



UNIVERSITY OF
BIRMINGHAM

**MATERIAL DEVELOPMENT AND PROCESS
OPTIMISATION FOR DIGITAL LIGHT
PROCESSING OF TRANSLUCENT ALUMINA**

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ABSTRACT

In the last decade, the urge to conduct additional research on viable production approaches for advanced ceramics has been arising in order to fully leverage the promise of ceramic materials and connect their distinctive thermomechanical capabilities with increased advanced features. It has been widely proven that Additive Manufacturing (AM) is a technology that is capable of integrating geometrical complexity and precision with fine microstructure and improved mechanical qualities while eliminating concerns about tool accessibility and reducing the costs associated with production assets. As a result, the ability to produce optimised components with extremely complicated geometries via AM, while simultaneously guaranteeing high standards of thermomechanical characteristics and delivering additional capabilities, has been a topic of significant interest among academics and businesses. In particular, Digital Light Processing (DLP) has been demonstrating the potential to rapidly manufacture intricate components suitable for a wide range of technological applications.

In this research, the production, formulation and optimisation of a slurry with high flowability as well as broad DLP printability were set as the first targets of the investigation. Subsequently, the main focus was shifted towards the determination of the optimal parameters for the fabrication of green ceramic samples that incorporated advanced characteristics. A photosensitive slurry with a high concentration of alumina particles and appropriate rheological properties was successfully formulated adopting a full-factorial design of experiments (DoE) and the influence of printing settings on the density and dimensions of the green samples was investigated. Afterwards, thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were employed to determine the optimal thermal debinding parameters. Upon examination of various debinding regimes, the debinding heat rate of 0.2 °C/min and increased dwell times contributed to reducing defects and enhancing densification. Samples

exhibiting a relative density higher than 99.0% and displaying translucent characteristics were fabricated by adopting a rapid high-temperature sintering cycle.

Furthermore, since the post-processing of AMed ceramic components has been demonstrated to be crucial to enhance the geometrical accuracy and mechanical properties of the finished product, especially the resulting density, numerical modelling was used to further optimise the sintering parameters and support experiments design. A thermo-viscoelastic model of the sintering process was formulated and validated against experimental data. The experimental findings and simulation results exhibited a discrepancy of less than 2% and, therefore, the numerical model demonstrated the potential to accurately forecast the characteristics of sintered alumina ceramics manufactured using DLP.

In addition, the effect of additives and different sintering regimes was investigated to further improve the translucency level of the produced samples. Magnesia and magnesium aluminate were incorporated into the ceramic slurry formulation and samples were sintered at different heating rates, dwelling times and sintering atmospheres. Finally, fine-grained translucent alumina discs sintered in air and exhibiting a maximum total transmittance of 90.4% and a maximum Real In-line Transmittance (RIT) of 16.9% in the visible and near-infrared regions were successfully fabricated.

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*To my wife Rosanna,
to my daughter Vittoria
and to whomever I will be blessed
to welcome as part of my beloved family*

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LIST OF ABBREVIATIONS

3DP	Three-Dimensional Printing
a	Radius of the interparticle boundary
A	Absorption coefficient
A_d	Attenuation coefficient
AlON	Aluminium oxynitride
Al_2O_3	Aluminium oxide (or Alumina)
AM	Additive Manufacturing
ANOVA	Analysis of Variance
ASM	Advanced Structured Material
BET	Brunauer-Emmett-Teller
BJT	Binder Jetting
BM	Ball milling
B_2O_3	Boron oxide
BPR	Ball to Powder Ratio
c	Speed of light in vacuum
CAD	Computer Aided Design
CaO	Calcium oxide
C_d	Cure depth
CIP	Cold Isostatic Pressing
COD	Crystallography Open Database
d	Thickness
D	Diameter
D50	Mean particle size
D_{eff}	Effective grain boundary coefficient
DED	Direct Energy Deposition
D_{gb}	Grain boundary diffusion coefficient
DIW	Direct Ink Writing
DLP	Digital Light Processing (or Process)
DMD	Digital Micromirror Device
DOD	Drop-On-Demand
DoE	Design of Experiments
D_p	Penetration depth
DSC	Differential Scanning Calorimetry
E	Energy dose
E_c	Critical energy dose
EP	Exposure Power
ET	Exposure Time
Eu_2O_3	Europium oxide

FE	Finite Element
Fe_2O_3	Iron oxide
FDM	Fusion Deposition Modelling
FEM	Finite Element Model (or Modelling)
FFF	Fused Filament Fabrication
F_n	Normal force
G	Average grain dimension
G_0	Initial average grain dimension
HIP	Hot Isostatic Pressing
HP	Hot Pressing
HTP	High-Test Peroxide
IJP	InkJet Printing
K	Grain growth time coefficient
K_0	Material-dependent grain growth constant
k_B	Boltzmann constant
La_2O_3	Lanthanum Oxide
LCM	Lithography-based Ceramic Manufacturing
LOM	Laminated Object Manufacturing
LT	Layer Thickness
MEX	Material Extrusion
MgAl_2O_4	Magnesium aluminate spinel
MgO	Magnesium oxide (or Magnesite)
MJT	Material Jetting
MnO	Manganese oxide
MSLA	Masked Stereolithography
n	Refractive index
Na_2O	Sodium oxide
NH_4	Ammonium
NIR	Near-Infrared
p	Hydrostatic pressure
PBF	Powder Bed Fusion
PCC	Polycrystalline Ceramic
PCA	Polycrystalline Alumina
P_L	Laplace pressure
PMAA	Poly(methacrylic acid)
PSA	Particle Size Analysis
$\tilde{q}$	Deviatoric stress
Q	Grain growth activation energy
Q_v	Viscous flow activation energy
r	Single particle radius
r_0	Single particle radius at room temperature
R	Universal gas constant

R_s	Refraction losses at the outer surfaces
RIT	Real In-line Transmittance (or Transmission)
S	Scattering coefficient
Sc_2O_3	Scandium oxide
SEM	Scanning Electron Microscopy
SHL	Sheet Lamination
SiC	Silicon carbide
Si_3N_4	Silicon nitride
SiO_2	Silicon oxide
SL	Stereolithography
SLA	Stereolithography Apparatus
SLM	Selective Laser Melting
SLS	Selective Laser Sintering
SMA	Shape Memory Alloy
SMC	Shape Memory Ceramic
SME	Shap Memory Effect
SPS	Spark Plasma Sintering
STL	Standard Tessellation Language
T	Temperature
T_0	Room temperature
T_e	Eutectic temperature
T_g	Glass transition temperature
TG	Thermogravimetric
TGA	Thermogravimetric analysis
TIR	Total Internal Refraction
TPO	Diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide
TPP	Two-Photon Polymerisation
UV	Ultraviolet
v	Speed of light through a medium
VIS	Visible
V_{pores}	Pores volume
VPP	Vat Photopolymerisaion
V_{total}	Total volume
v_{rn}	Normal relative velocity
XRD	X-Ray Diffraction
YAG	Yttrium Aluminate Garnet
YAM	Yttrium Aluminate Monoclinic
Y_2O_3	Yttrium oxide (or Ytria)
$\text{Y}_3\text{Al}_5\text{O}_{12}$	Yttrium aluminate
YSZ	Ytria-Stabilised Zirconia
ZrO_2	Zirconium oxide (or Zirconia)
α	Thermal expansion coefficient

β	Powder morphology related parameter
$\alpha\text{-Al}_2\text{O}_3$	Alfa alumina
δ	Grain boundary width
$\dot{\gamma}$	Shear strain rate
γ_s	Surface energy
$\dot{\epsilon}$	Total strain rate
$\dot{\epsilon}^e$	Elastic strain rate
$\dot{\epsilon}^{th}$	Thermal strain rate
$\dot{\epsilon}^{visc}$	Viscous strain rate
η	Apparent viscosity
η_0	Material-dependent viscous constant
η_b	Viscous bulk modulus
η_d	Dynamical shear viscosity
η_s	Viscous shear modulus
θ	Porosity fraction
λ	Wavelength
λ_0	Wavelength in vacuum
ρ	Relative density
$\hat{\rho}$	Initial relative density
$\dot{\sigma}$	Stress rate
σ'	Deviatoric stress tensor
$\dot{\sigma}^s$	Sintering stress rate
τ	Shear stress
φ	Effective shear modulus coefficient
ψ	Effective bulk modulus coefficient
φ_c	Dispersed ceramic volume fraction
Ψ	Dihedral angle
Ω	Atomic volume

LIST OF PUBLICATIONS AND PRESENTATIONS

The following publications and conference presentations are a result of the investigations carried out during the fulfilment of the PhD research and parallelly conducted collaborations.

Journal article publications

- De Lisi, M.; Kovacev, N.; Attia, U.M.; Essa, K. Numerical Simulation of Sintering of DLP Printed Alumina Ceramics. *Aerospace*. 2022, 9, 336. <https://doi.org/10.3390/aerospace9070336>.
- De Lisi, M.; Shu, C.; Attia, U.M.; Essa, K. DLP of Translucent Alumina: In-Depth Investigation on Slurry Development and Debinding Regimes. *Machines*. 2023, 11, 321. <https://doi.org/10.3390/machines11030321>.
- De Lisi, M.; Careri, F.; Attia, U.M.; Essa, K. Effect of different additives and sintering regimes on the optical properties of DLP printed translucent alumina. *Ceram. Int.* 2024. <https://doi.org/10.1016/j.ceramint.2024.04.348>.
- Shu, C.; Chen, S.; Zheng, Z.; Lu, X.; Li, W.; De Lisi, M.; Bidare, P.; Shu, X.; Essa, K. Fabrication and strengthening mechanism of crack-free nano-TiC reinforced IN738LC with enhanced mechanical properties by laser powder bed fusion. *J. Mater. Res. Technol.* 2023, 27, 3835–3848. <https://doi.org/10.1016/j.jmrt.2023.10.283>.
- Almadani, M.; Guner, A.; Hassanin, H.; De Lisi, M.; Essa, K. Contactless single point incremental forming: Experimental and numerical simulation. *Int. J. Adv. Manuf. Technol.* 2023, 129, 5167–5179. <https://doi.org/10.1007/s00170-023-12401-1>.

Conference presentations

- De Lisi, M.; Essa, K. 4D printing of smart ceramic structures, Manufacturing Technology Centre PhD Conference, Coventry, United Kingdom, 2021.
- De Lisi, M.; Kovacev, N.; Attia, U.; Essa, K. Numerical simulation of sintering of DLP printed alumina ceramics. ASTM International Conference on Additive Manufacturing; California; USA; 2021.

CHAPTER 1. INTRODUCTION

Optical transparent materials conventionally comprise polymers, alkali hydrides and glasses and have found extensive applications in both industrial and everyday settings. Nonetheless, these materials possess comparatively inadequate mechanical strengths and, at times, insufficient chemical and physical stabilities. Relevantly, conventional transparent materials exhibit a high degree of absorption in the infrared spectrum [1], rendering them unsuitable for utilisation within applications operating within this particular spectral range. In addition, it is noteworthy that these materials typically demonstrate comparatively diminished melting points, below 600°C, thereby limiting their utility in high-temperature applications. Some transparent materials can change their optical properties with temperature fluctuations or exposure to environmental factors such as humidity and UV radiation. This can lead to variations in performance over time [2]. Consequently, there is a need to create stable transparent materials suitable for deployment in severe and challenging conditions. Although not easily fabricated through conventional manufacturing routes, components made of ceramic materials are able to meet both the optical and thermomechanical requirements that harsh environments present, proving to be reliable candidates in multiple fields of applications, from military to electronics [3]. The capability of additively manufacturing translucent ceramic components would effectively provide a novel degree of geometrical flexibility in the production of complex translucent structures with significant thermomechanical and corrosion resistance, overcoming the difficulties of conventional manufacturing and, in turn, reducing associated costs.

1.1 Background

1.1.1 General overview of Additive Manufacturing working principle

The concept of Additive Manufacturing (AM) refers to a relatively new production process capable of constructing exceedingly complex items in terms of geometry and characteristics that are unreachable using normal manufacturing procedures. AM makes use of the concept of making a three-dimensional object by successively adding adjacent two-dimensional layers of material until the product has been completely shaped (Figure 1.1).

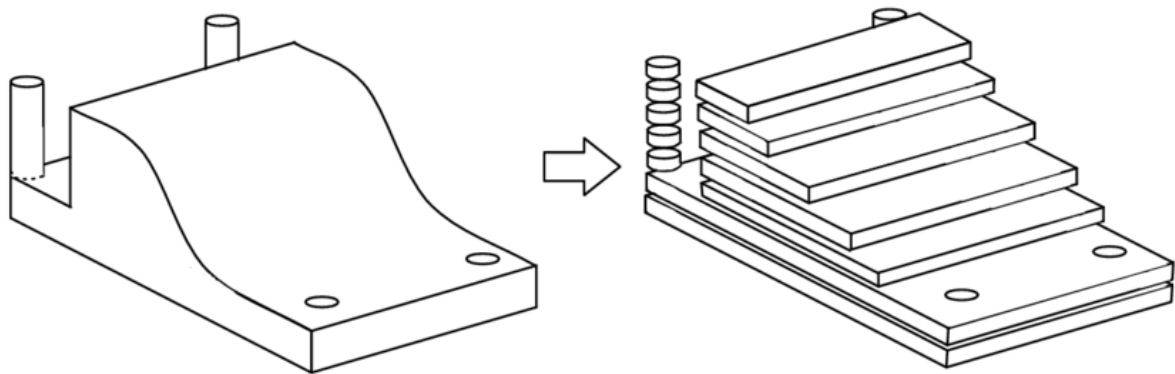


Figure 1.1 - Sketch of the 3D model slicing procedure into additively manufactured layers [4].

This fabrication process is in contrast to traditional manufacturing methods, which shape objects by removing material in order to achieve the desired final geometry. As a consequence, tools aren't necessary, issues about accessibility are avoided and the geometrical complexity is simply limited by the product designer's creativity, who can take advantage of a bigger workability window. Extensive research has been conducted to investigate and optimise the capabilities of additive manufacturing since its earliest experiments and implementations in the

late 1950s to adapt additive manufacturing to a variety of materials and applications [5]. As a direct result of this enhanced collaboration between academics and corporate research and development teams, substantial strides have been achieved toward the commercial implementation of additive manufacturing. As this sector was in continuous expansion, several new manufacturing processes were developed and the range of materials that could be used widened, including polymers, metals and, subsequently, ceramics. Among these, the Digital Light Processing (DLP) technique for ceramic 3D printing was presented as one of the more modernised, more effective and faster production approaches (Figure 1.2).

Figure 1.2 - Schematic of a DLP machine with foil transportation system [6].

As a consequence of the relevant progress made in the AM field, the idea of fabricating advanced materials exploiting the advantages of AM has been attracting increasing research interest. In fact, the possibility of 3D printing materials with complex structures and geometries

able to systematically respond within a predefined amount of time to external stimuli in different ways, such as being transparent to certain wavelengths, changing shape, colour, structure or initiating chemical reactions, defined a specific niche named as 4D printing [7,8]. However, there is currently a lack of specified criteria for the production and optimisation of advanced materials in the field of Additive Manufacturing. Nevertheless, the prospects of employing AM techniques for the fabrication of advanced materials are highly appealing. Advanced ceramics have the potential to be utilised in a variety of applications, such as controlled camouflage textiles, personalised medicines that respond to the values of body chemicals, programmable one-of-a-kind biological materials and temperature-responsive safety actuators.

In particular, transparent polycrystalline ceramics are versatile, finding utility in a range of fields including but not limited to laser systems, protective armaments and illumination devices. Nonetheless, polycrystalline ceramics have the advantageous characteristic of being capable of large-scale production, rendering them an appealing choice for the development of high-power lasers with tailored specialised capabilities and potentially resulting in cost-effective commercial manufacturing. Additionally, these materials possess the ability to serve as gain media for fibre lasers exhibiting superior beam quality ($M^2 < 2$, where M^2 is a quality factor measuring the degree of divergence of a beam from an ideal Gaussian beam where $M^2 = 1$) and media efficiency ($\eta > 55\%$), even when compared to single crystal ceramics ($\eta \sim 55\%$) in certain instances. They may also be utilised as composite laser media, enabling the creation of intricate structures that would otherwise pose challenges in fabrication when employing single crystals. Their exceptional compressive strength and hardness (> 8 on the Mohs scale) have rendered them viable candidates for substituting ballistic glasses in transparent armour applications. For example, alumina can tolerate compressive stresses of 3GPa and is nearly

three times harder than steel and second in hardness on the Mohs scale only to diamond and a few other ceramic carbides and borides. In fact, spinel or magnesium aluminate (MgAl_2O_4), aluminium oxynitride (AlON), and sapphire (Al_2O_3) have proved to have comparable performance characteristics to conventional armour glasses, if not superior. Finally, transparent ceramic materials with suitable thermal and mechanical characteristics are highly advantageous when employed as enclosures for focused-beam, short-arc lamps that incorporate diverse fillers and operate at very high temperatures. For almost a century, transparent polycrystalline alumina ceramics with a coarse grain structure have indeed been employed as protective coverings in discharge lamps [3].

While transparent glasses, alkali hydrides, and polymers generally possess low mechanical strengths and low melting temperatures, may lack necessary chemical and physical stabilities and be significantly affected by investigated wavelengths, operational temperatures and environmental conditions, transparent polycrystalline ceramics offer the potential to be adopted even in harsh environments while maintaining their exceptional chemical and thermophysical properties, improving on the performances of other transparent candidate conventional materials in the same application. However, even though the DLP of transparent ceramics is attractive, it comes with challenges. The porosity of ceramics is the primary determinant of their transparency. The interface of a pore delineates the separation between phases exhibiting distinct optical properties, resulting in increased light scattering and, thus, the opacity of ceramics can be attributed to the abundance of intergranular and intragranular pores. The removal of the latter, even those of submicron dimensions, is a greater challenge and requires more effort compared to the eradication of closed intergranular pores, which are situated at the borders between grains, serving as sites for vacancy accumulation and facilitating their removal. When there are variations in attributes between grains and grain boundaries, their

interfaces will promote light scattering. In order to ensure transparency, it is imperative to minimise the discrepancy in optical characteristics between individual grains and grain borders. In fact, the prevailing cause of opacity in most cases is the occurrence of a secondary phase at the borders of grains. Therefore, in order to produce translucent and transparent ceramics, raw materials with a high degree of purity and meticulously preventing any potential contamination throughout the manufacturing stages are of relevant importance. Finally, the transparency of a ceramic sample can also be influenced by exterior factors such as its thickness and surface polish. A surface that is rough can promote significant light scattering, thus it is desirable for the sample to possess a high degree of surface smoothness and lower values of thickness since the number of defects increases with the increased amount of grain layers through which wavelengths have to propagate.

1.2 Motivation

Due to its wide employability and geometric versatility, AM has found applications in a vast range of fields, ranging from military and aeronautical to biomechanical and advanced electronics as well as tissue engineering. Although metallic alloys and polymers applications to 3D printing of advanced or smart structures have been fairly investigated in the literature [9–12], only very few studies have been done on 3D printing of transparent ceramic structures [13]. Furthermore, transparent ceramics provide several benefits compared to single crystals. These advantages include a greater doping concentration, reduced processing time, cheaper manufacturing costs and the ability to be produced on a bigger scale. Nevertheless, the fabrication of translucent ceramics poses challenges and necessitates the use of machining techniques. Ceramic shaping is commonly conducted at the green body processing stage by

techniques, typically powder pressing or slurry casting, which include the utilisation of moulds [14–16]. In order to mitigate the expenses associated with moulds and cater to the increasing need for personalised manufacturing within the industry, AM production of transparent ceramics would be beneficial. The Direct Ink Writing (DIW) approach has been the foundation for the majority of successful demonstrations [17]. This technique employs material extrusion to fabricate ceramics with a 3D structure, offering the notable benefit of being applicable to various materials. Nevertheless, the DIW approach has a drawback in terms of inadequate printing resolution, hence imposing restrictions on its applicability to relatively uncomplicated printing geometries.

On the other hand, when comparing different methods, it is evident that lithography-based 3D ceramic printing, which utilises photon-initiated polymerisation, has superior capabilities in terms of printing resolution and obtainable mechanical strength. This possibility enables the fabrication of intricate structures with enhanced support. The Stereolithographic (SLA) and Digital Light Processing techniques are extensively researched lithography-based 3D printing technologies that are often employed in the production of high-density ceramics. However, very little research has been conducted on the DLP of translucent ceramics [18], which exhibits significant industrial scalability. Therefore, further investigations are deemed to be necessary to fully exploit DLP printing capabilities and translucent ceramics properties, especially their unique thermal and chemical stability and high-temperature resistance. Exploring DLP workability and applicability windows to advanced materials will promote its adoption and facilitate its application, especially in those fields where enhanced mechanical properties are combined with relevant geometrical complexity.

