a microscale brick and mortar structure composed of Al_2O_3 (brick) and Al–Si (mortar) exceeded the fracture toughness predicted using the rule-of-mixtures by a factor of four while reducing the weight versus pure Al_2O_3 by 25% [2]. Their fabrication process, however, is only compatible with a narrow range of materials and provides limited control over the final structure.

Similarly, there is a significant amount of theoretical work in the literature that predicts arrays of microscale bi-material lattices could dramatically reduce thermal expansion and/or density while maintaining material strength [3-6]. In principle, this type of design could provide materials with the strength of steel and the density of polymers or also zero thermal expansion with controlled stiffness. To date, no manufacturing process has demonstrated the necessary 3D microscale control and material flexibility required to fabricate these designer materials, but emerging additive manufacturing techniques may soon be able to meet these needs.

We aim to fundamentally understand and develop new additive micro-manufacturing techniques that enable designer materials on demand. To achieve these goals, the processes must: (1) be compatible with multiple materials (polymers, metals, ceramics, etc.), (2) be capable of creating heterogeneous or multi-material structures, (3) produce complex 3D mesoscale geometries with micron scale precision, and (4) be scalable to eventually achieve high manufacturing volumes at low cost. There are no current fabrication technologies which adequately address all of these needs. Therefore, we are developing three new additive micro-manufacturing processes because they have the potential to meet these needs. These techniques are: Projection Microstereolithography (PμSL), Electrophoretic Deposition (EPD), and Direct Ink Writing (DIW).

2. Results and Discussion

2.1 Designer Materials on Demand

"Designer materials on demand" refers to the ability to design and fabricate a "new" material with specified properties, either structural or functional, that exceed those attainable with bulk materials processed via traditional synthetic or manufacturing methods such as mixing and alloying. Control of these properties can be obtained by advanced design of the structural architecture at the micron scale. This capability will dramatically expand the design space for many applications ranging from aircraft to microelectronics. We are designing and manufacturing new micro-architectures based on desired structural or functional properties for particular applications. These designs have been both analytically and compu-

tationally derived. In addition, our efforts are guided by the open literature where many microstructures have been theorized, but few have been fabricated due to the relative lack of suitable manufacturing techniques. For example, materials with ultra-low or negative thermal expansion and controlled stiffness have been reported [3-6]. Typical theoretical structures which exhibit this combination of properties are bi-material lattices with void space. By carefully designing a structure with both high and low expansion materials, growth or shrinkage due to temperature changes can be accommodated locally by the void space or by small amounts of bending or twisting of a structural member.

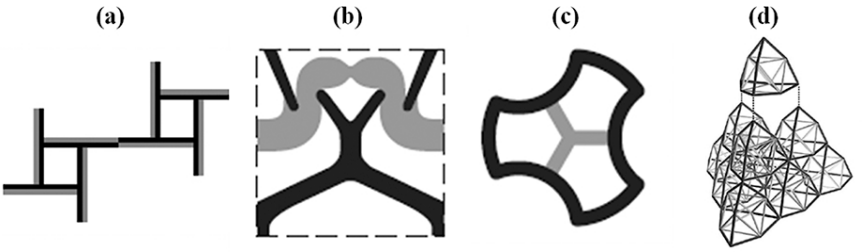

Figure 2. *Unit cells of bi-material lattice structures for low or neutral thermal expansion. Light gray indicates high thermal expansion material and black indicates low thermal expansion. These geometries have been proposed by (a) Lakes [4], (b) Sigmund and Torquato [5], and (c) Jefferson [3]. The structure in (d) is a low thermal expansion 3D lattice proposed by Steeves et al. [6].*

Unit cells of some of the designs for which thermal and mechanical properties have been derived in the literature are shown in Figure 2. Although these geometries have theoretically excellent properties, they have yet to be fabricated as the building blocks of a bulk material due to the absence of a fabrication technology with the suitable materials flexibility, three-dimensionality, and range of length scales. The high-throughput, multi-material, 3D micro- and nano-manufacturing tools being reported here are well-suited to achieving these structures. Ultimately, this combined design and manufacturing approach will result in the ability to generate volumetric lattices and truss-like structures at the microscale which exhibit these previously unobtainable property combinations.

2.2 Projection Microstereolithography (PμSL)

Projection Microstereolithography (PμSL) is a low cost, high throughput, microscale, stereolithography technique which uses a spatial light modulator, typically a digital micromirror device (DMD) or a liquid crystal on silicon (LCoS) chip as a dynamically reconfigurable digital, photomask [7-9].

PμSL is capable of fabricating complex three-dimensional microstructures in a bottom-up, layer-by-layer fashion. In this process, a computer aided design CAD) model is first sliced into a series of closely spaced horizontal planes. These two-dimensional slices are digitized as an image and transmitted to the spatial light modulator which projects the image through a reduction lens on the surface of a photosensitive polymer resin bath. The exposed liquid resin material then rapidly cures and solidifies. Next, the substrate on which the part rests is lowered to repeat the process with the next image slice.

