Title: The influence of precursor derived secondary structures on the sintering behavior of binder jet 3D printed titanium dioxide

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Abstract: Binder jet 3D printing is a solid-state additive manufacturing technique that constructs near net-shaped green bodies layer-by-layer by iterating between stages of powder deposition and binder patterning. The green bodies are then densified during a sintering step, during which the green body can distort due to creep. The aim of this work is to understand how the introduction of nanocrystalline ceramic necks, derived from a liquid precursor, affect creep, distortion, and densification. In a series of dilatometry experiments, radial and axial length measurements were collected while sintering cylindrical specimens under a uniaxial load. Samples treated with the ceramic precursor exhibited a lower axial strain than the untreated samples, but a high load sensitivity was observed in both samples, suggesting both are susceptible to high-temperature creep.

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Binder jet 3D printing is an additive manufacturing process that builds a component layer-by-layer by selectively joining powder particles with an organic fluid binder. This technique is compatible with a variety of feedstock materials and has been used to print metal drill bits [1], refractory molds for castings [2], and ceramic glasses for biocompatible scaffolds [3] with a single system. During the print process, each layer is deposited in two steps: (i) powder is spread on a build plate and (ii) binder is deposited in a pattern predefined by the computer-aided design (CAD) model. Once the build is complete, the binder is cured to hold the particles together in a structure known as a green body. The green body can then be fired to fuse its constituent particles together in a post processing step called pressureless sintering [4]. During pressureless sintering, the as-printed components are exposed to high temperatures that activate mass transport between adjacent powder particles. This mass transport leads to interparticle junction growth and densification, as the particles' centers approach each other [5]. Ideally, a component should shrink uniformly in three dimensions when it is sintered; however, high temperature creep can lead to distortion of unsupported features [6].

A promising approach for mitigating such distortion is to incorporate additives into the green body that form interparticle necks during the early stages of sintering. Several different types of distortion-mitigating additives, including metallic salts [7,8], nanoparticle dispersions [9,10], and a metallo-organic inks [11], have been demonstrated. Building on these studies, we recently developed a method to mitigate distortion in a ceramic (TiO_2) using a water soluble ammonium titanium lactate complex [12], titanium (IV) bis(ammonium lactato) dihydroxide (TALH) [13]. In the present work, we use dilatometry to understand the mechanism by which the precursor-derived interparticle necks mitigate creep in TiO_2 components.

An ExOne Innovent binder jet 3D printer was used to print cylinders from rutile TiO_2 powder (Saint-Gobain S.A.) with an average particle size of 16 μm. The cylinders had an initial radius (r_0) of 3.15 mm, an initial height (h_0) of 6.3 mm, and an average relative density of 0.42. To increase the handling strength of the as-printed cylinders, they were heated to 1100 °C at a rate of 6 °C/min and then held at this temperature for 1 hr. **Figure 1a** shows a neck that formed during this pre-sintering process. After pre-sintering, select cylinders were vacuum infiltrated with an aqueous TALH solution (50 wt% water, Sigma-Aldrich). The TALH was thermally decomposed by heating the infiltrated cylinders to 600 °C at a