1.3 Research aim and objectives

This research project aims to assess the feasibility of using the Digital Light Processing manufacturing technique as an Additive Manufacturing route to produce translucent ceramic components. In particular, the project is focused on the fabrication of translucent alumina parts.

To achieve the aforementioned purpose, the following objectives will be met:

- To examine and simulate numerically via Finite Element Modelling (FEM) the sintering processes of Al_2O_3 to understand process material interactions and, upon model validation, reliably predict post-processing results to programme tailored experiments for obtaining the desired final properties
- To develop in-house ceramic slurries formulations compatible with DLP, based on Al_2O_3 powder in the sub-micron range. Once feasible mixtures have been created and assessed, the main aim will be to optimise the slurry formulation procedure by varying process parameters and conditions.
- To investigate and optimise the impact of various process factors in the DLP additive manufacturing technique, especially layer thickness (LT), exposure power (EP) and exposure time (ET), on the dimensional accuracy and density of the produced samples to achieve high packing levels in the green parts.
- To investigate the influence of different sintering additives on the densification process and the final part optical properties, while assessing the effect of heating rates, holding temperatures and dwell time on the microstructure evolution of the additively manufactured parts.
- To fabricate lightweight translucent ceramic cylindrical demonstrators via DLP.

1.4 Thesis structure

The first chapter introduces the reader to the research topic and describes the motivation behind the effort. Furthermore, this section introduces the project, together with its goals, objectives and thesis structure.

The second chapter examines the state of the art in the primary research fields on which this thesis is based, including ceramic additive manufacturing and photopolymerisable ceramic slurries, numerical modelling of ceramic sintering processes and developments in the fabrication of advanced ceramics and their applications.

The third chapter analyses the influence of printing patterns and sintering parameters such as dwelling time and holding temperature on the final properties of sintered alumina samples in terms of dimensions and geometry. A finite element model is also developed and validated against experimental results obtained from alumina cylindrical samples. The geometrical dimensions and the densities of the alumina cylinders were evaluated at the green, brown and fired stages and the results when the axial direction was parallel or perpendicular to the building direction were compared and investigated. Furthermore, the effect of the principal sintering parameters on final geometric properties, shrinkage and density was studied using numerical simulations.

The fourth chapter reviews photopolymerisable ceramic slurry preparation procedures in order to acquire adequate rheology and curing conditions for usage in DLP additive manufacturing to produce translucent ceramic structures. The effects of ball milling parameters, slurry composition, layer thickness, exposure power and exposure time on the density, dimensional accuracy and integrity of the printed samples were investigated using statistical methods, including a full-factorial Design of Experiment (DoE) and Analysis of Variance

(ANOVA). The ideal processing window was determined by a methodical examination of printing factors. In addition, alternative debinding regimes were investigated in order to determine the ideal conditions for maintaining sample integrity and preventing undesirable fractures that could impair the samples ultimate translucency. After determining the ideal parameters from the previous experiments, additional samples were produced using sintering aids and, with the newly established optimal approach, translucent samples were produced.

The fifth chapter provides analyses of the effect of various sintering regimes and different sintering aids on the final optical properties of the fired sample fabricated adopting the DLP process. Various heating rates, holding times and sintering atmosphere were tested as well as the use of two distinct additives, MgO and MgAl_2O_4 . Upon examination of the physical, crystallographic and optical properties of the fabricated sample discs, the optimal post-processing conditions were evaluated and the improved transmittance properties were assessed.

Lastly, the sixth and final chapter presents a broad conclusion to the thesis, which serves as a summary, providing the major results from each chapter, followed by recommendations for the current work future development.

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CHAPTER 2. LITERATURE REVIEW

This chapter commences by providing an introductory overview of Additive Manufacturing techniques. It delineates the fundamental process characteristics, performance limitations, challenges and recent advances in the field aimed at overcoming these challenges. Subsequently, it conducts a thorough examination of techniques pertaining to ceramic additive manufacturing, with a specific focus on photopolymerisable ceramic slurries. This scrutiny encompasses an exploration of the current process design aspects and the additive manufacturing of ceramic structures. Following this, the chapter delves into the categorisation of smart and advanced ceramics, with particular regard to the analysis of translucent and transparent ceramics. Afterwards, a brief but exhaustive review of the current state of numerical modelling in the sintering process of ceramics is presented. In this section, attention is directed toward elucidating the underlying assumptions and constraints associated with various models. Moreover, this segment underscores the selection of the most appropriate models to be employed in the context of this research, aligning it with its intended objectives. Lastly, the chapter provides a concise summary of the research scope and its contribution to the ongoing advancement of state-of-the-art knowledge in the field.

2.1 Ceramics Additive Manufacturing Overview

AM offers several advantages, including cost-effective component manufacturing by reducing lead times and materials wastage, eliminating tooling expenses and increasing production flexibility. In the additive manufacturing industry, plastics and metals are the predominant materials due to their favourable processing and post-processing capabilities.

However, recent research has extensively explored the AM of ceramic materials, opening up new possibilities for creating intricate ceramic components for various industrial applications [1]. Since the creation of complex three-dimensional objects through the successive addition of adjacent two-dimensional layers has been demonstrated as a viable and effectively applicable method across a wide spectrum of applications, additive manufacturing has garnered significant attention for its capacity to produce components that are either net shape or nearly net shape. In fact, AM techniques have the ability to replicate fine geometric details and structural features that are typically unattainable through conventional manufacturing methods, often leading to enhanced mechanical performance and characteristics. Based on whether the AM process is carried out in a single step (Direct AM or Single-step AM) or in a multi-step approach which usually includes thermal postprocessing (Indirect AM or Multi-step AM) depending on the material and according to the ISO/ASTM 52900-21 standard, the AM process categories can generally be classified as reported below in Table 2.1.

Table 2.1 - AM process categories according to the ISO/ASTM 52900-21 standard.

Process category	Related AM technology	Direct / Indirect
Binder Jetting (BJT)	Binder Jetting	Direct or Indirect
	Three-Dimensional Printing	
Direct Energy Deposition (DED)	Laser Metal Deposition	Direct
	Laser Engineering Net Shaping	
Material Extrusion (MEX)	Fused Filament Fabrication	Indirect
	Direct Ink Writing	
Material Jetting (MJT)	Multi-jet Modelling	Indirect
	InkJet Printing	

Powder Bed Fusion (PBF)	Electron Beam Melting	Direct
	Selective Laser Melting	
	Selective Laser Sintering	
	Direct Metal Laser Sintering	
Sheet Lamination (SHL)	Laminated Object Manufacturing	Direct or Indirect
	Ultrasonic Additive Manufacturing	
Vat Photopolymerisation (VPP)	Stereolithography	Indirect
	Digital Light Processing	
	Two-Photon Polymerisation	
	Photopolymer Jetting	
	Continuous Liquid Interface Production	

Furthermore, novel hybrid AM approaches have recently emerged, which integrate both additive manufacturing and in-situ machining. The aforementioned method has demonstrated the potential to create alumina components that are virtually completely dense, exhibiting a substantially enhanced surface polish when compared to identical components produced without the utilisation of subtracting manufacturing processes [2,3]. In addition, combinations of different additive manufacturing processes are increasingly becoming a topic of interest. Simultaneously combining the advantages of various AM techniques in a symbiotic relationship while accurately removing their undesired countereffects is gaining attention among researchers [4].

According to Chen and colleagues [5], ceramic-based 3D printing processes can be also broadly classified based on the physical form of the base material employed and, in particular, they can be categorised into bulk solid-based, powder-based and slurry-based technologies (Table 2.2). The subsequent section will provide a brief overview of available ceramic AM methods, which are ultimately different in terms of printing resolution, accuracy, final quality

and product density as well as manufacturing speed [5,6]. A more comprehensive examination of Digital Light Processing Technology, which has been adopted as the primary AM process in this investigation, will follow.

Table 2.2 - Ceramic 3D printing technologies [5].

Feedstock form	Ceramic 3D printing technology	Direct / Indirect	Abbreviation
Slurry-based	Stereolithography	Indirect	SL
	Digital Light Processing	Indirect	DLP
	Two-Photon Polymerisation	Indirect	TPP
	InkJet Printing	Indirect	IJP
	Direct Ink Writing	Indirect	DIW
Powder-based	Three-Dimensional Printing	Indirect	3DP
	Selective Laser Sintering	Indirect	SLS
	Selective Laser Melting	Direct	SLM
Bulk solid-based	Laminated Object Manufacturing	Indirect	LOM
	Fused Deposition Modelling	Indirect	FDM

2.1.1 Bulk solid-based technologies

Fused Filament Fabrication (FFF) and Laminated Object Manufacturing (LOM) stand out as the most renowned methods within the realm of bulk solid-state manufacturing techniques. FFF, which received its first patent and became commercially available around 1989, and LOM, originally developed for applications involving plastics, metals and paper, were first put to the test on ceramic sheets composed of Al_2O_3 and ZrO_2 a few years later in 1994 by Griffin and colleagues [7,8]. In LOM, the procedure typically entails the utilisation of computer-controlled laser technology to cut thin sheets of materials into cross sections based on digital CAD models. These cut sheets are then adhered layer by layer, with each sheet coated with adhesive agents,

to create three-dimensional components. The process of achieving bonding and lamination between consecutive layers may be effectively carried out with the simultaneous application of heat and mechanical compression. In FFF instead, filaments of material are consistently provided and subjected to heating within a mobile nozzle. The temperature of the filament is maintained slightly higher than its melting point, thus facilitating its smooth extrusion through the nozzle to create successive layers. Upon the process of extrusion, the material undergoes rapid solidification, effectively forming a solid layer on the previously printed one. Similar to several other 3D printing methodologies, the platform is then lowered to facilitate the extrusion of the subsequent layer. The vertical dimensional resolution of the component is then dictated by the size of the nozzle [9].

While Fused Filament Fabrication for ceramics exhibits substantial versatility and is capable of effectively utilising filaments with high solid loading, reaching up to 60% in volume percentages, its limitations become apparent in terms of resolution along all axes. This issue is greatly influenced by the viscosity of the used material and the geometrical properties of the extruding nozzle. Tsang and Bhatia also observed that the FFF working principle itself leads to the creation of staircase defects and the formation of undesired anisotropic structures, both of which directly impact the final mechanical properties and surface quality of the manufactured part [10]. These constraints have restricted the use of FFF to applications where only minor dimensional accuracy is required, such as in general biomedical and tissue engineering applications.

On the other hand, LOM demonstrates its ability to effectively reduce or eliminate thermal stress-induced distortion and deformations due to its working principle. Nonetheless, limitations such as delamination caused by weak interlayer bonding, overall resolution, generally reduced surface quality which requires post-processing [11] and the specific

properties of the feedstock material have curtailed its applications and discouraged further exploration of its potential use with ceramic materials.

2.1.2 Powder-based techniques

Selective Laser Sintering (SLS), Selective Laser Melting (SLM) and Three-dimensional printing (3DP) are notable examples within the category of powder-based additive manufacturing techniques. While both SLS and SLM employ laser beams to consolidate powder beds, they differ in the crucial aspect that only SLS does not reach the material's melting temperature during the process. In contrast, 3DP is easily recognisable by its use of low-temperature binders that connect ceramic particles together to achieve the desired shape for the final product. In 3DP, the application of an organic binder solution in the form of droplets is achieved by spraying it through printheads onto specific areas of a surface consisting of a bed of powder particles. Solid layers are created by the process of solidification, wherein the penetrating liquid binder adheres to the powder and forms a cohesive structure. Subsequently, a further layer of powdered material is introduced and evenly distributed over the preceding stratum, initiating the iterative construction procedure until the desired component is fabricated. Afterwards, the loose powder is eliminated in order to expose the component. The primary drawbacks of 3DP include final limited surface finish, reduced density, generally weaker mechanical properties and notably, low dimensional resolution. However, since it offers a high degree of design flexibility and opportunities for experimentation, 3DP finds its primary applications in the realm of porous ceramics.

Conversely, SLS and SLM have the capability to fabricate nearly fully dense components, achieving higher levels of density and packing, along with significant mechanical strength, with

the latter being closely dependent on the properties of the feedstock material. In SLS, a high-power laser beam is employed to selectively expose the surface of the powder bed. Subsequently, the powder undergoes heating and sintering processes and then an additional coating of powder is applied onto the preexisting surface in preparation for the subsequent cycle of heating and sintering. This procedure is iteratively executed, with each layer being replicated until the desired three-dimensional component is successfully manufactured. On the other hand, in SLM, the materials melting temperature is locally reached and, hence, the joining process is achieved via the fusion of the powder particles without the use of secondary low-melting additives. Although Wilkes and co-workers and Deckers and colleagues demonstrated the feasibility of using SLM and SLS for ceramic materials [12–14], limitations such as porous microstructures caused by gas inclusions, resulting in low dimensional accuracy and poor surface quality, as well as issues related to high shrinkage and distortion, can hinder their application in high-value products and limit their industrial scalability.

2.1.3 Slurry-based processes

Stereolithography (SL), Digital Light Processing (DLP), Two-Photon Polymerisation (TPP), Inkjet Printing (IJP) and Direct Ink Writing (DIW) fall within the slurry-based macro-category of additive manufacturing technologies. IJP typically utilises low-viscosity inks in a drop-on-demand (DOD) mode, which are subsequently dried and sintered. On the other hand, SL, DLP and TPP rely on photopolymerisation reactions to create solid green parts that undergo conversion into brown parts following the debinding stage, culminating in sintering to produce the final products. For this category of slurry-based process, post-processing stages are particularly crucial as the complete removal of the organic components is significantly

challenging. Moreover, these methods are constrained in their applicability to a restricted selection of ceramic powders. For instance, the fabrication of ceramic materials with high refractive index is challenging due to the presence of considerable light scattering [15,16] and this phenomenon is particularly evident in oxide ceramics that do not exhibit a white colouration [17]. DIW, instead, employs nozzles to extrude high-solid-loaded slurries onto a building platform to determine the final component's geometry and shape. In comparison to the nozzles used in inkjet printing (IJP), the holes of the deposition nozzles need to be significantly bigger due to the increased viscosity of the materials employed in the deposition process. 3D parts are constructed by directing the nozzles in a manner that allows for the precise formation of each layer of the desired shape until the final item is fully fabricated. The droplet size and droplet-substrate interactions determine the possible feature size of a component [18]. Subsequently, debinding and sintering processes are carried out in order to eliminate any undesired component from the part.

Due to the adaptability of slurry-based technologies and their potential to produce virtually any desired geometrical feature or shape while maintaining good mechanical properties and surface finish, this macro-category has garnered interest from various audiences and has stimulated a wealth of studies in the literature. Like other AM processes belonging to different classes of techniques, slurry-based technologies do have their limitations, such as the consistent risk of nozzle clogging in IJP when very low solid loading is used, suboptimal density in the case of DIW and challenges like light scattering and refractive index mismatch in the case of photopolymerisation-based techniques. Nevertheless, slurry-based AM manufacturing remains the most extensively researched approach among ceramic AM methods [5].

In particular, DLP machines have proven to be easier to maintain compared to SLS, SLM or even SL machines. They are relatively cost-effective while ensuring optimal outcomes in

terms of accuracy, resolution, final density and mechanical performance. Jiang and co-workers also demonstrated that DLP offers higher accuracy for post-processed components compared to other slurry-based technologies, making it an attractive choice for AM ceramic parts and offering the best quality-to-cost ratio [19].

2.2 Digital Light Processing Overview

The stereolithography process is based on the photopolymerisation of a photocurable resin by irradiation with a laser beam, which provides the required energy to initiate the curing reaction and converts the liquid resin into a solid layer, resulting in a highly cross-linked polymer. Before Griffith and co-workers proposed to extend SL to ceramic materials by applying the resin curing technique to aqueous alumina and silica ceramic slurries in 1994 [20], SL was restricted to polymeric materials. On this occasion, SL-printed 3D ceramic components were successfully fabricated for the first time. While the first SLA machines were equipped with a UV laser beam source positioned above the building platform and the parts were then fabricated in a vat where an elevator moved the component down while being printed (top-down approach), following models allowed the laser source to be positioned at the bottom of the machine while the printed part was moved up by the worm screw mechanism (bottom-up approach) (Figure 2.1).

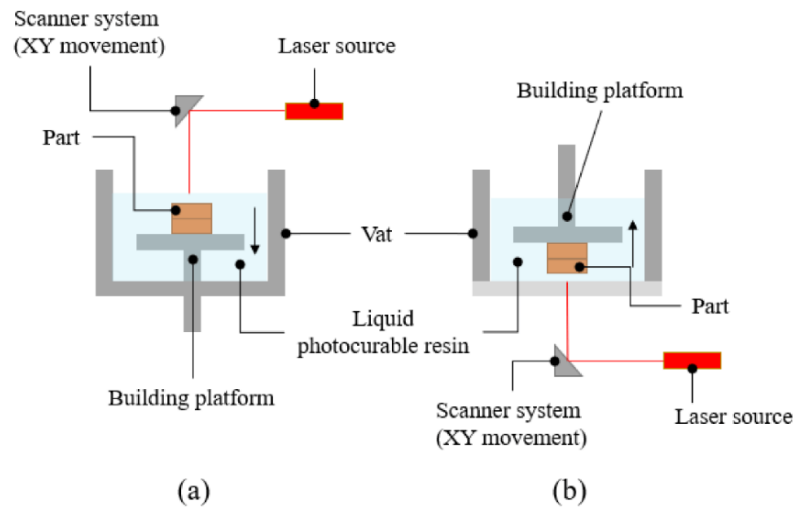


Figure 2.1 - Top-down (a) and bottom-up (b) approaches of SLA [21].

Following in-depth research and investigations, the process was able to evolve into a more mature version of itself and, as a consequence, the Digital Light Processing technique for ceramic 3D printing was established, representing a modernised, more time-efficient and effective production approach than SL. The primary difference between the two is the light source, with SL adopting a UV laser to expose the slurry to the light source curing along one line over time while DLP uses a projector screen with a Digital Micromirror Device (DMD) to cure a whole layer at once and offering faster print speeds. The printing resolution is then determined by the size of each mirror, which represents a single pixel of the picture [22]. The slurry transportation system evolved too in some instances, from being statically contained in a vat to being moved via a foil transportation system in order to reduce slurry usage, minimise waste and provide a better layer coating control. In fact, while vat-based SLA relies on slurry flowability to ensure a complete layer recoating, foil transportation systems ensure a consistent and stable supply of slurry for the entirety of the layer due to the shear action of a blade onto the slurry itself, distributing the slurry homogenously on the transported foil before curing. A schematic illustration of the DLP method on a foil transportation system is reported in Figure

2.2. A slight variation to DLP is Masked SLA (MSLA) where a light source, usually an LCD screen, is selectively covered or masked and, hence, only the desired cross-section of the part is cured.

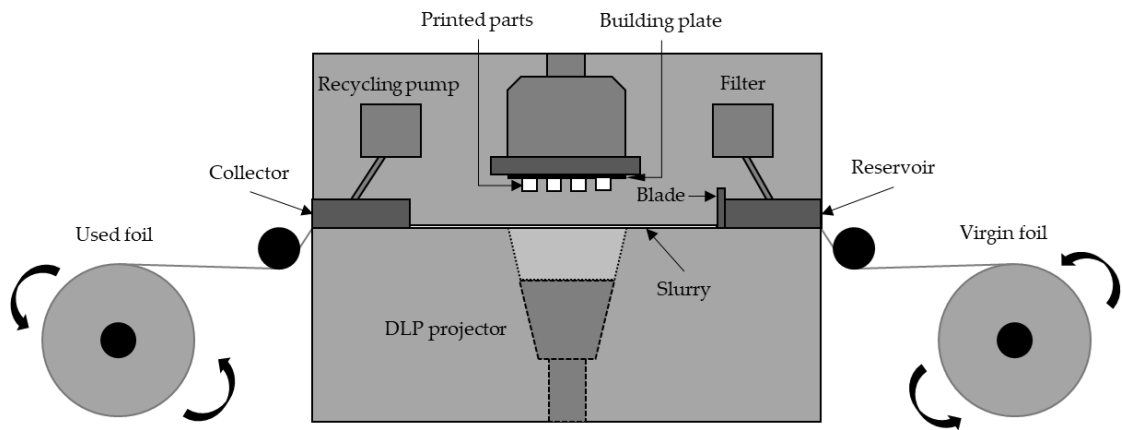


Figure 2.2 - Schematic of the DLP process based on a foil transportation system [23].

In DLP, similarly to other additive manufacturing techniques, the designed component is initially created using Computer-Aided Design (CAD) software and then converted into the Standard Tessellation Language (STL) format. Subsequently, the file is transmitted to the printing apparatus, whereupon the 3D model is transformed into a series of 2D pictures, each possessing a layer thickness that spans from 10 to 200 μm and representing a slice of the initial 3D model. The DLP procedure consists of projecting each picture layer onto a layer of photosensitive slurry, which undergoes hardening upon exposure to the light source. This iterative process is continued until the desired green body is achieved. After the completion of the green body shaping, the component is detached from the construction platform and undergoes a cleaning process to remove any remaining uncured slurry [24]. Subsequently, the part is debound and sintered in order to achieve the desired final density.