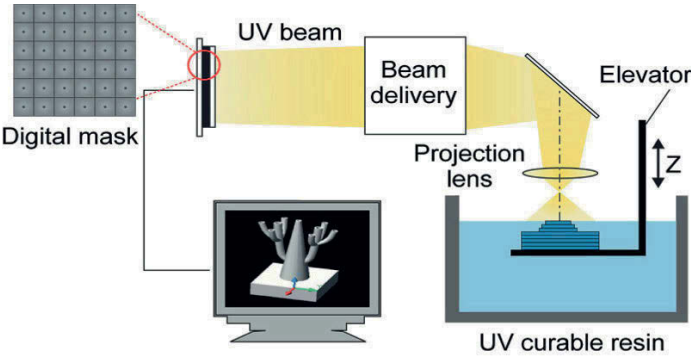

Figure 3. *Process schematic of PμSL.*

Figure 3 shows a schematic illustration of this process. The process is currently capable of rapidly generating complex 3D geometries such as those shown in Figure 4. These structures were fabricated in minutes out of hexanediol diacrylate (HDDA) and have features spanning size-scales from 10-500 μm [8].

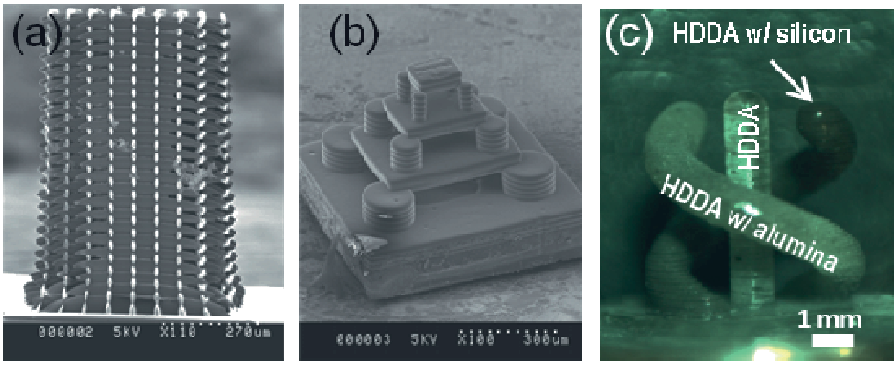

Figure 4. *SEM images of (a) lattice structures, (b) 3D components with void spaces, and (c) heterogeneous materials. For (c), the light curved helix is formed with Al_2O_3 nanoparticles in HDDA, the straight center post is pure polymer (HDDA), and the dark curved helix is silicon powder dispersed in HDDA [10].*

Currently, we are able to fabricate structures with micro or nanoparticles suspended in the photosensitive polymer resulting in a hybrid material with loadings of ~50 wt% of the nanoparticle material. An example of this is shown in Figure 4(c). A subsequent burn-out and sintering process can remove the organic polymer and densify the remaining inorganic material. It is also possible to fabricate a bi-material hybrid component with void space similar to those that may be required for a designer structural material by incorporating microfluidic material delivery systems.

The quality of a component fabricated by PμSL depends on the light uniformity at the image or polymerization plane and both the lateral and depth resolution of the system. The light uniformity is influenced by the performance and alignment of the various optical components, especially the LED array, and optimization of the projected image is achieved through careful selection and installation of these components. The fabricated resolution is limited both by the optical resolution and the physical-chemical characteristics of the exposed monomer solution. In order to optimize the fabrication procedure we have developed a process model that incorporates the chemical kinetics of photopolymerization, fluid dynamics, and optical effects. At the core of the process model is a set of differential equations that describe the evolution of the reaction in the resin during its transition from liquid resin to solid polymer. These equations include the effects of light attenuation as well as the kinetics of the various stages of polymerization coupled with heat and mass transport. In addition to improving our understanding of the underlying physics, this model also provides a means to optimize the fabrication parameters to obtain a desired resolution. For example, since the polymerization is driven by light intensity but limited by diffusion, there is a trade-off between fabrication speed and feature resolution.

2.3 Electrophoretic Deposition (EPD)

Electrophoretic deposition (EPD) is a bottom-up fabrication process that utilizes electric fields to deposit charged nanoparticles from a solution onto a substrate [11]. EPD can be used with a wide range of nanoparticles including oxides[12], metals [13], polymers [14], and semiconductors [15]. Once the particles are deposited, the green body can be post-processed (e.g., sintered, hot isostatic pressed, etc) to produce the final part. One-dimensional (1D) density and composition gradients in coatings have also been demonstrated by exchanging the nanoparticle suspension during the deposition process [16-19]. Hayward et al. demonstrated that EPD could be used to pattern particles in the plane parallel to the deposition surface, which is an important step in eventually patterning complex 3D geometries [16]. To date, this type of 2D patterning has been limited to fixed patterns and generally films only a monolayer thick.

