Bio Focus

3D printing sends ceramics to the queue

Advances in three-dimensional (3D) printing are expected to one day revolutionize industrial manufacturing as well as everyday life: imagine edible inks for downloaded dinners, and customized jet-engine parts synthesized on demand. At present, however, the range of materials that is 3D printed is relatively limited. To address this limitation, researchers at HRL Laboratories have introduced a strategy to efficiently print high-strength ceramic parts with complex shapes. The results are described in a recent issue of *Science* (DOI: 10.1126/science.aad2688).

Ceramics have many technologically valuable properties, including high hardness, strength, heat resistance, and resistance to abrasion and corrosion. These properties make ceramics attractive across diverse applications areas ranging from microelectronics to aerospace engineering. Achieving high-performing ceramic components, however, often requires demanding processing conditions, including high temperatures and pressures. Conventional processing routes based on consolidation of powders introduce defects such as porosity and cracks and also limit the diversity of shapes that can be achieved. Many previous ceramic printing techniques have followed this convention, using slow, layer-by-layer approaches to spatially consolidate binder resins around unformed ceramic powders.

In their newly demonstrated technique, the HRL research team, led by Tobias Schaedler, utilizes specialized pre-ceramic "inks" in the form of silicon-based resins, combined with a rapid lithography approach known as self-propagating photopolymer waveguide technology (SPPW). "With this new fabrication approach, we can combine the desirable properties of ceramic materials with the processing convenience of 3D printing," Schaedler said. The pre-ceramic resins are composed of monomers of siloxane, silazane, or carbosilane with organic side chains, such as vinyl or epoxy groups, that enable UV polymerization. This permits laser-directed polymerization in a spatially programmed manner (see Figure).

A separate study by a group based at the University of Padova, Italy, has recently demonstrated 3D printing from preceramic polymers using conventional layer-by-layer lithography, as reported in *Advanced Materials* (DOI: 10.1002/adma.201503470). However, with HRL's SPPW process, fabrication times are accelerated by 100–1000x for component thicknesses less than 1–2 cm. Additionally, a unique feature of the silicon-based precursors utilized by the HRL team is that, upon polymerization, the materials undergo a shift in index of refraction that helps trap the incident UV light within the solidified material. This decreases the requirement for additives to control light scattering and adsorption, ultimately improving the ceramic's structural integrity.

When polymerized scaffolds formed from a mixture of siloxanes are washed of excess resin and subject to pyrolysis at 1000°C, they undergo a 42% mass loss (through escape of volatile organics) and 30% shrinkage while converting into a SiOC ceramic. Notably, shrinkage is uniform, resulting in an absence of porosity. Printed feature sizes, however, must be limited to less than 3 mm to allow gases to escape during pyrolysis. Regardless, the new additive fabrication process achieves unique architectures such as honeycombs and microlattices, resulting in components with impressive strength. SiOC microlattices exhibited 10 times higher compressive strength relative to commercially available ceramic foams of similar density. The printed components also exhibited excellent high-temperature stability and survived 3 hours at 1700°C with some surface degradation. "The authors provide a much larger set of experimental data than available before that demonstrates how stereolithography can be favorably exploited using pre-ceramic polymers to generate components with outstanding properties," said Paolo Colombo (leader of the Padova-based team) about the recent work from HRL.

The introduced 3D printing approaches are anticipated to generate additional ceramic materials as well, such as SiC, Si_3N_4, and SiOCN, through use of alternate precursor chemistries. Overall, the use of polymer-derived strategies to print ceramics significantly expands the potential of additive manufacturing beyond simple metal and polymer products. And the future queue for industrial printing is looking as exciting as ever.

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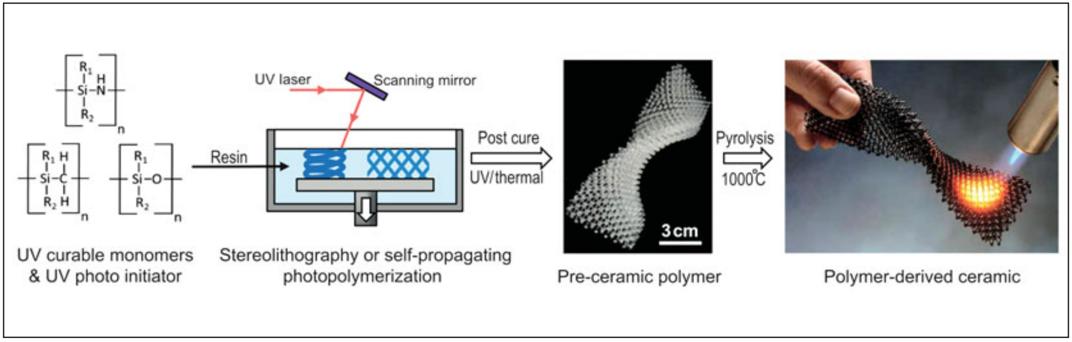

Workflow for three-dimensional printing ceramics as introduced at HRL Laboratories. Reproduced with permission.

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