2.2.1 Effects of DLP printing conditions

In the digital light processing technique, a high-powered projector serves as the forming tool, selectively curing the slurry layer by layer until the 3D part is fully formed. Consequently, similarly to all processes relying on laser or light sources such as SL, DLP is susceptible to various failure modes associated with its operational principles and the power source. Failures can easily occur when the printing conditions are not adequately considered. Firstly, failing to allocate sufficient time for the initial layers to securely adhere to the building platform can lead to procedure failure as proper adhesion is crucial for the structural integrity of the final product. Secondly, the compatibility between the building platform and the material being processed must be carefully assessed since their incompatibility can result in poor outcomes as the material may not adhere as required. Moreover, choosing the incorrect exposure time can have adverse effects on the photopolymerisation process since an inaccurate exposure time or exposure power can cause problems such as undesired tension positive forces at the interface between the green part being built and the slurry [25]. In addition, accurate positioning of the light source is critical for precise curing as incorrect locating can lead to irregular curing patterns and compromised part quality. Finally, unforeseen viscosity effects can impact the photopolymerisation process and lead to inconsistent curing and defects in the final product. Overall, meticulous attention to these factors is essential to ensure the success of the DLP processing method and to mitigate the risk of procedure failures.

In terms of the placement of the light source, DLP printing may be classified into two primary methodologies: the top-down approach and the bottom-up technique. The former method necessitates a lengthier duration of exposure in order to produce intricately constructed parts, but allows a major flexibility in terms of shape and geometry designs without generating excessive stress in the fabrication of the part during the process. It also offers greater

reproducibility and is more suitable for porous components and photosensitive resins that necessitate higher energy inputs [26]. Conversely, the bottom-up method is capable of generating robust components in a shorter exposure time. This is achieved by preventing air exposure to the layer being printed, thereby inhibiting the oxygen from impeding the radical photopolymerisation reaction [27]. The use of the bottom-up strategy yields a more efficient methodology for handling large-sized components, as it affords greater precision in regulating both the thickness of each layer and the impact of viscosity on such thickness, delivering components with smoother surfaces, in contrast to the top-down approach. Additionally, the effective construction of the component necessitates a very modest quantity of photosensitive resin, as the housing vat might be half-filled. Nevertheless, it is important to acknowledge that there are some significant drawbacks associated with this approach. For example, it is necessary for the bottom of the vat to possess transparency in order to not impede the passage of light and facilitate the printing of the slurry. Furthermore, subsequent to undergoing processing, each layer is effectively affixed to the bottom of the vat, necessitating the interruption of this contact by a movement of the vat. Hence, the bottom-up approach exhibits a longer total printing time when compared to the top-down approach and repetitive introductions of stress in the part can be more easily introduced, which can then lead to undesired deformations and failure [26].

2.2.2 Photocurable slurries components

Photopolymerisable monomers, ceramic fillers, dispersants and photoinitiators are the four main components of ceramic slurries. Prepolymers, diluents and, if needed, a diverse range of additives, including inhibitors and UV absorbers can be added to the mixture(Figure 2.3).

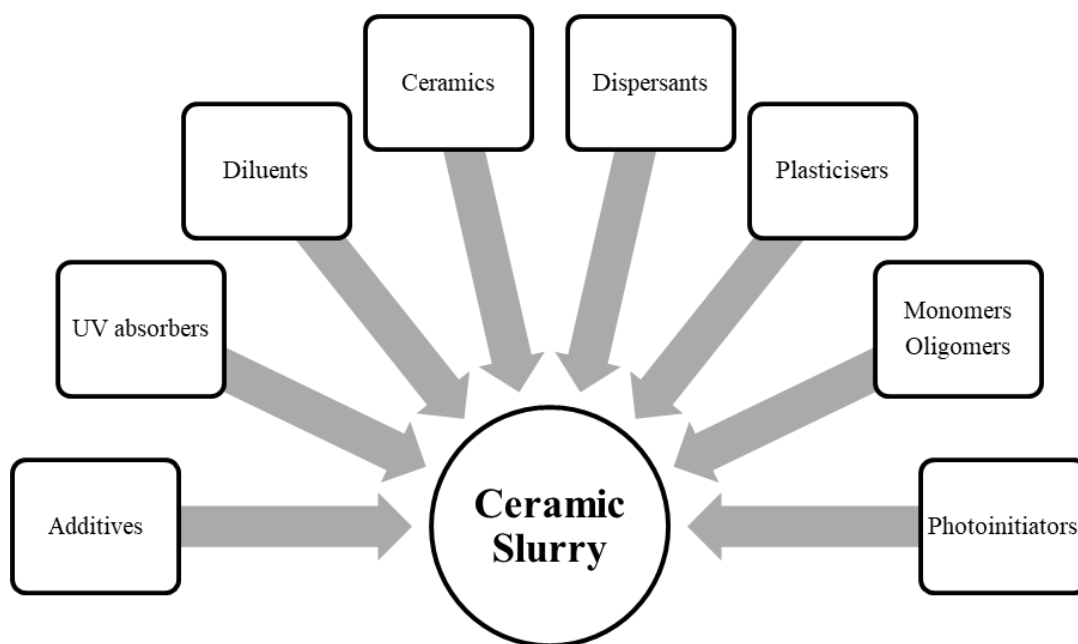


Figure 2.3 - Possible components of a 3D printable photocurable slurry.

In general, existing photocurable ceramic resins may be categorised into two groups: aqueous resins (based on acrylamide) and non-aqueous resins (based on acrylate and epoxy). Griffith and colleagues pioneered the use of the first aqueous photocurable solution in ceramic SLA. The aqueous solutions containing acrylamide were produced with a low refractive index ranging from 1.38 to 1.44 [20]. Therefore, the refractive index mismatch between was significant, leading to a reduced cure depth due to light scattering. Hence, the selection of ceramic powders that can be combined with aqueous resins is restricted. Despite the several benefits of this particular set of ceramic resins, such as their low viscosity, ease of dispersion oxide ceramic powders, lack of volatile organic compound emissions and, subsequently, being more environmentally friendly, they do have one significant drawback: the relatively poor strength of the fabricated green bodies. Furthermore, the presence of a significant quantity of water in the suspension gives rise to several issues, such as the occurrence of cracks, and, due to these limitations, this particular category of ceramic resins has not been extensively utilised

or researched for ceramics applications. On the other hand, non-aqueous ceramic resins have the benefit of greater strength in the cured green body, as opposed to aqueous ceramic resins, attracting more research attention. The acrylate- and epoxy-based resins often exhibit higher refractive indexes, in particular typically between 1.47 and 1.55, reducing light scattering phenomena and significantly enhancing the obtainable light penetration. Therefore, the energy requirements sufficient to cure a certain cure depth are less demanding, leading to a shorter duration of operation. Non-aqueous ceramic resins are also preferred for processing non-oxide ceramics because of the issues caused by the hydrolysis and oxidation of non-oxide particle surfaces in aqueous resins. Nevertheless, this particular category of ceramic slurries has the drawbacks of having greater viscosities compared to aqueous suspensions, when identical ceramic solid loadings are adopted, and the acrylate- and epoxy-based resins result in less environmentally friendly suspensions which require specific waste disposal procedures to be in place.

In terms of components of a photopolymerisable slurry, while UV absorbers can effectively modify the light penetration and the way in which it propagates through the medium [28,29], the diluents directly influence the rheological characteristics of the slurry, namely the viscosity, its refractive index and, consequently, the insurgence of defects that can alter the final properties of the green sample [30,31]. A thorough description of the concepts of viscosity and light penetration in photopolymerisable slurries is provided in section 2.2.3.

The dispersants purpose is to promote the diffusion of hydrophilic ceramic particles throughout the hydrophobic resin. Since unbound dispersant molecules between the ceramic particles create aggregates and flocculation when the dispersant concentration exceeds the optimal dose, eventually increasing the slurry viscosity, the type and the added quantity of dispersant should be chosen with care for each specific slurry formulation [32]. The dispersant

can be introduced in the slurry by adding it during the preparation stages of the used ceramic powder [33–35] or at a later stage when the photocurable resin and the ceramic particles are incorporated together in a slurry [36–38]. However, either way, its presence is fundamental in achieving the desired viscosity for additively manufacturing stable components.

Dispersant types and content have also to be taken into account as their impact on the slurries viscosity and the final microstructure is relevant [39]. While Johnson & Vogel proved that adding a mixture of dispersants may lead to better results and more performing properties when well coupled to optimal solid loadings [40], Zhang et al. showed that PMAA-Na should be preferred to PMAA-NH₄ when fabricating alumina-based parts. Despite they both avoid significant agglomeration and flocculation phenomena, PMAA-Na presence decreases the milling time by 80% compared to the latter while improving the strength of the green body and increasing the dielectric loss [41]. Chen et al. reported that there is an optimal percentage of dispersant that should be added to the mixture. In fact, in their experiments based on the Taguchi method, they proved that an addition of 5 wt.% of dispersant rather than 2.5 wt.% or 7.5 wt.% resulted in a decrease of both the sedimentation rate and the viscosity and an increase of the usable maximum solid loading percentages [42]. As also demonstrated by Zhang et al., varying the types of dispersants may have a positive effect on the maximum loadable content of ceramic powders and, hence, on the slurry viscosity. The addition of KOS110 in 5 wt.% concentration rather than 1 wt.%, 3 wt.% or 7 wt.% led to a better grade of homogeneity, higher long-term stability and greater solid loading to viscosity ratio due to the increased steric hindrance provided on Al₂O₃ particles surfaces [37] (Figure 2.4). In this regard, the Krieger-Dougherty viscosity model [43] significantly aligned with their results due to the spherical shapes of the particles processed, which also influenced dispersibility and randomisation in the slurry.

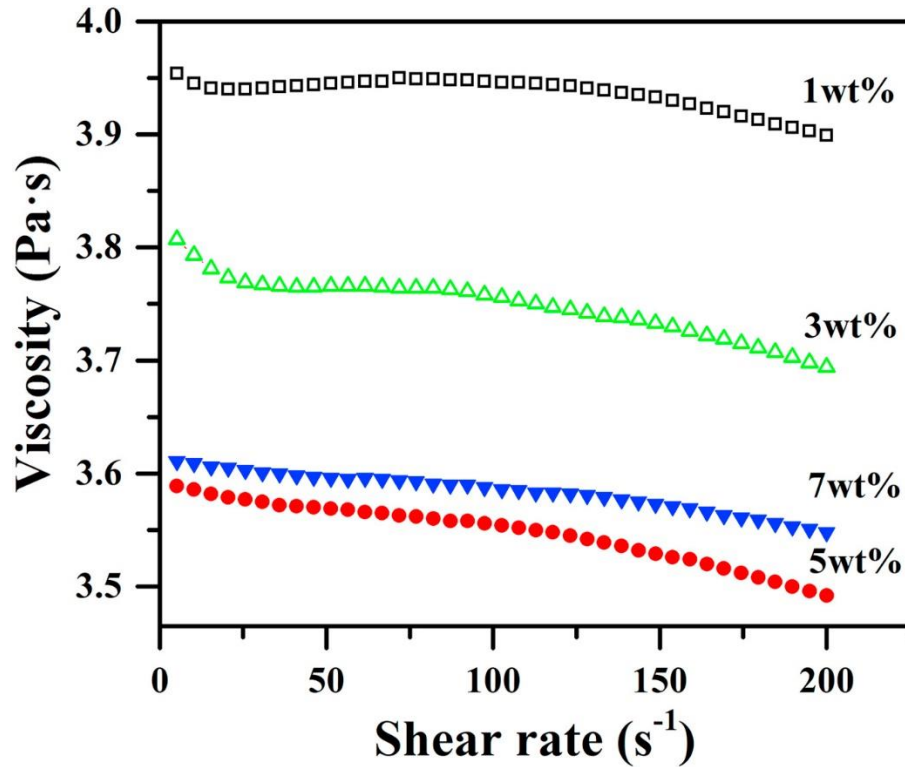


Figure 2.4 - Viscosity of Al₂O₃-resin slurries prepared with different dispersant concentrations [37].

In addition to dispersants, the presence of plasticizers and certain pH values affect the viscosity reduction and the mechanical performance as demonstrated by Ewais [44]. While plasticizers avoid the formation of possible breaking spots in correspondence to interlayer boundaries, preventing delamination and resulting in mechanical properties of sintered parts comparable to those of ceramics fabricated via conventional techniques [45], pH values play a role in the particles aggregation and flocculation dependently on the ceramic powder adopted [44].

Starting powder chemical composition, solid loading and additives inclusion in the solid loading also play a significant role in the slurry properties and the final obtainable microstructure. Choosing ethanol as a solvent for the functionalisation of the ceramic loading, for instance, could cause irregularities in the final part surfaces due to its low evaporation

temperature easily reachable during printing, resulting in even worsened geometries after the sintering at high temperatures. Therefore, using 2-butanol or solvents with higher boiling points may prevent the formation of the above-mentioned surface irregularities [36]. In addition, Ibrahim et al. illustrated how the mechanical properties of the final product are strictly dependent on the curing exposure time of the polymeric photosensitive slurry, solid loading and printing layer thickness [46]. The greater the solid loading, the higher will be the expected green part density, although it has been demonstrated that above saturation values ceramic particles in excess may result in loose powder barely attached to the printed part [36]. However, optimal conditions have to be found since increments in the initial solid loading correspond to higher viscosities, which instead should be maintained low for facilitating layer coating, avoiding delamination and, thus, promoting structure homogeneity. Varghese et al. demonstrated that for a ceramic-loaded photosensitive resin of Al_2O_3 , YSZ (i.e. Yttria Stabilised Zirconia), poly (ethylene glycol) diacrylate, phenyl bis (2,4,6-trimethyl(benzoyl)phosphine) as photoinitiator and ethanol, a solid loading saturation point is reached at 60% in weight, above which loose powder appears on the final part. On the other hand, excessively low solid loading, in particular below 25% of weight, led to printable structures that collapsed upon the sintering step, which was also strongly affected by significant shrinkage and, consequently, increased the obtained z-axis resolution at higher sintering temperatures [36].

Regardless of the adopted dispersant, the appropriate choice of the most suitable monofunctional and multifunctional monomers in the resin leads to different outcomes in terms of green body strength. In fact, while an excess of multifunctional ones creates stronger cross-linked polymers that enhance the stability and the mechanical properties of the printed part [26], a higher amount of monofunctional monomers will result in a weaker sacrificial polymer matrix that can, however, be removed more easily during the postprocessing stages. Furthermore, to

avoid the creation of internal stresses and delamination defects in the printed part, even the cleaning agent to remove external resin residuals after AM has to be chosen accurately. In fact, an incorrect choice can lead to geometrical inaccuracies at the green stages and to the insurgence of cracks during thermal postprocessing. Schwarzer and colleagues proved that ethanol is an effective cleaning agent for green parts due to its low viscosity and good solubility in nonpolar phases. However, its tendency for diffusion into the polymer network of alumina-based built parts can make the whole part swell, leading to undesired internal stresses and subsequent delamination [47]. According to their research, different cleaning agents, cleaning methods and sample ageing times effectively influenced the presence of building defects, the general printing quality and the overall suspension state. Cotton swabs impregnated with glycerol together with compressed air and avoiding ageing or solvent baths have been proven to be optimal cleaning methods for Al_2O_3 -based slurries, achieving the best green part quality in their experimental campaign [47].

Finally, the photoinitiator splits after being irradiated, resulting in the connection of monomers and oligomers that form the structural framework of the three-dimensional polymer network. The photopolymer precursor exhibits light absorption properties, whereby its photoinitiator system facilitates the conversion of photolytic energy into reactive species, therefore initiating the process of polymerisation [48]. Optimally curing the photopolymerisable resin is then crucial to obtain cohesive parts and avoid delamination as well as reducing the building time of 3D printed components. In fact, in recent years, photoinitiators or photoinitiating systems have witnessed significant development to enhance the pace of 3D printing and facilitate the creation of objects using low-energy visible light [49].

2.2.3 DLP printable slurries rheology and photopolymerisation

As previously mentioned, the rheological properties of the ceramic slurry are significantly influenced by several factors, including the characteristics of the ceramic powder such as starting particle size, distribution and shape, the surface potential, the adopted dispersant and the resin formulation. In order to provide uniform recoating and avoid the settling of ceramic particles, it is necessary for ceramic slurries used in polymerisation processes within the shear rate of the AM machine to exhibit non-Newtonian behaviour, namely shear thinning [50] (Figure 2.5).

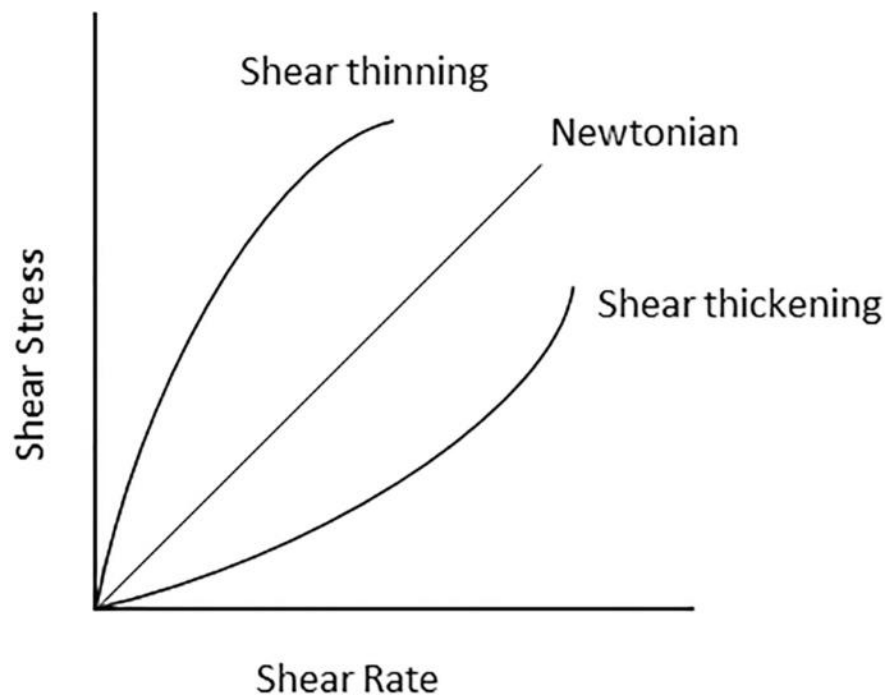


Figure 2.5 - Schematic rheological behaviour of shear-sensitive fluids [51].

While in the context of shear thickening slurries, it can be observed that the shear stress and, hence, the viscosity of the fluid increase as the shear rate increases, in shear thinning slurries the viscosity lowers at increasingly higher shear rates. The former phenomenon is

commonly found in suspensions characterised by a large particle loading, as it results in an increased occurrence of particles collisions, or inadequate dispersion of ceramic powder inside the resin. In this particular scenario, the phenomena of aggregation, jamming and flocculation are noticed, resulting in a notable elevation in the viscosity [34,52] (Figure 2.6).

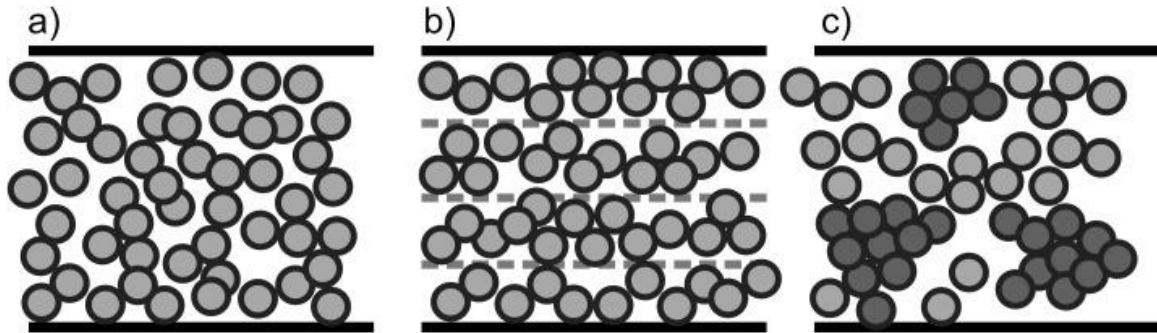


Figure 2.6 - Organization of particles according to the flow in a highly loaded suspension. a) Particles at rest; b) the ordering of particles in layers promotes shear-thinning; c) destruction of the layered organization of the particles and subsequent jamming promote shear-thickening [50].