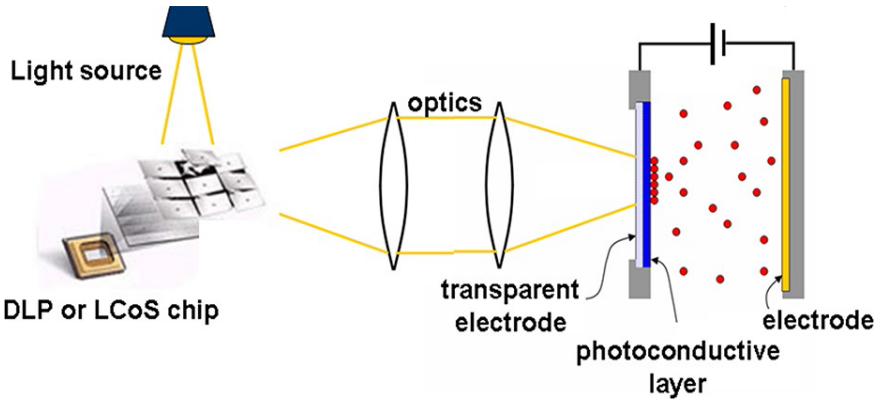

Figure 5. *Illustration of the dynamic electrode system using a spatial light modulator.*

We can precisely pattern different geometries and additively build structures on the deposition plane by modifying the electrode pattern because EPD occurs only where the field is applied. To enable this capability, we use dynamic, optically defined electrodes. The dynamic electrodes utilize a transparent photoconductive layer (such as α-H:Si) that can be illuminated in specific regions using either an optical mask or a dynamic optical pattern from a spatial light modulator as shown in Figure 5. By changing the optical mask during the deposition process, we can adjust the 2D pattern on the deposition plane to build complex 3D structures.

In order to accurately fabricate new designs, we must be able to predict the necessary process parameters to achieve the desired deposition thicknesses, feature widths, and resulting particle packing structure based on the particle material(s). To do this, we have developed a Stokesian dynamics simulation that captures the physics relevant to this process including: electrophoresis, dielectrophoresis, hydrodynamic interactions and Brownian motion of the particles during the deposition process as well as the particle-particle and particle-wall interactions (e.g., van der Waals and electrostatic interactions) that determine the resulting packing structure. Figure 6 shows simulation results of the first few layers of polystyrene particles as they deposit onto a uniform electrode surface. Additional functionality is required in this model to accurately predict 3D patterning as the electric fields generated by the electrode patterns at the surface will quickly diverge away from the surface (this is a work in progress). Using finite element modeling to capture these features in the field, we can predict the appropriate electrode spacing away from the deposition surface to maintain the desired 2D pattern at the surface.

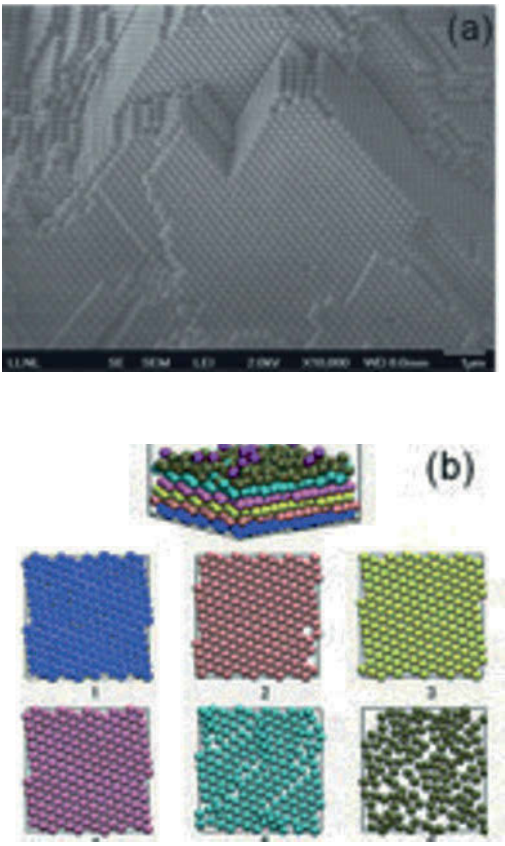

Figure 6. *Comparison of the experimentally observed (a) and predicted (b) structure for polystyrene particles deposited from an ethanol solution in an electric field of approximately 20 V/cm. The numbered images in (b) represent different layers of the deposition at a given time and correspond to the colored layers in the isometric view above.*

2.4 Direct Ink Writing (DIW)

Direct ink writing (DIW) is a layer-by-layer printing approach in which concentrated inks are deposited in planar and 3D layouts with lateral dimensions (minimum ~200 nm) that are at least an order of magnitude lower than those achieved by conventional printing methods. Paramount to this approach is the creation of concentrated inks that can be extruded through fine deposition nozzles as filament(s) which then undergo rapid solidification to maintain their shape even as they span gaps across unsupported regions (see Figure 7(a) for a schematic illustration). Direct-write techniques offer an attractive alternative to conventional manufacturing technologies due to the low-cost of the printing equipment, ease of manufacture, and flexibility in material systems, dimensions, and designs.

