Abstract

The aim of this PhD work is to explore and develop printable slurries via DLP (Digital Light Processing) Stereolithography having, as a ceramic matrix, a biphasic($Ce_{11}ZA_{16}$) or triphasic ($Ce_{11}ZA_{8}Sr_{8}$) composite powder in the zirconia-alumina system. A powder engineering strategy made possible the tailoring of the composition, the microstructure, and the features of the final materials. The methodological approach taken allowed the exploitation of the high potentiality ofthe Ce-TZP composites to explore the feasibility of obtaining printable formulations for complex composition ceramics, while maintaining the morphological and microstructural characteristics that characterize such composites when obtained by conventional shaping methods, thanks to the high- resolution offered by the stereolithographic additive manufacturing technique.Extensive research in the field of stereolithography has been carried out, but it is evident the paucity of publications on Ce-TZP composites. Thus, filling the gap in the previously published studies was one of the objectives of this research joining the outstanding aging resistance of the material to the extremely high dimensional resolution of DLP-stereolithography, laying the groundwork for future biomedicalapplication.

In the first chapter, through detailed bibliographic research, the state-of-the-art of zirconia-alumina composites obtained by additive manufacturing methods was developed, paying particular attention to the DLP-stereolithography. The first part of the chapter deals with the transformation toughening proper of zirconia and the beneficial effect of alumina addition in the powder composition and the advantageous influence of the ceria in the aging resistance of zirconia. The secondpart is focused on the DLP-stereolithography features of the printable slurries, the resin, and on the removal of the organic fraction for the consolidation of the parts through debinding and sintering.

The second chapter deals with the elaboration process of $Ce_{11}ZA_{16}$ composite powders demonstrating an optimum control of the entire process. The raw powders'dispersion with the addition of the suitable dispersant (Disperbyk-103 in our case) and the proper ball milling time allows the preparation of homogeneous slurries obtaining outstanding microstructures of the fired parts.

The third chapter shows the elaboration process of $CeZA_8Sr_8$ via surface modification of a zirconia-based composite powder with inorganic precursors of the secondary phases. The final formulation contains 8 vol% of alumina and 8 vol%of an aluminate phase. The adopted approach such as the powder dispersion, addition of the dopants, spray drying, and the thermal treatments for the decomposition of the nitrates guarantees to the final composite powder to be uniformly dispersed in the acrylic resin and printed at the end. Highly dense sinteredparts were then obtained.

The fourth chapter is dedicated to the development and characterization of slurriesprintable with DLP-stereolithography. The slurries without and after the addition of the dispersant were characterized from the point of view of the rheology, while the effect of the solid loading and the amount of dispersant on the slurry behaviourwere investigated, and the characteristics of the printed parts. In the closing sectionof the chapter the printing process parameters, and their correlations, were studied through the Principal Components Analysis (PCA).

In the last part of the thesis, the main results of a full description of the printed partsin terms of phase composition, microstructure, and mechanical characterization of the hardness and fracture strength are presented. The adopted procedure for the preparation of the powders and the slurries was successful in developing composites having highly homogeneous microstructures. Particularly, in the $Ce_{11}ZA_8Sr_8$ acomplex microstructure was obtained with an excellent distribution of the round- shaped alumina and elongated strontium aluminate grains, as secondary phases, inside the fine zirconia matrix. A strong influence of the printing parameters and the debinding cycle on the microstructure and on the mechanical features was revealed.