When the solid fraction is held constant, reducing the particle size results in an increased particle count inside a certain volume. Consequently, smaller particles can have a significantly greater surface area, often by several orders of magnitude, and result in a higher number of collisions. Particles of minuscule size exhibit Brownian motion in opposition to an externally applied shear force. Hence, hydration, surface charge and adsorption can significantly influence the effective hydrodynamic particle size, especially for smaller particles. However, The discrepancy in viscosity between small and big particles decreases with increasing shear rates due to the favourable reorganisation of particles in relation to the direction of flow (Figure 2.6b). Furthermore, The maximum packing density and solid percentage are enhanced by the presence of particles with varying sizes (i.e. a polydisperse particle size distribution), as it allows for more effective filling of the space and, in particular, the wider the particle size

distribution, the more significant are the beneficial effects on the powder packing, but, in contrast, the lower is the control on the manufacturable layer thicknesses and, hence, on the building axis resolution. In addition, even the morphology of the powder should be considered. Spherical particles generally lead to lower viscosity as they don't deflect flow lines, but elongated particles, while performing worse at rest, can reorient themselves and align their elongated dimension to the flow direction. However, in any typical scenario, completely irregularly shaped particles result in a more viscous suspension. Finally, the particles surface charge and surface potential affect the inter-particle behaviour. When the surface charge is considerable, the repulsion between particles becomes more significant than the attraction caused by van-der-Waals force and an energy barrier prevents the particles from getting near to each other. Conversely, particles with a surface charge close to zero experience less repulsion, promoting accumulation or flocculation and a structured arrangement of the particles. Nonetheless, considering the particle size in combination with the surface potential, while high surface charges in smaller particles may lead to high viscosities when the slurry is at rest and shear-thinning behaviours at high shear rates, due to the reduced significance of gravitational forces for smaller particles compared to the Brownian motion, larger particles ($>1\ \mu\text{m}$) generally possess at rest higher values of viscosities at low surface potentials due to sedimentation and lower viscosities at increased shear rates with the same surface charge levels.

Ideally, the AM machine should always work in the shear thinning window as a shear thickening behaviour may lead to process failures since, in this case, small increases in the shear rates correspond to rapid growths in stress and viscosity, which can cause layers delamination and the consequent detachment of the body from the building platform [47]. In fact, in the case of components with intricate geometries, it is often preferable to utilise low-viscosity slurries in order to mitigate the occurrence of excessive stresses during the separation process of the

solidified layer. While values of $\sim 3 \text{ Pa}\cdot\text{s}$ in the workability window of the adopted AM machine usually represent the viable upper limit of viscosity for a successful print, modern DLP machines, like the Admaflex 130 used in this research, can efficiently handle higher levels of viscosity up to $\sim 10 \text{ Pa}\cdot\text{s}$ when the shear rate ranges from 10 to 300 s^{-1} [53]. Nevertheless, the slurry viscosity needs to be low enough to ensure the coverage of the last printed part slice in the layer-by-layer manufacturing to promote interlayer cohesion and avoid delamination, but, at the same time, since very diluted slurries won't remain within the borders of the transportation foil system of the machine, could escape the reservoir before printing as well as moving out from the printing zone when the building platform is moved against the foil. In this case, there won't be enough slurry between the cured layer and the slurry itself, exposing the already cured layer and the previous ones that fall within the slurry curing depth to an excessive energy input that worsens the mechanical properties of the printed layers, causes swelling, reduces interlayer adhesion and increases the risk of delamination.

In fact, when tailoring the properties of the photosensitive ceramic slurry, its photopolymerisation reaction has to be observed and documented through the analysis of parameters, such as cure depth, refractive index, critical energy dose, light absorption and scattering [54]. The ceramic slurry's working curve illustrates the relationship between the curing depth of the slurry and the light dosage applied by a certain light source. The cure depth, denoted as C_d , can be determined by the use of Jacob's equation [20]:

$$C_d = D_p \ln \left(\frac{E}{E_c} \right) \quad (1)$$

where the factor D_p represents the penetration depth, which refers to the distance at which the intensity of light decreases by a factor of e^{-1} [55], E denotes the surface exposure energy density and E_c represents the critical surface exposure energy density for the slurry [56]. E_c specifies the minimum energy density required for the photopolymerisation of the slurry [57]. Hence,

when the penetration depth is higher and the E_c is lower, a reduced energy density is necessary to achieve a certain cure depth. The values of E_c and D_p are commonly regarded as resin-specific measurements that are not influenced by various exposure circumstances [58] and can be determined by evaluating the y-axis and the x-axis intercepts of the cure depth fitted function on a semilogarithmic graph where $\ln\left(\frac{E}{E_c}\right)$ is reported on the x-axis. This study employed a single-layer curing method to estimate the critical exposure energy and depth of penetration. This was achieved by evaluating the cure depth at different levels of exposure energy and exposure times. An example of the obtainable graph and subsequent information can be seen in Figure 2.7.

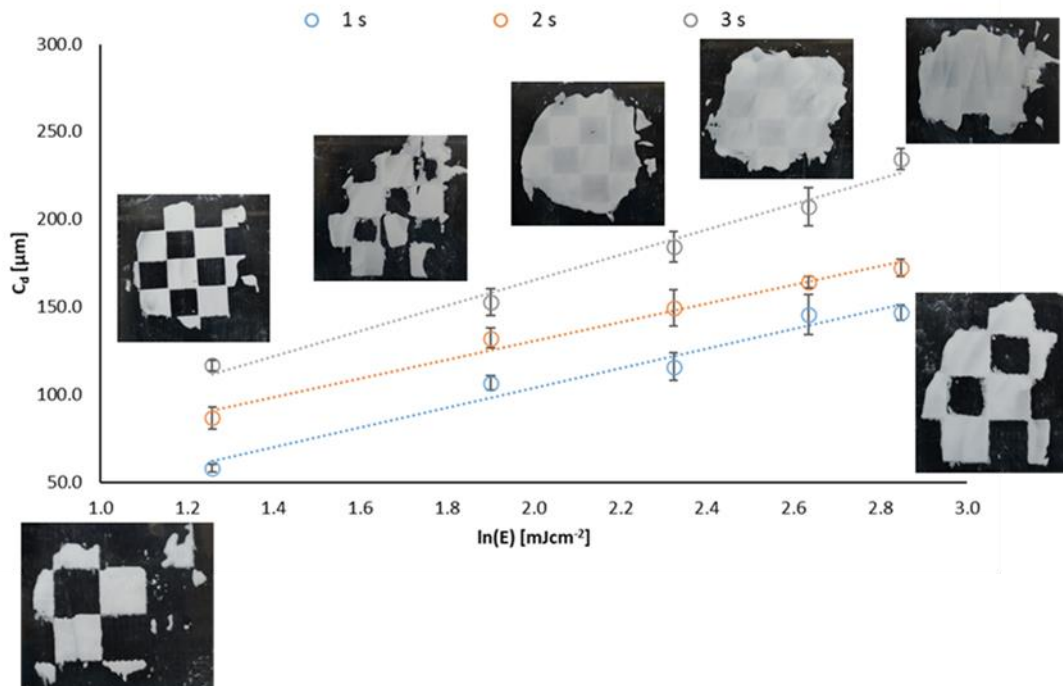


Figure 2.7 - Example of the analysis of a slurry cure depth at different exposure energies and time, corresponding to different morphologies of cured single layers.

The cure depth and the optimal photopolymerisation of the ceramic slurry are also affected by light scattering and absorption. The phenomenon of scattering is typically accompanied by absorption in the process of energy conversion from the source, resulting in competition for the attenuation of the light beam [59,60]. These phenomena arise when a ceramic particle in the slurry causes a beam to stray from its original path. One often employed method involves the consideration of the scattering coefficient, which serves to quantify the reduction of D_p and, hence the deflection of light by particles. The absorption model takes into account the dual contributions of scattering and absorption when evaluating the correlation between D_p and the scattering coefficient [61]:

$$D_p = \frac{1}{S + A(1 - \varphi_c)} = \frac{1}{A_d} \quad (2)$$

where the scattering coefficient, denoted by a S , is the inverse of the scattering length, a dimensional quantity that represents the distance over which the propagation of photons becomes randomised [54], the factor φ_c represents the volume fraction of the dispersed ceramic material, A is the absorption coefficient and A_d the attenuation coefficient. As it can be noticed, the higher the scattering coefficient, the lower is the penetration depth and, thus, the higher the energy input needed to reach a certain cure depth (Figure 2.8).

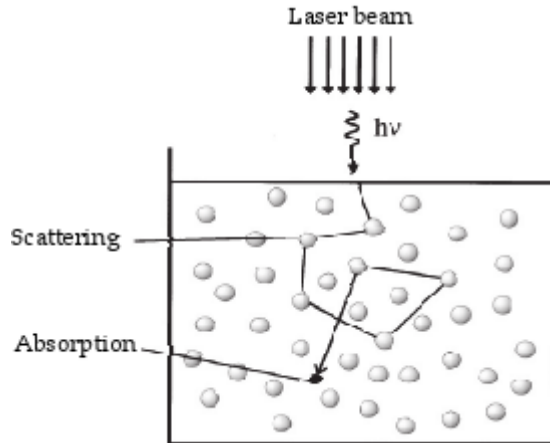


Figure 2.8 - Light scattering and absorption phenomena in ceramic slurries [62].

The scattering effect is strictly correlated with a quadratic proportional dependence to the refractive indexes of the ceramic powder and the medium in which it is dispersed. In fact, the higher the difference between them, the higher will be the internal light refraction and the horizontally dispersed photonic energy [38,54,57]. Minimising this difference is therefore the key to ensuring that the optimal cure depth is achieved.

In summary, the accuracy of components produced using Digital Light Processing is influenced by intricate relationships among process parameters, printer resolution and the composition of the photopolymerisable slurry. Given the relative novelty of DLP technology in ceramic materials manufacturing, it is imperative to be able to customise the rheology and photopolymerisation characteristics of ceramic suspensions for particular purposes. Additionally, a comprehensive investigation into the impact of printing parameters on the attainable geometric precision and physical attributes of DLPed alumina green parts is essential. In order to customise specific qualities to meet specific demands, it is necessary to assess the effects of various powder pre-treatments, slurry components and subsequent curing behaviours by examining the density evolution and geometrical precision at varied layer thicknesses and energy doses throughout the entire manufacturing process chain.

2.2.4 DLP postprocessing

In order to remove the resin components and create a dense product, DLP-manufactured parts require thermal postprocessing. The ceramic green body produced through the method of 3D printing undergoes debinding and sintering to obtain a sintered body with the necessary final characteristics (Figure 2.9).

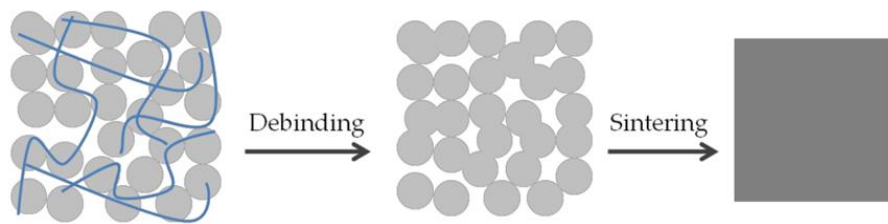


Figure 2.9 - Steps of the thermal treatment after green body fabrication: debinding and sintering [63].

The method changes based on the chemical composition of the resin, the solid loading of ceramic powder in the slurry and the geometric dimensions of the component [64]. During the debinding process, it is necessary to efficiently eliminate the organic constituents from the ceramic slurry using the process of pyrolysis. Wang and colleagues showed that the rapid increases in temperature, inadequate holding zones and prolonged holding periods result in the formation of microcracks due to the diffusion of the binder from the ceramic green body [65]. The presence of microcracks during the sintering process leads to a degradation of the mechanical characteristics, hence, it is imperative to precisely ascertain the heating rate and holding zone within a certain temperature range where the binder undergoes decomposition. This is crucial in order to effectively achieve thermal stabilisation of the ceramic green body by the use of an appropriate holding period [66]. Furthermore, slow heating rates and adequate holding temperatures are required to prevent delamination, cracking, deformation or collapse

brought on by thermal stress induced by the breakdown of organic components [65,67]. In addition, it is of significant importance to utilise an optimum sintering temperature in order to achieve complete ceramic densification throughout the sintering process and avoid the degradation of physical properties. During sintering, ceramic particles are completely joined together by heating the debound component to a high temperature and, in turn, the part volume slightly decreases and its relative density rises [63,68] (Figure 2.10).

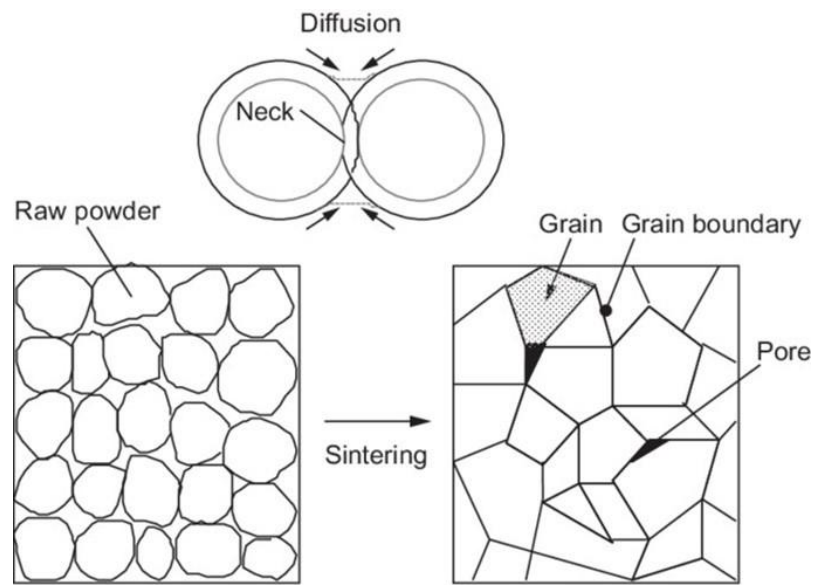


Figure 2.10 - Schematic diagram of the sintering process [69].

The process of solid-state sintering for alumina ceramic entails the consolidation of a porous brown body into a compact and solid structure, achieved by subjecting it to elevated temperatures in the range of 1600-1800 °C, but below the melting point. Pressureless sintering in electric or vacuum furnaces is capable of delivering fully dense parts even in the absence of inert atmospheres [70,71]. Al_2O_3 solid-state sintered samples are mainly influenced by the starting particle size, the debound body density, the sintering temperature, the heating rate and the holding sintering time. While the sintering rate can be increased and the dwell time reduced

when the starting grain size is finer, the correlation between dwell temperature and sintering rate is significant due to the thermally triggered nature of the sintering process since several factors, including diffusivity and viscosity, are usually described as exponential functions of temperature. However, it was shown that elevating the sintering temperature may result in enhanced grain development and decreased mechanical characteristics, thus tailoring the sintering parameters to the specific case investigated is of relevant significance [72]. Moreover, the influence of the holding time on the characteristics of sintered ceramics is relatively less significant when compared to the effect of the sintering temperature [73].

In addition, the incorporation of sintering aids can have a substantial impact on the diffusion and densification processes of the material. Silicon dioxide (SiO_2), magnesium oxide (MgO) and calcium oxide (CaO) are frequently cited and widely utilised sintering aids. However, it should be noted that lanthanum oxide (La_2O_3), boron oxide (B_2O_3), and scandium oxide (Sc_2O_3) have also been applied as additives to enhance the decrease of porosity and, thus, promote higher relative densities [74]. Magnesium oxide has demonstrated significant advantages in vacuum sintering procedures involving Al_2O_3 components, even when employed in minimal amounts, as evidenced by previous studies [75]. Its notable efficacy lies in its ability to significantly impede excessive grain formation, rendering it particularly well-suited for the sintering of transparent alumina [76,77]. La_2O_3 is a highly effective additive for sintering alumina components, especially when combined with Y_2O_3 and MgO [78,79]. Researchers have demonstrated that the incorporation of La_2O_3 using infiltration methods significantly improves transmittance at 800 nm wavelengths. Finally, in previous studies, MgAl_2O_4 has been identified as a sintering aid that actively enhances the densification process and improves the optical characteristics of translucent alumina by raising the highest relative density obtained [75,80]. In order to produce transparent ceramics, for instance, it is necessary to eliminate all

potential causes of light scattering. These include the presence of residual intragranular and intergranular voids, grain boundaries, the existence of secondary phases at the grain boundaries and the birefringence effect of noncubic materials. Hence, enhancing the densification process, even with the use of suitable sintering aids, has significant value in achieving the intended optical characteristics in the final component. While the effect of including additives in the powder mixture can be effectively investigated experimentally, the influence of the sintering parameters can be studied in advance in numerical modelling software and subsequently validated via experimentation. In fact, having the capability of relying on a digital simulation of the sintering process is particularly helpful when numerous sintering conditions have to be explored, when the material is significantly precious and when the significance of different parameters has to be assessed.

2.2.5 Brief overview of the solid state sintering theory

Solid state sintering refers to the thermal and mechanical process of consolidating a porous material into a solid mass without reaching its melting point and causing liquefaction. The diffusion of atoms within the materials usually involves the particles boundaries, which then coalesce, resulting in the formation of a unified entity. During sintering, ceramic particles get bonded together and, thus, as a consequence of the average grain growth, the surface energy decreases due to the reduction of free surfaces and grain boundaries. The formation of bonds results in enhanced mechanical strength, thermal and electrical characteristics and a reduction in the overall energy of the system. At the microstructural scale, the phenomenon of sinter bonding becomes apparent when the necks formed by particle contacts increase in size. Based on phenomenological findings, the sintering theory stipulates that there are three phases in the

sintering process, according to the geometric changes experienced by the grains during the densification process [81] (Figure 2.11).

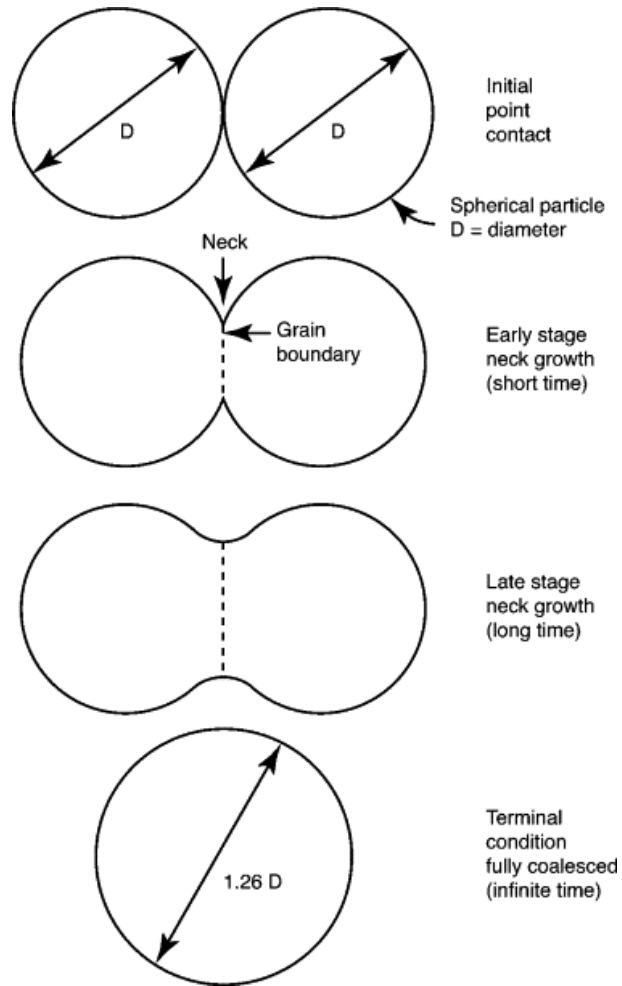


Figure 2.11 - Different stages of solid state sintering [82].

Firstly, the powder particles are combined together, resulting in particles that establish contact points randomly with one another. The early phase of sintering is distinguished by the rapid expansion of the sinter bond starting at the initial site of contact, also referred to as neck. However, the real change in volume of the porous body is negligible since just a tiny mass is required to create a neck. Typically, the grain size is not greater than the original particle size

and necks have a microstructure with substantial curvature gradients. During the intermediate stage, there is a reduction in pore volume and amount, as most of them become interconnected and round, thus significant compaction of the powder compact occurs. Nevertheless, the subsequent grain growth and the decreasing of the active surface area due to the reduction of free grain boundaries hinder the sintering process itself. Lastly, after long heat treatment times, the concluding phase of sintering is distinguished by the spheroidisation of pores and their isolation while, gradually, the rate of densification slackens and the grain expansion becomes obvious [83,84].

