Title: Elucidating the effects of reactive binders on sintering binder jet 3D printed materials

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Abstract: Reactive binders are a promising approach for increasing the green density and neck size in binder jet 3D printed components. Here we present a ceramic-precursor reactive binder that decomposes to form nanocrystalline necks in the printed compact prior to sintering. Using scanning electron microscopy, we characterized microstructural differences between samples with and without the reactive binder treatment. With a series of dilatometry experiments, we quantified the effect of increasing interparticle contact size on creep during sintering and found that samples treated with reactive binder are more creep-resistant. These results are used to develop quantitative sintering and diffusional creep models for binder jet 3D printed materials which integrate our microstructural observations to account for the increase in interparticle neck size introduced by reactive binders.

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Binder jet 3D printing forms near-net shaped green bodies that must be sintered to achieve adequate strength for load-bearing applications. Unfortunately, sintering is often accompanied by creep, which results in distortion and loss of dimensional accuracy. Creep is most rapid at the early stages of sintering, when the interparticle contact sizes are small. Thus, one approach to mitigating creep is to augment the interparticle bonds prior to sintering using reactive binders, which can be deposited as a liquid via the printhead, then decomposed after the printing step to form solid-state junctions between the individual particles [1-6]. Liquid-phase reactive binders are easier to print than nanoparticle-loaded binders, which suffer from problems with nanoparticle agglomeration and resulting clogging of the printhead. Binder jet 3D printing with reactive binders was first demonstrated by Sachs and coworkers [7], who applied silver nitrate metal salts to stainless steel powder to strengthen the green body. In the present study, we use electron microscopy and dilatometry to determine the effects of a reactive binder on the creep and densification behaviors of a sintering compact.

Here we use a model system of titanium dioxide (TiO_2) powder and a reactive binder comprising titanium (IV) bis (ammonium lactato) dihydroxide (TALH), a liquid-phase TiO_2-precursor. TiO_2 samples were printed with an ExOne Innovent binder jet printer and pre-sintered to 1100 °C to increase handling strength. The average relative density of the pre-sintered samples was 41%. A SEM micrograph of an interparticle neck formed during pre-sintering is shown in **Figure 1a**. Select samples were treated with the reactive binder and heated to 600 °C to precipitate TiO_2. This reactive binder infiltration (RBI) process increased the relative density of the samples to 42.5%. **Figure 1b** shows an interparticle contact in a sample that was treated with TALH. TiO_2 derived from the decomposition of the TALH is evident as a coating covering the particle surfaces. **Figure 1b** further shows that the TiO_2 coating partially fills the neck between particles. These observations suggest that the TiO_2 nanostructures could serve as a secondary binding agent that strengthens printed parts during and following binder burnout.