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3D printing of a new generation of structured non-oxide polymer derived ceramics

Preceramic polymers were proposed as precursors for the fabrication of mainly Si-based advanced ceramics, generally denoted as polymer-derived ceramics (PDCs). Precursor-derived covalent ceramics in general exhibit enhanced thermo-mechanical properties with respect to creep and oxidation, crystallization, or phase separation up to 1500°C and higher [1]. Preceramic polymers can be processed or shaped using conventional polymer-forming techniques but in this work, we will focus on additive manufacturing of PDCs. Two 3D printing technologies will be used: Fused Deposition Modeling (FDM) where a solid thermoplastic material in the form of a filament is pushed by rollers through a small heated nozzle where it is melted and then deposited as a thin layer on a substrate; the nozzle is moved according to the computer programmed pathway and a solid shape is slowly manufactured layer by layer [2] and stereolithography (SLA) based on photopolymerization [3,4]. Once formed, objects made from the preceramic polymers can then be converted to ceramic components by heating to temperatures high enough to consolidate the elements contained in the polymer structure to a ceramic [1]. Moreover, PDCs can possess functional properties such as electrical conductivity luminescence, and piezo-resistivity. Several key engineering fields suitable for application of PDCs include high-temperature-resistant materials (energy materials, automotive, aerospace, etc.), hard materials, chemical [1] and membrane application. Chemical modification of PDC's precursors by introduction of new element is possible and leads to a high degree of crosslinking [5].

We investigated the 3D printing of different PLA molds (going from simple cylindrical to honeycomb shaped molds) and their impregnation with commercial and synthetic preceramic polymers, precursors of respectively SiC and SiBC. Then, after optimization of the cross-linking of the preceramic polymers and decomposition of the mold while retaining the shape of the ceramic, we investigated the direct extrusion followed by the 3D printing of the preceramic polymers.

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