2.2.6 Sintering models and viscoelastic theory

Alumina particles sintering is mainly driven by grain boundary diffusion mechanisms, overall at high heating rates [85]. Various sintering models based on continuum mechanics and incorporating grain boundary diffusion have been created in the past literature. Riedel and co-workers [86] developed an isotropic linear viscous constitutive equation to explain sintering dominated by grain boundary diffusion and to investigate the influence of pore size distribution on the sintering process. However, grain growth was not considered. Another model was developed by Johnson and colleagues [87], who, in their research, defined a combined-stage sintering model for the complete sintering process, which encompasses the beginning, intermediate and final stages of sintering. Their developed model is capable of simulating situations within a wider relative density spectrum when compared to linear viscoelasticity models. However, it should be noted that all of the model parameters have broad distributions and it is challenging to identify them, particularly the scale parameter, which is correlated to the mean diffusion distance, the driving force and microstructural geometric characteristics.

Finally, Olevsky and his colleagues [88] constructed a phenomenological model of sintering based on the rheological theory of sintering previously developed [89]. In general, while the relationship between strain rate and sintering stress equations may be equally characterised by Riedel's creep law model or from Olevsky's linear viscoelastic model, the combined-stage model may not be suitable for the realistic modelling of the sintering process owing to the difficulty of quantifying the wide range of the parameters. Conversely, Riedel's model and Olevsky's model possess fewer parameters, which also have distinct physical meanings.

According to the theory of linear viscoelasticity, materials have the ability to both store and release mechanical energy. Generally, an externally induced stress may consist of mechanical force as well as thermally generated loading, such as the hydrostatic sintering stress. A condition of stress generates an immediate deformation in viscoelastic materials, which then usually causes a time-dependent flow process [84]. Therefore, the material reaction is dictated by the current level of stress and its stress history since the two components of creep and elastic deformation are present. At high sintering temperatures, the behaviour of materials with a significant volumetric void fraction is both elastic and viscous and, over the lengthy process, a time-dependent thermally induced strain will develop, usually referred to as sintering strain or creep strain. This phenomenon is comparable to conventional continual mechanical loadings and, consequently, makes the linear viscoelastic theory exploitable for the numerical modelling of sintering processes [84]. In fact, the set of equations that explain viscous flow is comparable to the Hooke's Law equations that describe elastic deformation. Newton's Law of viscous flow describes the relationship between the shear strain rate of a viscous material and the applied shear stress as:

$$\tau = \eta_d \dot{\gamma} \quad (3)$$

where τ is the shear stress, η_d the dynamical shear viscosity and $\dot{\gamma}$ the shear strain rate or, simply, the shear rate.

2.2.7 Numerical modelling of sintering

Among the several examples of numerical modelling of sintering processes that can be found in the literature [90,91], very few are related to ceramic components and even a smaller number are focused on the debinding operations [92]. Numerous investigations have been undertaken on the subject of sintering processing, a very intricate yet extensively utilised technology within the realm of powder metallurgy [93], and different model approaches have been distinguished: atomistic, micromechanical and continuum models. The distinction between these concepts is evident based on their respective names, which highlights their divergence in terms of the selected perspective. Atomistic models incorporate the dynamic positions and velocities of atoms, as well as the chemical compositions of the material analysed. Micromechanical models, on the other hand, focus on the microstructure of materials to study phase changes and the formation of necks. In contrast, the continuum approach treats the material as a continuous medium and employs modified equations from the theory of solid plasticity to model its thermomechanical behaviour. The utilisation of multiscale modelling may also be employed to examine the interactions occurring at various scales and assess the cross-interactions [94], although even more modelling complexities have to be taken into account as well as significantly longer computing time.

In regards of the microscopic model, Nosewicz et al. developed a rheological scheme based on a thermo-viscoelastic model which considers the effects of significant configuration

changes during sintering, fluid-like behaviours of the material while sintered and thermal stress induced by temperature variations [95].

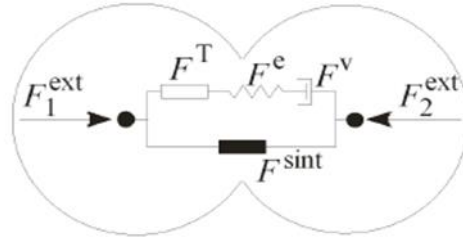


Figure 2.12 - Nosewicz et al. rheological scheme of thermo-viscoelastic model [95].

Analysing stresses and mass transportation phenomena between two sintered particles, Nosewicz et al. obtained the following equation for the normal force:

$$F_n = \frac{\pi a^4}{8D_{eff}} v_{rn} + \pi \gamma_s \left[4r \left(1 - \cos \frac{\Psi}{2} \right) + a \sin \frac{\Psi}{2} \right] \quad (4)$$

where a is the radius of the interparticle boundary, v_{rn} is the normal relative velocity, γ_s is the surface energy, r is the single particle radius, Ψ the dihedral angle and D_{eff} the effective grain boundary coefficient (Figure 2.13), which is given by:

$$D_{eff} = \frac{D_{gb} \delta \Omega}{k_B T} \quad (5)$$

where D_{gb} is the grain boundary diffusion coefficient, δ is its width, Ω is the atomic volume, k_B is the Boltzmann constant and T is the temperature.

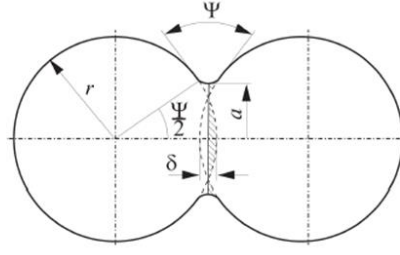


Figure 2.13 - Schematic representation of rheological parameters defined by Nosewicz and colleagues [95].

In order to consider the thermal expansion in the model, r has to be calculated following the linear thermal expansion rule, which is represented by the following formula:

$$r = r_0[1 + \alpha(T - T_0)] \quad (6)$$

where r_0 is the particle radius at room temperature, α is the thermal expansion coefficient proper of the material being sintered and T_0 is the room temperature.

From a macroscopic point of view, instead, the material is believed to behave as a continuum and, hence, follows the modified plasticity theory for solids. As it is well known according to the above-presented thermo-viscoelastic model, the total strain rate is given by the addition of three different components i.e. elastic, thermal and viscous ones. Therefore:

$$\dot{\boldsymbol{\varepsilon}} = \dot{\boldsymbol{\varepsilon}}^e + \dot{\boldsymbol{\varepsilon}}^{th} + \dot{\boldsymbol{\varepsilon}}^{visc} \quad (7)$$

and, hence, the constitutive equation assumes the following aspect:

$$\dot{\boldsymbol{\sigma}} = \mathbf{D}\dot{\boldsymbol{\varepsilon}}^e + \dot{\boldsymbol{\sigma}}^s = \mathbf{D}(\dot{\boldsymbol{\varepsilon}} - \dot{\boldsymbol{\varepsilon}}^{th} - \dot{\boldsymbol{\varepsilon}}^{visc}) + \dot{\boldsymbol{\sigma}}^s \quad (8)$$

where the thermal strain, viscous strain rate and sintering stress are respectively expressed by:

$$\boldsymbol{\varepsilon}^{th} = \alpha T \mathbf{I} \quad (9)$$

$$\dot{\boldsymbol{\varepsilon}}^{visc} = \frac{\boldsymbol{\sigma}'}{2\eta_s} + \frac{tr(\boldsymbol{\sigma}) - 3\sigma^s}{9\eta_b} \mathbf{I} \quad (10)$$

$$\boldsymbol{\sigma}^s = \sigma^s \mathbf{I} \quad (11)$$

$$\sigma^s = \frac{\beta \gamma_s \rho^2}{r_0} \quad (12)$$

where:

$$\rho = \hat{\rho} e^{-(\varepsilon_x + \varepsilon_y + \varepsilon_z)} \quad (13)$$

where η_s is the viscous shear modulus, η_b is the viscous bulk one, β is a parameter related to the powder morphology and $\hat{\rho}$ the initial relative density, which are all strictly connected to microscopical properties and functions of porosity and temperature [96].

Olevsky and co-workers [88,97,98] elaborated a phenomenological model of sintering. The theory of sintering based on rheology, formerly built by Skorohod [89], was the fulcrum of the model. The stress-strain rate equation obtained from the theory is:

$$\sigma_{ij} = 2\eta(\phi \dot{\varepsilon}'_{ij} + \psi \dot{\varepsilon}_{ii} \delta_{ij}) + P_L \delta_{ij} \quad (14)$$

where η is the apparent viscosity of the porous body skeleton, P_L is the effective Laplace pressure (sintering stress, σ^s), ϕ and ψ are the coefficients of the effective shear and bulk moduli, respectively:

$$\phi = (1 - \theta)^2 \quad (15)$$

$$\psi = \frac{2}{3} \frac{(1 - \theta)^3}{\theta} \quad (16)$$

where the porosity θ can be estimated as:

$$\theta = \frac{V_{pores}}{V_{total}} \quad (17)$$

As a result of mathematic considerations involving the equivalent hydrostatic pressure p and the Mises equivalent deviatoric stress $\tilde{q}$, the stress-strain rate equation can also be rewritten in the following terms:

$$\sigma_{ij} = p \delta_{ij} + \tilde{q} \quad (18)$$

since:

$$p = \frac{1}{3} \text{tr} \sigma = 2\eta\psi\dot{\epsilon}_{ii} + P_L \quad (19)$$

$$\tilde{q} = \sqrt{\sigma'_{ij}\sigma'_{ij}} = 2\eta\phi\sqrt{\dot{\epsilon}'_{ij}\dot{\epsilon}'_{ij}} \quad (20)$$

where σ'_{ij} is the deviatoric stress tensor component. Olevsky and co-workers [88] have also proved that, adopting a stochastic approach, the actual Laplace pressure can be defined as:

$$P_L = \sigma^s = \frac{3\gamma_s}{r_0}(1 - \theta)^2 \quad (21)$$

where γ_s is the surface tension energy and r_0 is the mean radius of the pores or the powder particles [88] used in the fabrication of the material compact. Considering that grain boundary diffusion is one of the main mass transport routes in solid-state sintering for the majority of crystalline materials, the sintering should be a function of surface tension, relative density and average grain size. Therefore, σ^s can be defined as:

$$\sigma^s = \frac{6\gamma_s}{G}(1 - \theta)^2 \quad (22)$$

where the average grain size, which can reasonably be approximated to the average diameter of the powder particles, is expressed by the variable G .

In regard to the viscosity, which can be looked at as the material resistance to viscous flow, it has to be considered that temperature is an important player in the viscosity determination and, since it widely changes during the sintering process, the material will behave accordingly in terms of viscosity. Then, an Arrhenius equation should be reasonably able to estimate the viscosity fluctuation across the sintering cycle; in particular, it should assume the form:

$$\eta = \eta_0 e^{\frac{Q_v}{RT}} \quad (23)$$

where Q_v is the activation energy for the viscous flow, η_0 a pre-exponential material-dependent constant, R is the universal gas constant and T is the temperature in Kelvin. The above-

presented equation is deemed to be more precise as the material assumes a quasi-liquid status, which effectively happens at high sintering temperatures.

However, the parameters in the continuous viscoelasticity theory should be modified accordingly taking into consideration the porosity. Specifically, the shear viscosity and the bulk viscosity modulus above mentioned and introduced in the viscous strain definition, should be evaluated as:

$$\eta_s = (1 - \theta)^2 \eta \quad (24)$$

$$\eta_b = \frac{4(1 - \theta)^3}{3\theta} \eta \quad (25)$$

where θ is the porosity and η is the apparent viscosity estimated with the Arrhenius equation. Taking into consideration all the described relationships at both micro and macro scale conditions, numerical modelling of sintering processes allows for predicting final part properties.

As previously briefly mentioned, other numerical models of sintering can be found in the literature. However, there are just a few attempts in the literature on the combination of AM of ceramics and numerical modelling of the sintering stage and most of the published work is either missing important details on the used numerical approach, experimental validation or development of adopted ceramic AM technique. Introducing a well-known viscoelastic model, paired with accurate temperature and density dependent material properties of alumina and capable of predicting with good reliability dimensions and density of sintered samples, will constitute a novel and strategically helpful tool in the process of ceramic DLP postprocessing optimisation. In fact, understanding the impact of the additive manufacturing working principle on the initial conditions of the sintering process is necessary in order to produce high-density, defect-free, alumina ceramic parts using DLP, which will enable them to be used to their full potential. The objective can be accomplished by developing and utilising a numerical model

grounded on the principles of thermo-viscoelasticity theory, with the aim of investigating the impact of various sintering process factors.

2.3 Advanced and Smart Ceramics

Additive manufacturing of smart ceramics has just started to be explored as a topic of research since the literature around is mainly focused on the AM of common ceramics. Smart materials can be categorised as responsive materials and advanced structured materials (ASMs) [99]. The former class includes all the materials that interact with the surrounding environment modifying their structure and/or their phase configuration to answer to external stimuli such as mechanical loading, pH value changes, pressure/temperature variations or light incidence. The way in which they answer to these stimuli can be programmed. The latter group, instead, comprises all the materials that react to one or more predefined stimuli without self-transforming over time. Therefore, according to this classification, Shape Memory Alloys (SMAs), self-crack-healing and piezoelectric materials belong to the former category [99].

Standards for the use of smart materials in Additive Manufacturing have not been defined yet, but the potentialities of manufacturing smart materials via AM are very attractive. Controlled camouflage textiles, personalised medicines responding to body chemicals' values, programmable one-of-a-kind biological materials, stimulated tissue regeneration and temperature-responsive safety actuators with optimised geometries are just some potentially viable applications for smart ceramics. Whilst for metals and polymers some studies have been carried out on 3D printing of smart structures for advanced applications, 3D printing of ceramic with added or advanced properties is still in its infancy, but the capability of fabricating, for instance, transparent ceramics for defence, lasers, aerospace and military applications or

producing materials that can self-heal in critical environmental conditions such as aeronautical ones or yet creating stronger though smaller actuators made out of Shape Memory Ceramics (SMCs) is attractive to many industries for its great potential [99].

In recent years, there has been a notable global focus on the advancement and exploration of transparent polycrystalline ceramics for optical purposes in order to overcome the utilisation of traditional single crystal and glass materials and the manufacturing challenges associated with them. Within the realm of optics, while transparency denotes the inherent physical characteristic of materials that enables the transmission of light without any significant scattering, translucency indicates an optical characteristic of materials to permit the transmission of light while not strictly adhering to Snell's law on a macroscopic level. [100]. Currently, transparent ceramics are mainly fabricated via well-known manufacturing routes such as Hot Pressing (HP), Hot Isostatic Pressing (HIP) [101] and microwave sintering. In fact, in their review of the current manufacturing state of the art, Wang et al. limited the currently viable routes to HP, HIP, vacuum sintering, Spark Plasma Sintering (SPS) and microwave sintering, excluding any additive manufacturing methods preprocessing [100]. With regard to the investigations on transparent ceramics, the porosity is the primary determinant of their transparency. In fact, by varying heat treatment conditions and regimes, the principal scope is to achieve finer microstructure and to improve the densification process in order to obtain optimal light transmittance. This can be conventionally done with several different approaches, such as using multi-step sintering processes [102], including sintering aids and additives [103] or adopting advanced thermal treatment techniques [79,104]. Either way, the feasibility of producing polycrystalline transparent ceramics has been extensively proven and studied in the literature, even though their manufacturability has been revealed as very costly and not really prone to flexibility in design and geometries. Additive manufacturing has been transversally

imposing across the whole spectrum of manufacturing processes as the most green and flexible in terms of design and tuning of components properties, being able to accommodate exacting requests and overcome issues otherwise insurmountable. However, their production via AM has yet to be explored as there is little to no information in the literature regarding the challenges and possibilities associated with it, overall when taking into consideration alumina as the processed material. Therefore, the lack of information about AM of transparent ceramics, together with the industries interest in minimising costs while providing the best possible solutions, paves the way for making this type of advanced ceramic an interesting and sought-after field of research with huge potential to exploit.

2.4 Polycrystalline transparent ceramics

In optics, the interactions of electromagnetic radiation with media are directly associated with the optical characteristics of materials. The small area of the electromagnetic spectrum between 380 nm and around 700 nm is where visible light wavelengths are located and represent the region of the spectrum to which the human eye is responsive (Figure 2.14).

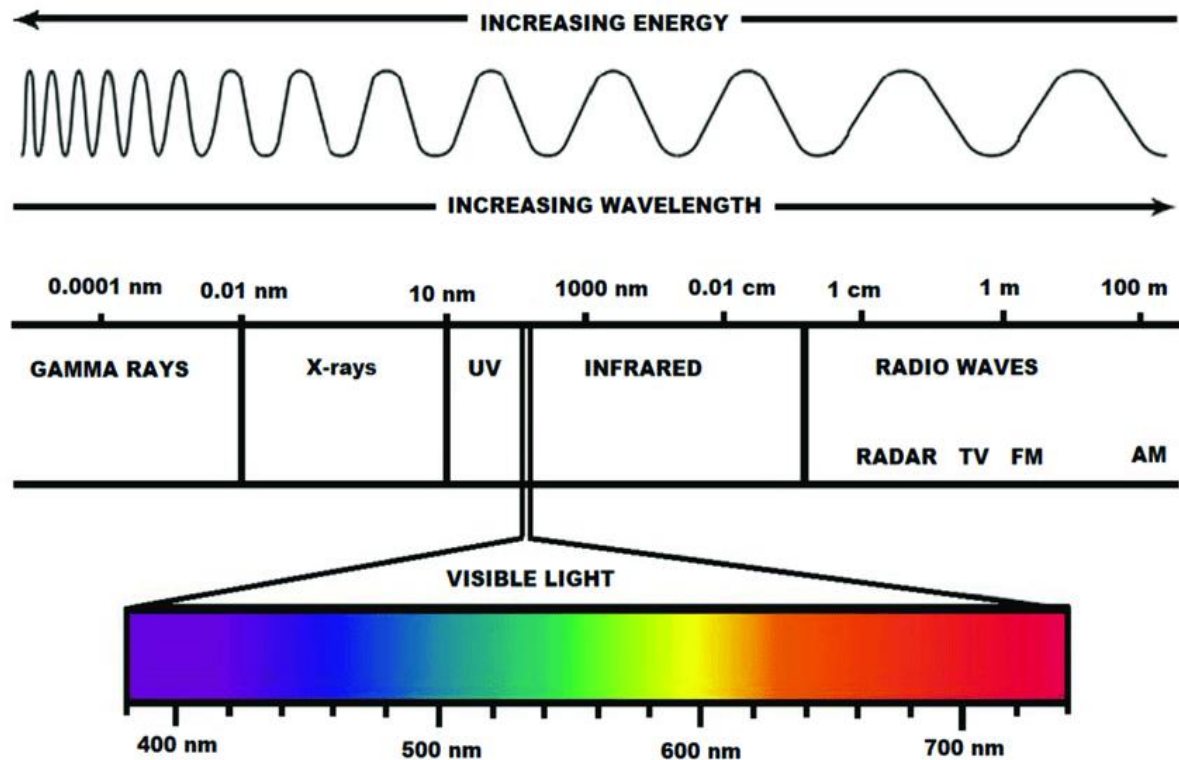


Figure 2.14 - The electromagnetic radiation spectrum [105].

As it transitions from one medium to another, according to their respective refractive indexes, part of the light propagates into the body and is transmitted through it, while another portion is absorbed and a further one is reflected at the interface between the two media. In fact, the way in which a medium interacts with light is defined by its refractive index n , which can be defined as:

$$n = \frac{c}{v} \quad (26)$$

where c represents the speed of light travelling in vacuum and v is the speed of light when passing through that specific medium [106]. The refractive index n illustrates the speed reduction experienced by light when travelling through a particular medium and is crucial for defining the optical properties of the said medium. Snell's law equation determines the relationship between refractive indexes and actual bendings of light rays (Figure 2.15):

$$n_1 \sin \theta_1 = n_2 \sin \theta_2 \quad (27)$$

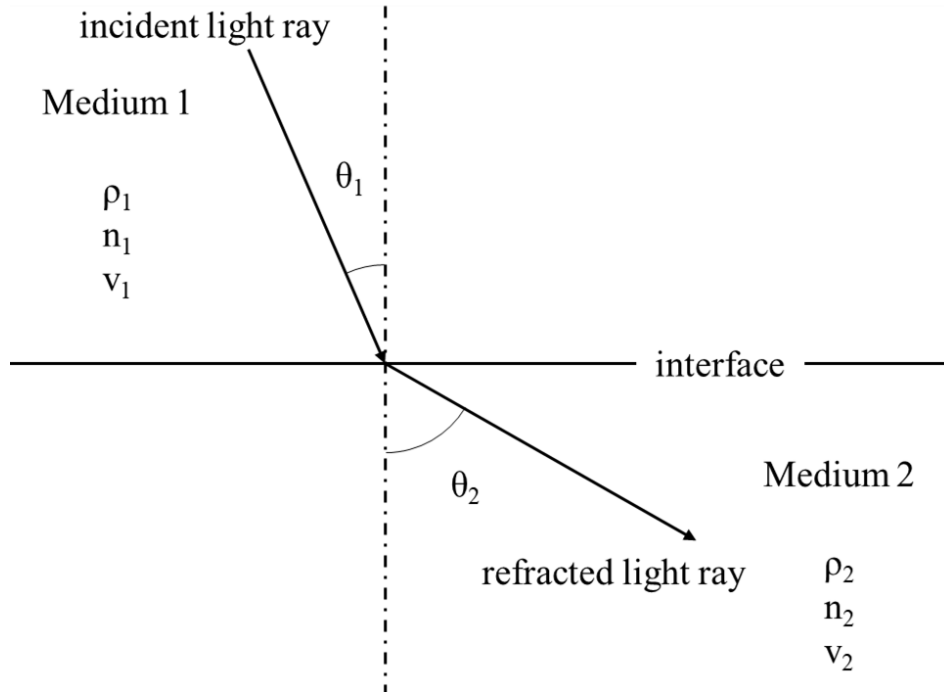


Figure 2.15 - Light transmission at the interface between media according to Snell's law.