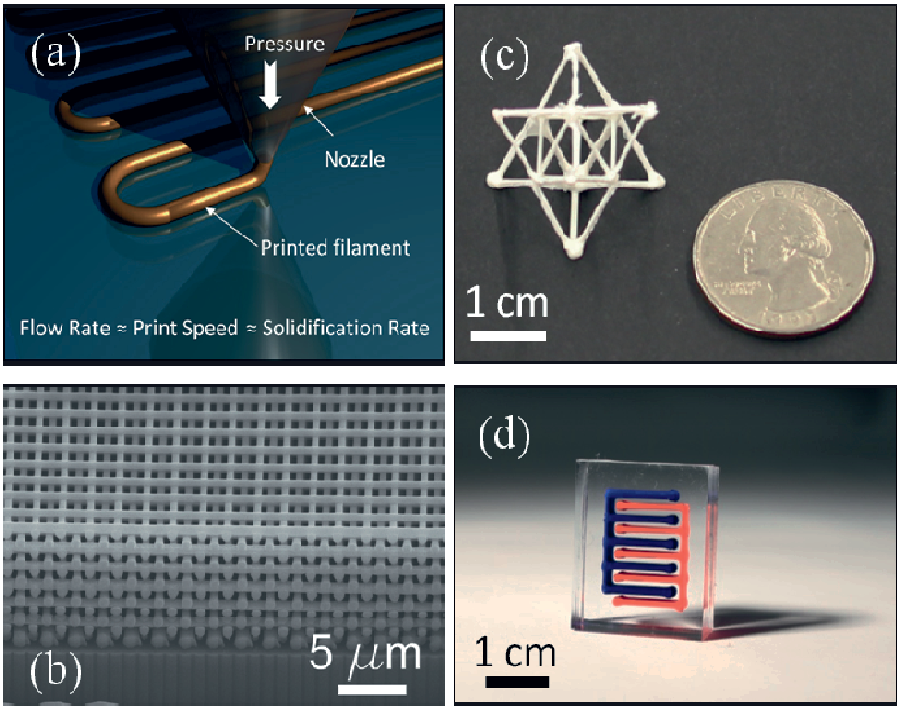

Figure 7. *(a) Schematic illustration of DIW process, (b) woodpile structure printed with a titania-based sol-gel ink [20], (c) octet-truss structure printed with an alumina-based ink with a wax support material (wax has been removed), (d) multi-material silicone structure (e.g., red and blue materials) printed with two nozzles and infilled with a third silicone material.*

The real strength of the DIW approach is the materials flexibility due to functional ink design. To date, DIW has been demonstrated with a wide variety of functional inks, including colloidal gels [21, 22], organic waxes [23], concentrated polyelectrolyte complexes [24], silk [25], sol-gel materials [20], and metallic nanoparticles [26]. In general, DIW inks are designed to exhibit shear thinning behavior so they will easily flow through micro-nozzles, but rapidly gel and solidify upon exiting the nozzles. Typically, 3D structures are assembled in a layer-by-layer build sequence with this filamentary printing technique to create scaffolds that resemble a log-pile structure (Figure 7(b)). In another approach, one may also print support materials (e.g., similar to fused deposition modeling processes) that can be subsequently removed to obtain an arbitrarily complex 3D structure (Figure 7(c)). In addition, DIW is used to pattern heterogeneous structures with the use of multiple nozzles loaded with different inks, akin to an inkjet print-head, to microfabricate composite structures from different materials (Figure 7(d)). Presently, we are developing a process model to capture the relevant physics for improved patterning capability. To achieve this, we are creating computational fluid

dynamics models that capture ink rheology and flow behavior during printing as well as shape retention and uniformity after deposition.

3. Conclusions

We are developing three new additive micro-manufacturing techniques that will enable production of designer materials on demand. These techniques, Projection Microstereolithography, Electrophoretic Deposition, and Direct Ink Writing, are capable of patterning multiple materials (polymers, metals, ceramics, etc.) within a single structure to produce complex 3D mesoscale geometries with micron scale precision. These processes were selected, in part, due to their eventual scalability to high manufacturing volumes at low-cost.

Acknowledgments

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