

Digital Light Processing of ceria-stabilized zirconia and Ce-ZrO₂/Al₂O₃/SrAl₁₂O₁₉ composites: role of powder pre-treatment on printability and physico-mechanical properties

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Abstract

This study focuses on the elaboration of ceria-stabilized zirconia (Ce-TZP) ceramics by Digital Light Processing (DLP), with the aim of deepening the role of the ceramic powder features on the different steps involved in the process and then transmit this acquired knowledge on Ce-TZP-based composites. Therefore, commercial Ce-TZP powders were submitted to mechanical and thermal pre-treatments, to investigate the impact of surface and structural modifications of the powders on the slurry printability, as well as on the sintered density, microstructure and mechanical behaviour.

Ball milling effectively reduced the size of micron-scale agglomerates in the un-milled batch, resulting in a loosely dispersed ultrafine powder. However, the mechanical treatment increased the monoclinic zirconia phase content and induced the appearance of oxygen vacancies, likely due to the partial reduction of cerium from its tetravalent to trivalent state. The presence of surface oxygen vacancies, combined with certain ceria segregation on the zirconia surface, led to increased UV absorbance, thereby hindering effective photopolymerization of the slurries. The subsequent calcination step successfully restored the tetravalent oxidation state enabling the production of nearly defect-free samples.

For the optimized material, the best sintering conditions were identified as 1350 °C for 0.5 h, yielding a dense ceramic with a fine microstructure ($0.60 \pm 0.23 \mu\text{m}$, Figure 1a) and a low monoclinic phase content, resulting in a remarkably high flexural strength ($561 \pm 15 \text{ MPa}$).

On the ground of the preliminary results achieved on the monophasic Ce-TZP, it was possible to develop a triphasic composite powder comprising 8 vol% $\alpha\text{-Al}_2\text{O}_3$ and 8 vol% SrAl₁₂O₁₉, to be successfully used in the DLP process. Sintered samples (1h at 1500 °C) achieved an Archimedes' density of $97.9 \pm 0.3 \text{ \%TD}$ and a flexural strength equal to $465 \pm 26 \text{ MPa}$. FESEM observations confirmed the expected finer microstructure compared to the monophasic composition sintered at the same temperature (Figure 1b) with a good distribution and dispersion of the three phases (Figure 1c).

Finally, an endosseous dental implant (Figure 2a) was selected as representative prototype to demonstrate the high accuracy and printing resolution of the triphasic ceria-stabilized zirconia composite (Figure 2b-c).

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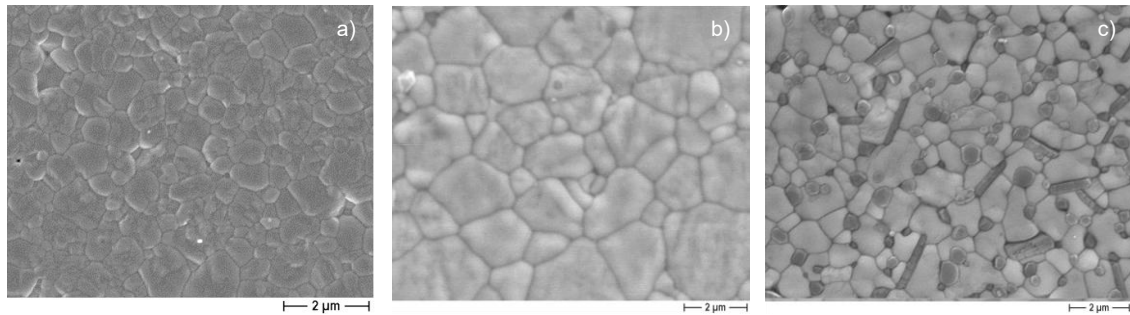


Figure 1. FESEM micrographs of 3D printed samples, a) and b) monophasic sintered 0.5 h at 1350 °C and 1 h at 1500 °C, respectively; c) triphasic sintered 1 h at 1500 °C

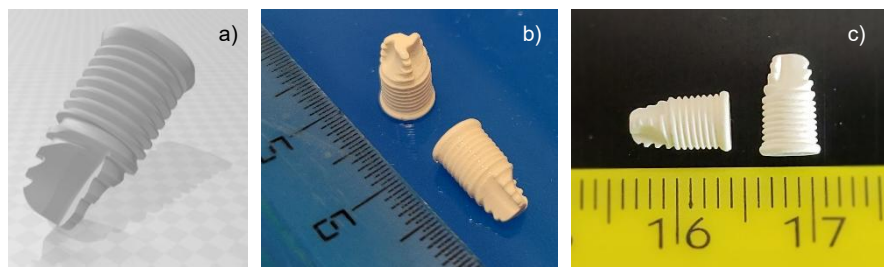


Figure 2. a) CAD model, b) triphasic as-printed sample and c) sintered at 1500 °C for 1 h