When light travels through an ideally perfectly homogeneous medium, the refractive index is constant in all its parts, so, when an imaginary hypothetical interface line is drawn, $\theta_1 = \theta_2$ since $n_1 = n_2 = n$ and the light is not deviated. However, when considering different media where $n_1 > n_2$, then $\theta_1 < \theta_2$ and light is refracted. It exists a critical value of $\theta_1 = \theta_c$ at which the refracted light rays are deviated along the interface between the media ($\theta_2 = 90^\circ$) and above which the incident light is refracted completely internally at the first medium ($\theta_1 > \theta_c$ and $\theta_2 > 90^\circ$), resulting in the phenomenon of Total Internal Refraction or, shortly, TIR. From Snell's law equation, this value can be found by imposing $\theta_2 = 90^\circ$ so that:

$$\theta_1 = \theta_c = \sin^{-1} \left(\frac{n_2}{n_1} \right) \quad (28)$$

When $\theta_1 > \theta_c$ and $n_2 < n_1$, which generally entails that the medium from which the light source ray is incident is denser than the second medium ($\rho_1 > \rho_2$), TIR is noticed.

The aforementioned condition can be revisited in the context of transparent ceramics. In fact, when a light ray travelling through air hits the surface of an ideally perfectly smooth ceramic suspended in air, TIR cannot be observed. If the ceramic material is a single crystal without any impurities, the light would travel through its thickness with a different angle from the incident one and defined by Snell's law until it reaches the opposite outer surface, where it will be refracted with an angle equal to the initial incident one (Figure 2.16).

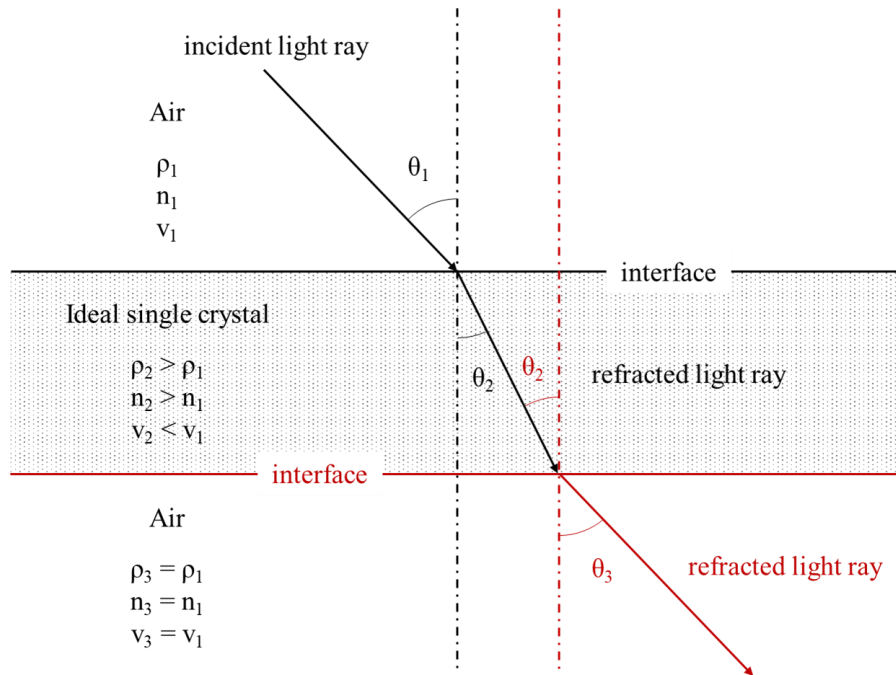


Figure 2.16 - Light transmission through an ideally perfect single crystal.

In fact, according to Snell's law:

$$n_1 \sin \theta_1 = n_2 \sin \theta_2 \leftrightarrow \theta_2 = \sin^{-1} \left(\frac{n_1}{n_2} \sin \theta_1 \right) \quad (29)$$

$$n_2 \sin \theta_2 = n_3 \sin \theta_3 \leftrightarrow \theta_3 = \sin^{-1} \left(\frac{n_2}{n_3} \sin \theta_2 \right) = \sin^{-1} \left(\frac{n_2}{n_3} \sin \left(\sin^{-1} \left(\frac{n_1}{n_2} \sin \theta_1 \right) \right) \right) \quad (30)$$

$$\theta_3 = \sin^{-1} \left(\frac{n_2}{n_3} \sin \left(\sin^{-1} \left(\frac{n_1}{n_2} \sin \theta_1 \right) \right) \right) = \sin^{-1} \left(\frac{n_2}{n_3} \cdot \frac{n_1}{n_2} \sin \theta_1 \right) \quad (31)$$

$$n_1 = n_3 \rightarrow \theta_3 = \sin^{-1}(\sin \theta_1) \leftrightarrow \theta_3 = \theta_1 \quad (32)$$

Even though single crystals are known for their exceptional optical properties, their production and flexibility in the designing stage is heavily restricted by the costs associated with lengthy grain growths and machining time and equipment. The only viable alternative to single crystal materials are transparent Polycrystalline Ceramics (PCCs), especially in harsh and demanding environments where glass is not adoptable. In fact, polycrystalline ceramics have demonstrated their capabilities of matching and, in some instances, overachieving the thermomechanical and optical properties of single crystals at significantly lower manufacturing expenses [107–109], rapidly finding application in aerospace, lasers systems, lighting, armour as well as defence equipment and lenses [100,110,111]. However, as soon as a light ray hits the surface, crosses the interface of PCCs and travels through a real polycrystalline ceramic medium, it encounters grain boundaries, irregularities, pores, impurities and defects that will affect its propagation direction (Figure 2.17).

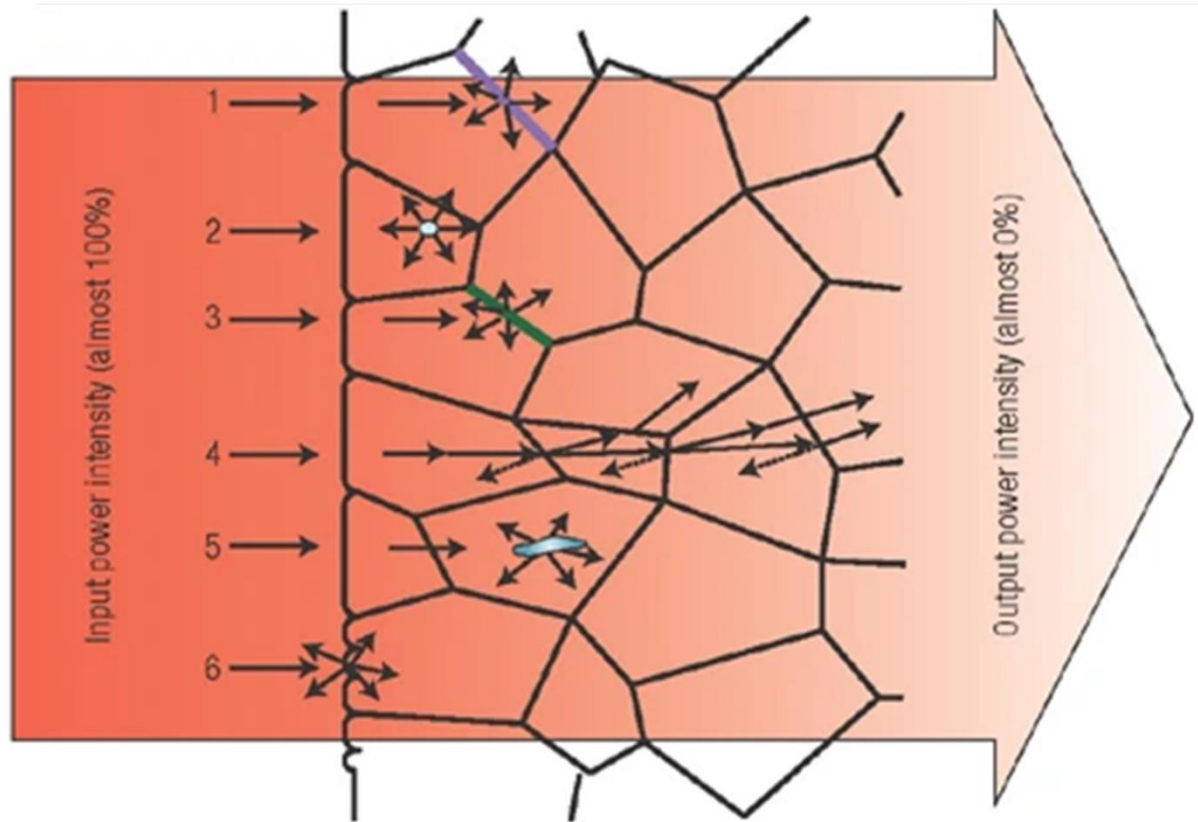


Figure 2.17 - Possible sources of light scattering in ceramics: (1) grain boundaries, (2) pores, (3) impurities, (4) double refraction, (5) secondary phase, and (6) surface roughness [111,112].

Nonetheless, although the attenuation of these undesired characteristics could be quite challenging and requires attentive experimentation to reduce the amount of light energy dispersed into the medium, transparent PCCs have been fabricated via advanced modern technologies. Optimising the manufacturing processes parameters to achieve fully dense and highly pure components with smooth surfaces and well-defined microstructure while avoiding contaminations and pores inclusion is the key to obtaining transparent polycrystalline ceramics and the aim of current research investigations.

2.4.1 Transparent ceramic materials and applications

Transparent polycrystalline alumina (PCA) can mainly be generally categorised in simple and complex metal oxide-based ceramics and non-oxide ceramics. The primary emphasis in research has been placed on transparent ceramics composed of oxides due to their enhanced chemical stability and simplified synthesis processes in comparison to non-oxides and their superior mechanical strength compared to fluorides. While among simple and complex oxide ceramics, yttria (Y_2O_3), zirconia (ZrO_2), alumina (Al_2O_3), yttrium aluminate ($\text{Y}_3\text{Al}_5\text{O}_{12}$ or YAG), magnesia (MgO) and magnesium aluminate spinel (MgAl_2O_4) are the most investigated ones, in the context of non-oxide ceramics the most renowned materials are aluminium oxynitride (ALON) and silicon nitrides (Si_3N_4) solutions.

Due to its exceptional physical and chemical characteristics as well as its remarkably wider transparency range (~ 0.2 to $\sim 8 \mu\text{m}$) compared to other PCCs materials, yttria is regarded as a very promising transparent polycrystalline ceramic. Y_2O_3 crystallographic structure is body-centred cubic material with bixbyite or cubic-C structure [113]. Originally developed in 1967 by Lefever and Matsko [114], translucent and transparent yttria ceramics have been mostly used in the development of infrared domes, semiconductors, refractories, scintillators and laser applications [100,115]. Despite its high melting point ($\sim 2400^\circ\text{C}$), significant resistance to corrosion, higher density and superior thermal conductivity as well as a reduced thermal expansion coefficient, which makes it an even more optimal choice for scintillators and lasers compared to single crystals YAG [116], yttria limited mechanical properties relegate it from its adoption in very harsh environments. However, the inclusion of additives and dopants, in particular La_2O_3 [117,118] and Yb [119], promoted the achievement of a finer microstructure and improved thermal management for high-power laser applications, respectively.

Zirconia has garnered significant attention and utilisation due to its remarkable mechanical and functional characteristics, including reduced thermal conductivity, enhanced oxygen diffusivity and elevated toughness. Under normal atmosphere, but at different temperatures, it has three well-defined crystal phases: cubic, tetragonal, and monoclinic [120]. Transparent ZrO_2 ceramics, particularly yttria-stabilised zirconia (YSZ) doped one to stabilise zirconia crystallographic structure when vacancies are present [121], have been the subject of substantial and widespread research due to their inherent qualities. The inclusion of Y_2O_3 leads to an enhancement in ionic conductivity, which facilitates its application as an electrolyte in solid oxide fuel cells. Due to its exceptional blend of mechanical and optical characteristics, in recent years, there has been a growing interest in the study of polycrystalline transparent cubic yttria-stabilized zirconia at different levels of Y_2O_3 -addition (usually from 3 mol% to 8 mol%). However, since cubic zirconia possesses a value of the refractive index that surpasses the ones observed in optical glasses and other oxides, specifically ~ 2.2 . its application to light-based manufacturing techniques is challenging, even though its specific combination of mechanical and optical characteristics is particularly interesting in the field of optical lenses of digital cameras and mobile phones [122].

Alumina can count exceptional resistance to corrosion, elevated hardness, notable strength and optical properties among its noteworthy characteristics, but possesses an anisotropic crystal structure consisting of a distorted hexagonal closest packed layer sequence of oxygen which causes birefringence and hinders transparency effects. When microstructural grain sizes below $1\text{ }\mu\text{m}$ are achieved through the addition of sintering aids, particularly MgO , the birefringence effect is reduced and Al_2O_3 can exhibit exceptional hardness, higher than the ones of other transparent materials to the point that polycrystalline alumina could potentially completely substitute sapphire in defence and armour applications [123]. In fact, even though

the grain size and residual porosity of transparent Al_2O_3 ceramics significantly influence their optical and mechanical characteristics [124,125], their obtainable transparency renders them highly promising options for several applications, such as transparent armour, electromagnetic domes and high-pressure metal halide lamps envelopes. However, due to the necessity of employing elevated sintering temperatures ($\geq 1900^\circ\text{C}$), the balance between optical transparency and mechanical properties is very delicate as high sintering temperatures will promote grain growth, lowering the achievable mechanical strength. Therefore, in order to decrease the needed sintering temperature while facilitating densification, the utilisation of sophisticated sintering procedures, such as vacuum sintering, SPS and HIP, the optimisation of sintering aids inclusion and the adoption of novel processing strategies are necessary.

Yttrium aluminium garnet, as the name describes, combines the advantages of yttria and alumina trying to mitigate their weaknesses. It possesses a cubic crystal structure and, hence, its crystallographic structure is isotropic which impedes the insurgence of birefringence effects. Transparent YAG ceramics serve as a significant structural material for high-temperature applications due to steady chemical properties, distinctive homogeneous optical properties and exceptional thermal stability. Moreover, thanks to its ability to readily replace yttrium ions in the host lattice, rare-earth ion dopants, especially neodymium, erbium and cerium, can effectively increase YAG potentialities in solid-state laser applications. In fact, since its introduction in 1995 as a transparent PCC thanks to the work of Ikuese et al. [126,127], Nd-doped yttrium aluminate has been consistently used as the main material for laser media, both as single crystal and PCC, while Ce:YAG is widely known for its adoption in scintillators and light-emitting diodes [100].

Polycrystalline magnesia cubic crystal structure allows MgO to possess crystallographic isotropic features, ideal for transparency effects. In fact, together with PCA, magnesia is

classified as a potential replacement for sapphire in sensor guarding in extreme environments and infrared windows. Although MgO has interesting optical and thermomechanical characteristics, its manufacturing for transparent applications has been proven really challenging by the elevated sintering temperature needed for achieving complete densification (melting point at ~ 2800 °C), even when fluorides and chlorides were added to improve its sinterability [128,129]. Presently, the optical characteristics of MgO ceramics documented in the available literature are notably inferior to those exhibited by their single-crystal equivalents.

Magnesium aluminate spinel is characterised by an isotropic face-centred cubic arrangement of oxygen atoms and any thermally induced phase alterations cannot be detected, hence no possible polymorphic transformation can be observed. Spinel stands out as an exceptional optically transparent ceramic due to its remarkable mix of distinctive thermal and mechanical qualities as well as its optical transparency to electromagnetic radiation throughout a broad spectrum, specifically within the range of 0.2 to 5.5 μm , surpassing the capabilities of its competitors, sapphire and AlON, over 4.5 μm in defence applications [100]. Furthermore, due to its physical properties, hardness and high transmittance in a wide electromagnetic spectrum, spinel has emerged as a very desirable material for the production of advanced optical components, including lenses, infrared protective windows and missile domes as well as transparent armours and windshields in military operative vehicles [130–132].

Among transparent non-oxide ceramics, aluminium oxynitride is probably the most renowned. It possesses a defect cubic structure which results in a cubic spinel structure in the presence of a small addition of nitrogen, which guarantees consistently enhanced transmission capabilities. When optimally manufactured, AlON is slightly harder than magnesium aluminate and almost as hard as single crystal sapphire, but it exhibits an exceptional transmittance of at least 80% in the wavelengths from 0.2 to 2.5 μm . Patented in 1985 by Raytheon Company,

aluminium oxynitride favourable optical and mechanical characteristics render it suitable mainly for deployment in various defence applications, predominantly transparent armour as well as domes for missiles and windows for aeroplanes [133].

Finally, silicon nitrides solutions, also known as Sialon ceramics hold significant importance in the field of engineering ceramics due to their exceptional strength throughout a broad spectrum of temperatures, notable resistance to thermal shock and reasonably good chemical stability. Furthermore, the addition of dopants, such as Y_2O_3 and Eu_2O_3 in Joshi et al. investigations [134], has been proven highly beneficial in the production of transparent yellow-coloured Sialon ceramics. However, the utilisation of advanced sintering processes like HP and SPS is still necessary to reach mechanical strength and optical properties comparable to the ones of other PCCs.

2.4.2 Transparent ceramics conventional processing

2.4.2.1 Shaping processes

The fundamental basis of every process aimed at producing transparent ceramics is the high purity of the materials involved, which has to be at least 99%, and the strict avoidance of cross contamination occurrences. In fact, the presence of impurities and inhomogeneities might lead to undesired scattering, hence diminishing the ultimate optical quality that can be attained by the PCC. Furthermore, the synthesis of the powder may strongly affect the characteristics of the resulting material, particularly its homogeneity and, consequently, its sintering behaviour.

The synthesis process known as solid state reaction is generally recognised as one of the most commonly employed techniques and consists of the mixing of ceramic powders in stoichiometric proportions, which are subsequently subjected to elevated temperatures. Then,

the occurring chemical reaction shapes the powder in the final solid phase compact [135]. On the other hand, widely used wet chemical methods, the sol-gel technique and the chemical co-precipitation are similar processes to synthesise ceramic powders for transparent applications involving the addition of organic components later precipitating. Despite both processes providing highly pure and homogenous powders [136,137], they come at a significant cost in terms of processing time.

Nevertheless, the most important part of the process chain in the fabrication of transparent ceramics relies on the various sintering techniques employed to achieve full densification with limited scattering sites. Among these techniques, hot pressing, hot isostatic pressing, microwave sintering, spark plasma sintering and vacuum sintering can be listed. In some instances, green bodies can be initially formed via dry pressing and cold isostatic pressing (CIP) or casting methods and then sintered to the desired final properties. The difference between these two methods mainly relies on the fact that the formers are predominantly mechanical processes, during which powders are compacted with a die upon uniaxial pressing or isostatic pressing conditions applied by a fluid to form the green body, although binders may be used to improve the green stage mechanical properties [138]. The latter category, instead, employs a chemical approach by using both aqueous and non-aqueous suspensions to form ceramic shapes into moulds subjected to air drying to obtain the final green parts, which are basically free of design constraints and usually more homogenous than dry pressed ones [138]. Irrespectively of the fabrication procedure chosen, debinding to remove organics and binders is necessary, followed by sintering or advanced pressing techniques.

2.4.2.2 Sintering consolidation processes

The method of hot pressing sintering is a powder metallurgy technique that involves subjecting a powder or powder compact to high pressure and low strain rate and, thus, it is mostly employed in the manufacturing process of hard and brittle materials due to its quasi-static nature. HP is conducted at an elevated temperature that facilitates the occurrence of sintering and creep phenomena by means of thermal energy and mechanical force with the aim of rearranging particles to achieve full densification and initiating the plastic flow occurring at the interfaces between particles (Figure 2.18).

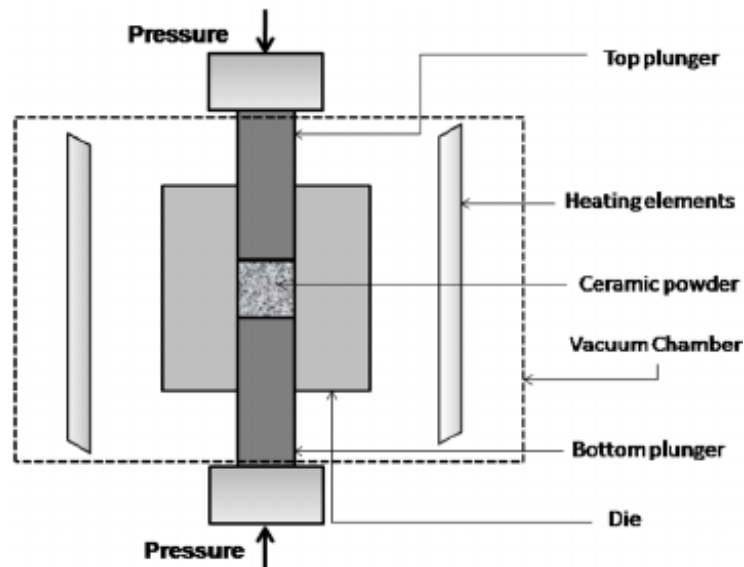


Figure 2.18 - Schematic of the hot pressing process [139].

HP has been successfully used for producing transparent ceramics and various examples can be found in the literature. Balabanov and co-workers managed to obtain highly transparent spinel, specifically with an in-line transmittance of 83.7%, at 1.1 μm by hot pressing previously sol-gel casted MgAl_2O_4 powders [137]. Due to its capabilities of impeding the development of grains and inducing plastic deformation at low temperatures and high pressures, hence

eliminating the presence of pores and extra phases that may be present, finer microstructures can be achieved and grain growth contained [140,141]. Similarly, YAG and yttria have also been produced via HP method. Liu and colleagues prepared yttrium aluminate garnet samples at high pressure (2-5 GPa) and modest temperatures (300-500 °C), which hindered the atomic diffusion among grain boundaries and resulted in fully dense parts with nanosized grains [142]. Podowitz and colleagues adopted HP and europium addition to further improve the optical properties of yttria by controlling ionic diffusivity by subjecting the samples to a pressure of 40 MPa and a maximum temperature of 1580 °C [143]. Finally, hot pressing has also landed excellent results in producing transparent Sialon ceramics and translucent magnesia [144,145], where pressures of 20 MPa and 24 or 45 MPa were used to improve and enhance transparency.

While HP and HIP are similar sintering procedures that differ only for the operating pressure conditions, as their names suggest, CIP and HIP are comparable in terms of process conditions, except that HIP is conducted at high temperatures and with inert gases as fluid media. The hot isostatic pressing technique involves exposing a component to elevated temperatures and subjecting it to isostatic gas pressure due to the administration of thermal energy within a high-pressure containment vessel, HIP is therefore mainly employed in the manufacturing industry to significantly enhance the density of metallic substances and to heavily mitigate the presence of porosity in several ceramic materials. In this method, the ceramic materials are usually pre-sintered to be able to handle HIP without cracking, which allows major parts design flexibility before HIP (Figure 2.19).

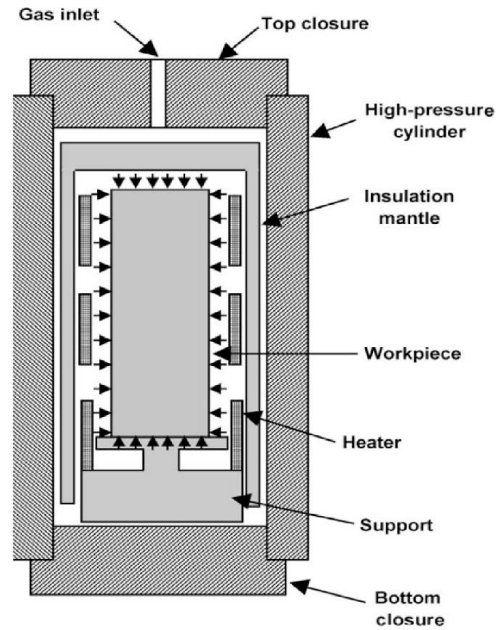


Figure 2.19 - Schematic of HIP [146].

Even though hot isostatic pressing is capable of delivering transparent components of superior quality, the costly equipment and experimental conditions are sometimes prohibitive. However, the fabrication of transparent PCCs via HIP is widely available in the literature [147–149]. Mizuta et al. managed to achieve in-line transmittances of 46% in 1 mm thick alumina samples by combining slip-casting technique and HIP under 150 MPa at 1400 °C to limit Al_2O_3 grain growth to a maximum of 15 μm [150]. Magnesium aluminate has been successfully sintered to almost full densification with in-line transmittance higher than 82% in the visible spectrum via HIP by Sutorik and colleagues [151]. Vacuum sintering to reduce closed porosity followed by HIP was also employed to fabricate transparent yttria components with in-line transmittance of 81.7% while reducing the risk of contamination due to HP graphite heating elements [152]. A similar procedure was also applied for the production of highly transparent Nd:YAG parts without the need for annealing procedures [153,154].

Microwave sintering is a distinct sintering method that deviates substantially from the standard sintering processes since the materials being treated absorb microwave power, which is then transformed into internal heat that rapidly increases the temperature of the samples from the inner core. Reduced holding times and lower dwelling temperatures achieve higher levels of transparency compared to other sintering techniques while operating at improved efficiency and increased heating rates. However, the ceramic subjected to this procedure has to be a good receptor within the operational frequency range of the adopted machine, otherwise the parts may not even reach the sintering temperature and result in poor outcomes (Figure 2.20).

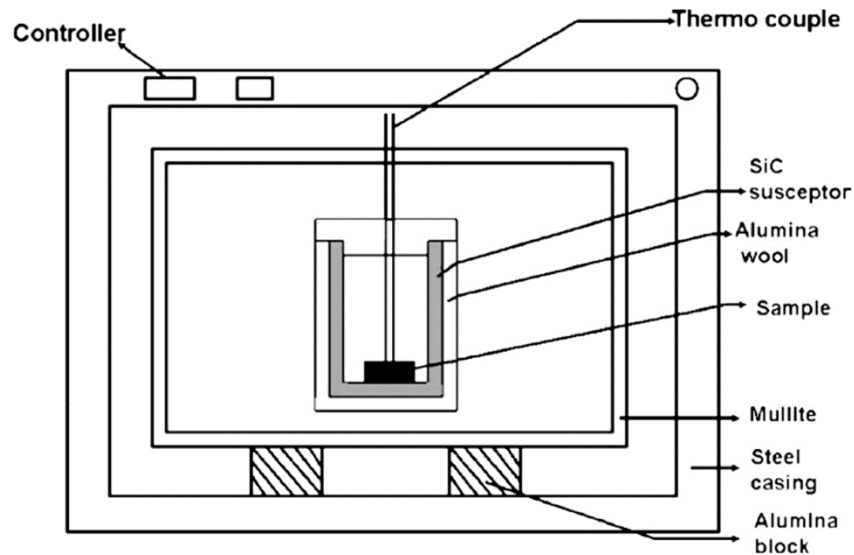


Figure 2.20 - Schematic of microwave sintering [155].

Fully transparent aluminium oxynitride with a transmission of 60% was achieved by Cheng and co-workers via microwave sintering at 1800 °C for 1 h using an in-house developed single mode applicator working at 2.45 GHz [156]. Afterwards, the same research group managed to obtain transparent alumina adopting microwave sintering as a post-sintering technique to achieve full densification. In fact, by only microwave sintering the samples at 1750

°C for 15 minutes, a gain of 20% in transmittance was obtained [157]. On the other hand, Kerbart and colleagues produced transparent spinel samples with submicron grains by means of uniaxial-pressure-assisted microwave sintering [158]. In their research inspired by the sinter-forging process, magnesium aluminate with high mechanical properties and a transmittance of 83% in the infrared range was fabricated in air with a very short thermal process. Furthermore, microwave sintering at a temperature of 1500 °C was proven capable of delivering highly transparent $\text{Y}_2\text{O}_3\text{-MgO}$ ceramics in the infrared region [159].

Spark plasma sintering is an emerging technique that has been developed to achieve high-density and fine-grained transparent ceramics at relatively low temperatures and in a short period of time. SPS employs a high-density current flux that passes through both the sample and the die, resulting in Joule heating within the sample. As a result of its narrow periods of time for consolidating the samples, it presents a promising approach for compacting nanoscale powders, circumventing the inevitable occurrence of substantial grain growth. The process of densification in spark plasma sintering is commonly categorised into three distinct phases [160] and it is promoted by the applied high pressure throughout all the stages. While the initial stage is distinguished by the compaction of the particles, the subsequent stage is associated with the particles necking and consequent sliding of grains. The last one, instead, primarily involves the elimination of pores (Figure 2.21).

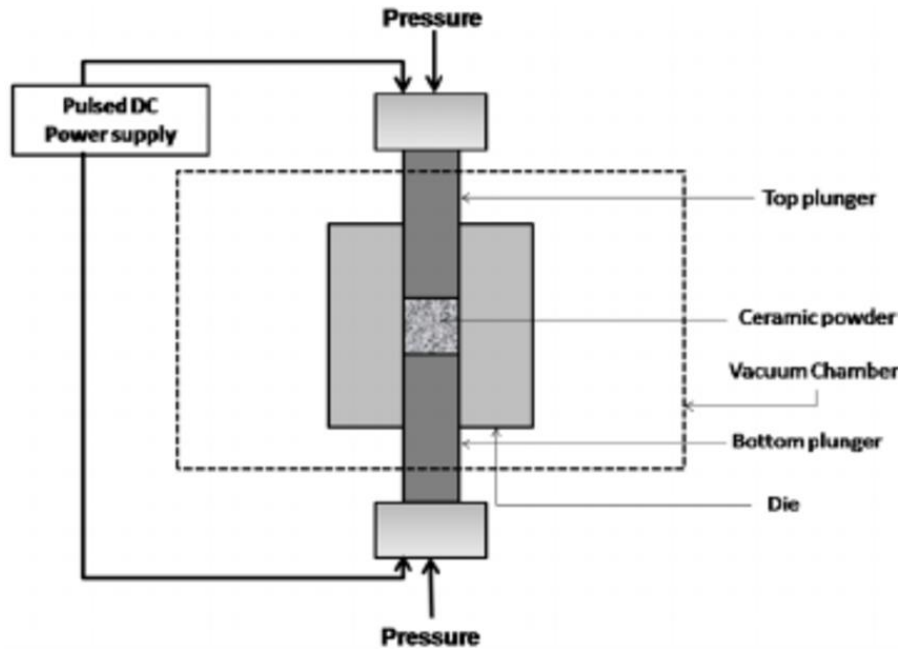


Figure 2.21 - Schematic of SPS [139].

SPS has been successfully used to sinter at lower temperatures most of the aforementioned PCCs to transparency, particularly alumina, which is affected by excessive grain growth due to the high sintering temperatures needed and the lengthy holding time durations [161,162]. Transparent spinel was also obtained by Wang and Zhao under the low pre-load pressure of 5 MPa at 1500 °C for 3 minutes following a heating schedule of 100 °C/min, landing on an outstanding transmittance of 85% at 2 μm [163]. In addition, laminated composites of spinel and alumina were fabricated via SPS after meticulous optimisation of the process parameters [164]. Magnesia [165], zirconia [166] and YAG [167] have also achieved translucency and transparency via SPS, demonstrating its wide adaptability and versatility to accommodate the requirements of the majority of transparent PCCs. However, SPS facilities require a substantial monetary investment.

Finally, vacuum sintering entails the utilisation of a vacuum apparatus to conduct sintering procedures with the aim of attaining superior outcomes compared to those executed

under atmospheric pressure conditions. It can be used for all the transparent PCCs hereby reported and, although it may require subsequent postprocessing and it may not lead to the same outcomes of the aforementioned processes, it is the relatively most diffused sintering method among the advanced sintering techniques presented in this section. Yttria [167], doped yttrium aluminate [168], and alumina [169] have all been vacuum sintered to translucency and transparency with successful and satisfactory results.

2.4.3 Additive manufacturing of transparent ceramics

Compared to the research and experimentation conducted on conventional manufacturing routes for transparent PCAs, the information on additive manufacturing of transparent ceramics that can be found in the literature is very scarce, specifically with regard to transparent alumina.

In this field, the main focus of research interest has been directed towards the additive manufacturing of yttrium aluminate garnet and zirconia-based transparent PCCs, most likely for their wide adoption and diffusion in the laser and biomedical sectors, respectively. Zhang and Wu produced Nd:YAG via DLP with a layer thickness of 25 μm with the aim of establishing a procedure to demonstrate the industrial scalability of digital light processing. In particular, the use of specifically designed pre-sintering procedures to induce the YAM phase formation, together with long sintering schedules in vacuum, avoided the insurgence of bubbling which could induce cracking and resulted in samples with a density of 99.9% and maximum in-line transmittance of 80% in the visible light spectrum. However, a further postprocessing of annealing was required to remove colouration and oxygen vacancies [170]. Hu and co-workers also adopted DLP as the 3D printing technique to produce ceramic phosphors for high-flux laser lighting exhibiting excellent luminescence of 20.7 W/mm², higher

than the one obtained via conventional dry pressing and vacuum sintering [171]. Cooperstein and colleagues used TPP to print miniature Nd:YAG samples in the micrometre range which were transparent in the visible light range and able to show infrared emission at 1064 nm, the wavelength at which commercially available Nd:YAG emit. In addition, they managed to print micrometre-sized ruby samples. However, due to the scale of the prints and the constraints in the size of TPP, their applications are limited although present [172]. 10 at.% Yb:YAG has been produced for the first time via SL by Hostaša et al. and it was subsequently vacuum sintered, achieving an output power of 2.16 W around 1030 nm with a slope efficiency of 17.6%. The research group itself declared that further optimisation of process parameters might lead to improved optical performances [173]. DIW was successfully employed to fabricate fully-dense transparent Nd:YAG in a top hat geometry [174] and rare-earth-elements-doped YAG rods in order to obtain a constant refractive index along the printed solid state laser media rods through gradient-based doping [175–178]. Nonetheless, the presented processes required further optimisation to reach their full potential. Furthermore, direct ink writing was proven to be able to produce 99.7% dense transparent YAG without recurring to cold isostatic pressing or HIP, even though the use of the latter was proposed as a possible post-treatment to improve outcomes and rapidly sharpen the in-line transmittance vs wavelength slope to match CIPed parts [179]. Finally, even IJP has been demonstrated as a viable alternative to fabricate YAG-based laser gain media [180].

Zirconia has been additively manufactured even though its high refractive index and density render the process quite challenging. 3D printing of ZrO_2 has been reported via DIW by Li and colleagues in their research [181], where 3 mol% yttria-stabilized tetragonal zirconia was manufactured starting from a high solid loading ink to reach the relative density of 99.85% only after subsequent debinding, sintering and HIPing. After polishing, the remarkable

transmittance of 71% in the mid-infrared wavelength was obtained. Partially translucent samples of ZrO_2 doped with 5 mol.% Y_2O_3 were also manufactured via robocasting [182]. However, most of the research on zirconia has been conducted on lithography-based additive manufacturing despite its refractive index. Translucent partially stabilised zirconia at 4 mol.% Y_2O_3 for dental application was manufactured by Kim and colleagues, obtaining good optical transmittance and almost full densification after air sintering at 1500 °C for 2 hours, mainly due to the high starting solid loading of 50 vol.% [183]. Another dental application was proven by Xiang and co-workers, who analysed the effect of different build orientations on the geometrical accuracy and optical translucency of pure zirconia and demonstrated that better physical properties at the expense of geometrical accuracy could be achieved when samples were printed vertically rather than horizontally [184]. Komissarenko et al. were also able to produce semi-translucent zirconia utilising low solid loaded slurries to produce complexly shaped pure zirconia. 35 vol.% loaded UV-curable slurries were prepared and their rheological properties were tailored to the research scope, achieving a relative density of 99.6% after undergoing DLP, slow debinding and air sintering at 1480 °C for 2 hours [185]. In addition, recently, Wang and colleagues explored the potential of 5 mol% yttria-partially stabilised zirconia (5Y-PSZ) for dental restoration applications by testing the influence of different solid loadings on the mechanical properties, microstructural evolution and translucency via SL and finding that the density of green and sintered samples, as well as the flexural strength and the translucency, is significantly affected positively by increases in the starting solid loading [186]. Even more recently, the same research group deepened the study on 5Y-PSZ loaded slurries, getting a better understanding of the zirconia fracture modes, which changed from intergranular to a mix of intragranular and intergranular in the temperature range in which they chose the sintering

temperature (1450-1550 °C). Moreover, they managed to obtain at 1500 °C the minimum value of 0.43 for the contrast ratio [187].

Transparent alumina has been reported to be additively manufactured only via 3D printing [110] or digital light processing [80]. In fact, due to its anisotropic crystal structure which causes birefringence and its high melting point, its sinterability is quite poor if transparent PCA has to be achieved. Carloni and co-workers 3D printed alumina parts which then underwent debinding, single-step and two-steps vacuum sintering at 1875 °C for 6 hours and, finally, polishing. In their work, maximum values of 99.92% relative density and 71% total transmittance in the near-infrared range were reached, with a slight decrease of the transmittance in the visible range, which was attributed to defects introduced during 3D printing that affected the maximum relative density obtainable. Nonetheless, total transmittance levels comparable to the ones obtained via CIP were achieved in the near-infrared zone. Even though Carloni and colleagues managed to produce transparent alumina samples via 3D printing and vacuum sintering without sacrificing physical qualities when compared to conventional CIPing, however, the slurry optimisation process was extended only to alumina solid content and isobam addition rather than including milling conditions, additives and debinding regimes. Moreover, the intrinsic properties of 3D printing constrained the definition of the features to a fraction between 25% and 70% of the adopted nozzle diameter, resulting in layer thicknesses of 0.2 mm and 0.6 mm, a printing resolution that hinders the adoption of the developed procedure in a wide variety of applications where high geometrical accuracy is needed. Further reductions of the layer height resulted in excessive printing time and poor interlayer adhesion due to premature drying of the slurry. Therefore, investigations on alternative approaches are needed to overcome these limitations. Conversely, Sun et al. [80] succeeded in producing translucent alumina through DLP by using a commercially available high solid loaded slurry

(55 vol.%) that included a prearranged amount of MgO as a sintering aid and after thermally treating the samples in a vacuum sintering furnace at 1700 °C for 2 hours. In their study, the effect of different exposure times at a fixed exposure power was investigated to better understand its effect on the interlayer cohesion by inspecting the degree of polymerisation conversion in order to minimise the insurgence of internal stresses during thermal postprocessing. It was concluded that the shortest exposure time to guarantee enough curing depth should be regarded as the optimal one for DLP as increased exposure time may negatively impact the sintering performance. After following an accurate debinding regime, sintering the samples in vacuum and polishing, intricately shaped crack-free translucent demonstrators with an in-line transmittance of 15% over 600 nm were successfully fabricated. Even though this pioneering work is crucial for the introduction of DLP as a feasible and promising technology to manufacture transparent PCA, however, no optimisation work or design of experiment was carried out to investigate the influence of slurry preparation techniques and slurry components on the continuously evolving relative density of the parts and the printing conditions. In addition, since the adopted slurry is commercially available, the process relies on the availability of the said slurry and the constancy of its rheological properties rather than on the in-house slurry formulation capabilities. Furthermore, the effects of different printing parameters, with the exception of the exposure time, were not tested while the shrinkages and the geometrical accuracy were not mentioned. Finally, the influence of different debinding and sintering regimes together with the effect of different sintering atmospheres and the inclusion of diverse additives on DLPed samples were not explored. Therefore, further research in these areas is needed to fully comprehend the DLP capabilities of manufacturing transparent PCA without resorting to costly advanced sintering procedures like HIPing.

In the context of non-oxide ceramics, silicon nitrides solutions were manufactured by DLP in the work of Chen and colleagues [188]. In their research, wave-transmitting $\text{Si}_3\text{N}_4\text{-SiO}_2$ composite ceramics with excellent wave-transparent performances were fabricated and the influence of the different sintering temperatures on the physical proprieties, phase composition and microstructure was systematically studied, particularly the dielectric properties.

Finally, magnesium aluminate spinel has also been produced via different additive manufacturing techniques. The constantly increasing research interest in this specific material is due to its exceptional blend of optical and mechanical properties. Pappas and Dong [189] focused their research very actively on laser direct deposition. After demonstrating the feasibility of producing in-situ thin walls of single phase transparent spinel from alumina and magnesia precursors with a layer thickness of 80 μm and a transmittance of 46%, they acknowledged that cracks and residual porosity impeded the achievement of high transparency able to match the theoretical one obtainable through conventional processing. The same research group addressed these problems in another publication providing possible strategies to overcome them [190]. Finally, transparent MgAl_2O_4 with an optical transmittance of 82% at the wavelength of 632.8 nm was produced via direct laser deposition after attentive tailoring of powder flow rate and laser power, providing components with mechanical properties comparable to their conventionally sintered counterparts [191]. However, the insurgence of cracking was still noticeable due to the high thermal gradients. Further studies conducted by the same research group addressed the persistent issue correlated with the use of high power lasers by introducing a filament-fed procedure rather than a blown powder one to dramatically reduce the cracking phenomenon and obtain results comparable with conventional direct laser deposition [192]. In conclusion, SL 3D printing of spinel was demonstrated feasible when subsequent debinding, pre-sintering at 1650 $^{\circ}\text{C}$ and HIPing at 1800 $^{\circ}\text{C}$ were included.

Following this lengthy and costly, but extremely effective process chain, samples reached the outstanding transmittance of 97% of the theoretical limit after optimising the dispersant concentration and the postprocessing dwell temperatures [193].

In summary, with the exception of the recent achievements by Carloni et al. in extrusion-based printing techniques for producing transparent alumina and the initial studies of Sun and co-workers on DLP of PCA, no further studies have been identified pertaining to the utilisation of additive manufacturing in the context of transparent polycrystalline alumina, probably due to the encountered difficulties in the production of transparent alumina in terms of limiting grain growth and hindering the birefringence effect while avoiding advanced and costly sintering equipment. Hence, further research is necessary to fully harness the advantages of digital light processing in combination with polycrystalline alumina-based ceramics thermomechanical and optical properties for promoting its adoption in industrial settings, particularly in defence and aeronautical applications.

2.5 Summary of research questions

Significant untapped potential for the additive manufacturing fabrication of advanced ceramics is yet to be exploited, particularly with respect to transparent alumina ceramics, as it still is in its early stages. The significant attention to density evolution, geometrical accuracy and microstructural modifications needed to ensure the successful production of transparent ceramics hinder their fabrication via additive manufacturing techniques. Controlled grain growth, purity, full density and reduction of defects and porosity in the ceramic matrix constitute the main obstacles to achieving translucency or transparency. However, conventional manufacturing routes are limiting the possible audience to which the production of transparent

ceramics can be exposed due to the high costs associated with their fabrication and machining. Nevertheless, in turn, conventional manufacturing of transparent PCA imposes heavy processing constraints in terms of geometrical flexibility and design at both small and big scales. In order to effectively tackle critical issues pertaining to the creation of transparent ceramics, the progress of additive manufacturing technology necessitates resolving the obstacles associated with the printing process. In order to fully realise the potential of ceramic additive processing, it is important to have a comprehensive understanding of its intricacies and it is crucial to possess the capability of tailoring the rheological properties and photopolymerisation features of the ceramic suspensions by formulating in-house developed slurries to appropriately meet the specific objectives. This can be achieved through a systematic and methodical examination of the influence of preprocessing steps and printing settings on the achievable geometric accuracy and physical characteristics of DLPed alumina green components.

Nonetheless, the importance of DLP thermal postprocessing to achieve the desired microstructure and physical properties should not be disregarded. In fact, thermal debinding is a determining step in the definition of alumina components quality and purity prior to sintering, hence a clear understanding of its process parameters and their influence on the brown parts is needed. Furthermore, comprehending the effects of DLP and subsequent debinding on the initial conditions of the sintering process is necessary in order to produce defect-free ceramic components that may be used to their fullest potential for a wide variety of applications. Examining the influence of the sintering process parameters in order to achieve alumina ceramic parts with high density and minimal defects via the development of a thermo-viscoelastic numerical model that considers the temperature and relative density evolution in the evaluation of alumina thermomechanical properties will serve to accurately depict the

sintering phenomenon of debound brown parts. Finally, even though different sintering aids and regimes have been investigated in the literature to further push the sinterability of alumina to its limit, an investigation of their influence on the resulting optical properties of DLPed components has yet to be conducted. Specific research on the effects of sintering regimes, firing conditions and additives on the enhancement of the densification process and the microstructural evolution of sintered alumina parts fabricated from an in-house developed slurry will illustrate the capability of AM to openly manufacture translucent and transparent ceramics and promote their widespread diffusion.

Therefore, the primary objective of this work is to address the aforementioned gaps in knowledge, thereby making a valuable contribution to the ongoing efforts aimed at demonstrating the wide applicability of AM and its versatility to be adopted as a preferential manufacturing route for the production of advanced translucent ceramics, in particular translucent PCA.

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CHAPTER 3. NUMERICAL SIMULATION OF SINTERING OF DLP PRINTED ALUMINA CERAMICS

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NUMERICAL SIMULATION OF SINTERING OF DLP PRINTED ALUMINA CERAMICS

Abstract

Digital Light Processing (DLP) technology exhibits the capability of producing components with complex structures for a variety of technical applications. Postprocessing of additively printed ceramic components has been shown to be an important step in determining the final product resolution and mechanical qualities, particularly with regard to distortions and resultant density. The goal of this research is to study the sintering process parameters to create a nearly fully dense, defect-free, ceramic component. A high-solid-loading alumina slurry with suitable rheological and photopolymerisable characteristics for DLP was created. TGA/DSC analysis was used to estimate thermal debinding parameters. The sintering process of the debound parts was studied by employing a numerical model based on thermo-viscoelasticity theory to describe the sintering process. The validated Finite Element Modelling (FEM) code was capable of predicting shrinkage and relative density changes during the sintering cycle, as well as providing meaningful information on the final shape. Archimedes' principle and scanning electron microscope (SEM) were used to characterise the sintered parts and validate the numerical model. Samples with high relative density (>98.5%) were produced and numerical data showed close matches for predicted shrinkages and relative densities, with less than 2% mismatch between experimental results and simulations. The current model may allow

to effectively predict the properties of alumina ceramics produced via DLP and tailor them for specific applications.

Keywords: additive manufacturing; DLP; alumina; sintering; numerical modelling

3.1 Introduction

Additive Manufacturing (AM) is a relatively recent manufacturing technique that is able to fabricate very complex products in terms of geometry and detail, which are unobtainable using traditional manufacturing techniques. Compared with conventional manufacturing techniques, whose working principle consists of subtracting material in order to shape the product, AM exploits the concept of creating a 3D object by the consecutive addition of 2D layers of material until the complete shape of the product is achieved. In this way, tools are not needed, accessibility issues are not present, and geometrical complexity is essentially limited by the creativity of the product designer, who can consequently take advantage of a wider workability window. Since its first experimentations and applications in the late 1950s, significant studies have been carried out in order to explore and optimise AM capabilities and potentialities, as well as adapt the approach to different materials and applications [1].

Due to the fact that the fabrication of complex 3D objects through the subsequent addition of adjacent bidimensional layers has been proven feasible and successfully employable to a wide range of applications, AM has generated significant interest due to its ability to produce net shape or near-net shape components even at small scales [2]. Fine geometric details and structural features, otherwise unobtainable via conventional manufacturing routes, are reproducible with AM techniques, frequently resulting in improved mechanical performances and characteristics [3–5]. In particular, slurry-based AM is one of the most highly investigated

approaches with regard to ceramic parts [1]. Since DLP machines are easier to maintain than other manufacturing machines and are relatively cheaper while guaranteeing optimal outcomes in terms of accuracy, resolution, final density, and mechanical performance, DLP has been proven to be one of the best candidates for the AM of ceramic parts. It also exhibits higher accuracy when it comes to postprocessed components compared with other slurry-based technologies, offering the best quality-to-cost ratio [6].

The forming tool in DLP processing is a high-powered projector, which selectively cures the slurry layer by layer until the completion of the 3D part. As a consequence, similar to all light-source-based processes such as stereolithography (SL), it is subject to different ways of failure linked to its working principle and the power source required. Underestimating the necessary time for the first layers to completely adhere to the building platform, as well as not taking into account the grade of compatibility between the platform and the processed material itself, may cause the failure of the procedure. The wrong choice of exposure time, bad positioning of the light source, and unforeseen effects of viscosity may all significantly affect the photopolymerisation phenomenon and create undesired tension-positive forces at the green part–slurry interface [7]. In fact, the mechanical properties of the final product are strictly dependent on the exposure time of the polymeric photosensitive slurry, the energy dose, the solid loading and the layer thickness. The greater the solid loading is, the higher the expected green part density will be; although, it has been demonstrated that above the saturation values, ceramic particles in excess may result in loose powder being barely attached to the printed part [8]. However, optimal conditions have to be found, since increments in the initial solid loading correspond to increasingly higher viscosities, which instead should remain low in order to facilitate layer coating, avoid delamination and promote structural homogeneity. In addition to layer thickness, exposure time and solid loading, the chemical composition and addition of

additives play a significant role in the slurry properties and the features of the final part. Dispersant types and contents also have to be taken into account, since their impact on the slurry's viscosity and the final microstructure of the part is significant, as their tailored and optimised addition can result in a decrease in both the sedimentation rate and the viscosity and in an increase in the usable maximum solid loading percentages [9–11].

However, the postprocessing of additively manufactured ceramic parts has been proven to be an even more crucial step in the determination of the resolution of the final product and its mechanical properties, particularly with regard to distortions and the resulting densities. The debinding and sintering heating rate, as well as the dwell temperatures and times, strongly affect the final characteristics of the product. Ceramic powders [12] as well as binders [13] and the type of debinding process [14], strongly influence the quality of the postprocessing steps and the strength of the final product. For instance, adopting a two-step debinding process in different atmospheres can help to tailor the reaction rate of the binder, and significantly limit defect formation in the alumina parts [15]. In addition, the presence of a nonreactive component within the photopolymerisable ones can reduce the shrinkage during debinding and, consequently, decrease the insurgence of both intralaminar and interlaminar fractures in the brown bodies [16]. Full-density final samples can be obtained at atmospheric pressure. Gradual heating in conventional and vacuum furnaces with diverse atmospheres [17–19], spark plasma sintering [20], or using a microwave furnace [21,22] are the main approaches to sintering ceramics to create fully dense parts, with alumina components among them. The initial particle size; the presence of defects and agglomerates; the starting density and, of course, the sintering cycle parameters, all affect the sintering process. Reducing the initial grain size helps the densification process while decreasing the needed dwell time, while increasing the sintering rate and temperature promotes the process activation more than the holding time, as the material

properties mainly involved are highly temperature-dependent. Nevertheless, higher dwell temperatures facilitate the lowering of the final mechanical characteristics and the increase in grain dimensions [23].

Since sintering is a complex but widely adopted powder metallurgy technique, many studies have been conducted on this topic and different modelling approaches have been adopted, such as atomistic, micromechanical and continuum models. As appears clear from the nomenclature, they differ with respect to the chosen point of view. Atomistic models [24,25] take into account time-dependent atomic positions and velocities and chemical compositions. Micromechanical ones [26,27] consider the material microstructure in order to observe material phase changes and necks formation. The continuum approach [28] models the material as a continuous medium whose thermomechanical behaviours are modelled on modified equations of the plasticity theory of solids. Multiscale modelling can also be adopted in order to investigate the interactions at different scales and for evaluating cross-interactions, although even more modelling complexities have to be taken into account, starting from the various interactions that are present across the different scales. However, due to the particular interest that AM of ceramics has attracted and due to its application to a huge variety of fields - including monolithic catalysts [29,30], aerospace, biomechanics, dentistry, microelectromechanical systems [31] and automotive ones, to mention only a few - it seems necessary to deepen the knowledge of AM techniques and their effects when applied to ceramics.

This is particularly useful in the aerospace sector, since AM of ceramics is able to provide lighter, more detailed components with enormous structural strength, hardness, and temperature resistance. High-purity aluminium oxides, for example, have a high level of hardness combined with excellent corrosion and temperature resistance. Alumina components are also electrically

insulating at high temperatures, which are commonly seen in aircraft systems. Alumina ceramics applications on HTP thrusters can be widely found in the literature. When compared to silicon, alumina is an attractive alternative that is able to reduce thermal losses thanks to its significantly lower thermal conductivity while resisting the highly corrosive action of liquid propellants such as hydrazine, although its forming process could be simplified if AM were adopted, avoiding the involvement of laser cutting and milling process [32]. Furthermore, AMed catalyst beds adopted for HTP thrusters have shown improved performance over other available coated pellets without compromising the drops in pressure [30]. In addition to the HTP thrusters, ceramic applications in the aerospace field range from brakes and wear-resistant components to seals, from electrothermal management structures to lightweight optical components and armours - such as, for example, transparent lookdown windows for aircrafts and ballistic protections, as well as missile domes, due to their capability of being exposed to harsh environments [33].

In order to obtain defect-free ceramic parts able to be exploited to their full potential for this vast range of applications, the need emerges to understand the impact of the additive manufacturing working principle on the starting conditions of the sintering process. Therefore, this investigation focuses on studying sintering process parameters to obtain high-density, defect-free, alumina ceramic parts using DLP as the additive manufacturing technique. This can be achieved by creating and exploiting a numerical model based on the thermo-viscoelasticity theory in order to describe the sintering process of debound brown parts.

3.2 Materials and Methods

3.2.1 Materials preparation

The details of the alumina slurry preparation procedure can be found in a previous study published by this research group [34]. Aluminium oxide powder (A16 SG, Almatix GmbH, Ludwigshafen, Germany) was chosen as the ceramic filler. The as-received ceramic powder was first pretreated with ethanol and 2 wt.% of dispersant (phosphoric ester salt of high molecular weight, BYK-Chemie GmbH, Wesel, Germany) to the powder content, followed by planetary ball milling. The mixture was dried first in air and then in an oven to allow solvent evaporation. Finally, the dried powder was sieved through a 250- μ m mesh. The resin preparation consisted of combining polyfunctional and monofunctional monomers (tetrafunctional = 18.6 wt.%; difunctional = 28 wt.%; monofunctional = 33.4 wt.%) together with a plasticizer (20 wt.%) to reduce delamination. Diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (Sigma Aldrich, Gillingham, UK) was then incorporated into the resin mixture as photoinitiator (0.13 wt.% to the prepared resin) (Table 3.1). The pretreated powder was incrementally added to the resin–photoinitiator mixture while continuously stirring, until a solid loading of 83 wt.% was achieved. Lastly, the slurry was mixed in a turbula mixer for at least 12 h. Prior to the printing, the prepared slurry was treated in a vacuum degasser for 10 min to remove air bubbles and to reduce the inhibition of the polymerisation.

Table 3.1 - Slurry composition.

Starting Materials	Powder	Resin–Photoinitiator Mixture
Chemical composition	Dispersant pretreated Al ₂ O ₃	Monofunctional, difunctional, tetrafunctional monomer, plasticizer, photoinitiator
Mass percentage	83 wt.% total	17 wt.% total

Laser diffraction particle size analysis was employed to measure the particle size distribution of the ceramic powder; it was carried out in a liquid dispersion composed of water and two drops of dispersant. SEM images were also taken to further investigate the morphology of the powder. To understand the flowability of the prepared suspension, the rheological behaviour of the ceramic suspension was analysed with AR 500 (TA Instruments, New Castle, DE, USA) using a 20-mm parallel plate geometry in the shear rate window starting from 0.1 to 300 s⁻¹ at a constant temperature of 20.0 °C as per the DLP printing conditions.

3.3 Digital Light Processing

The Admaflex 130 (Admatec Europe BV, Alkmaar, The Netherlands) was used as 3D printing machine, capable of obtaining a resolution of 40 µm on the layer plane with a light source of $\lambda = 405$ nm. The actual forming tool of the machine consisted of thousands of mirrors moving according to pixels to imprint the image on the viscous slurry work. As a transportation method, the Admaflex 130 adopts a rotating foil system that moves the slurry on the foil from the reservoir to the 3D building area and then to the collection zone, where a pump mechanism returns the unused slurry to the reservoir. The light-reactive slurry is exposed to light in the

working wavelength of the machine and, as a consequence, the whole layer is cured at one time due to the presence of the several mirrors. Curing repeatedly, layer by layer, the green body is then printed in its entirety.

A number of cylinders with a diameter of 5 mm and height of 10 mm were printed along the z-axis with a layer thickness of 25 μm and an energy density of 20.16 mJ/cm^2 (Figure 3.1). The printed parts were detached from the building plate and cleaned by using compressed air and dibasic ester (Sigma Aldrich, Gillingham, UK).



Figure 3.1 - Digital Light Processed green sample.

3.4 Debinding cycle

A crucial step in the post-treatment of the 3D printed parts is the removal of the photopolymerisable resin from the interspace of the ceramic particles. During the debinding process, as the temperature rises, the organic components in the green body decompose into gas molecules, which diffuse or penetrate into the surface of the green body and, in the end, get out of it while leaving behind voids inside the now brown body. Thermogravimetric (TG) and

Differential Scanning Calorimetry (DSC) analyses were carried out on a SDT NETZSCH STA in dynamic air (100 ml/min) with a heating rate of 5 °C/min [35], according to the accessible facilities availability, and were used to identify the rapid mass loss of the green body printed by the DLP process. These conditions for the TGA-DSC analysis were selected in accordance with the actual regime in which the debinding cycle was being carried out in the presented experiments. In particular, the selected debinding cycle was then performed in air in a tube furnace (TSH/1S/75/450, Elite Thermal Systems Ltd., Market Harborough, UK). However, after experiencing evident cracking adopting a heating rate of 5 °C/min, the experimental heating rate was kept to 0.2 °C/min to completely avoid the insurgence of cracks due to the binder removal and allow the parts to gradually release the decomposed resin.

3.5 Sintering cycle

Sintering experiments were carried out at different dwell temperatures and dwell times in order to analyse density developments and shrinkages of the DLP printed cylinders. Six different sintering cycles were performed as detailed in Table 3.2; the respective sintered demonstrators are as shown in Figure 3.2. Sintering cycles were chosen in line with guidelines that can be widely found in the literature and within the workability window of the available sintering furnace, whose maximum operating temperature was 1700 °C. In particular, the lowest sintering temperature of 1540 °C was selected as it was the sintering temperature adopted by the powder supplier. In the end, three dwell temperatures, ranging from 1540 °C to 1650 °C, and two different holding times were selected, while fixing the heating rate at 3 °C/min.

Table 3.2 - Sets of sintering experiments performed.

	T1	T2	T3	T4	T5	T6
Dwell temperature (°C)	1540	1600	1650	1540	1600	1650
Dwell time (h)	2	2	2	4	4	4

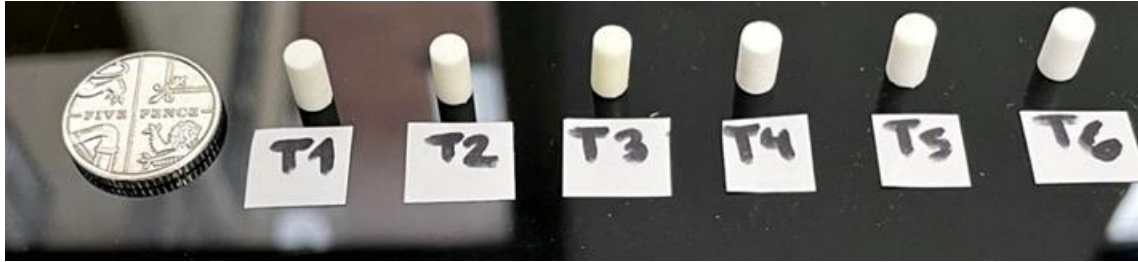


Figure 3.2 - Sintered samples resulting from the different sintering trials.

The diameter and height dimensions of the green, brown and sintered samples were collected. Four samples were fabricated for each sintering trial and the average values of diameters and heights, together with the corresponding standard deviations, were reported. In addition, SEM pictures at the green, brown, and sintered stages were taken to reveal the surface evolution.

3.6 Numerical Modelling

In order to predict the behaviour of the alumina ceramic samples undergoing different sintering cycles, a finite element model was developed using the ABAQUS software and user-defined subroutines. The FEM code is based on thermo-viscoelasticity theory, and thus, takes its constitutive equations from it. Variables such as surface tension energy, shear and bulk viscosity, and average grain dimension need to be taken into account. From a macroscopic point

of view, the material is believed to behave as a continuum and, consequently, based on the abovementioned thermo-viscoelastic model, the total strain rate is given by the addition of three different components, i.e., elastic, thermal, and viscous ones [28]. Therefore,

$$\dot{\boldsymbol{\varepsilon}} = \dot{\boldsymbol{\varepsilon}}^e + \dot{\boldsymbol{\varepsilon}}^{th} + \dot{\boldsymbol{\varepsilon}}^{visc} \quad (1)$$

Consequently, the constitutive equation assumes the following aspect:

$$\dot{\boldsymbol{\sigma}} = D\dot{\boldsymbol{\varepsilon}}^e + \dot{\boldsymbol{\sigma}}^s = D(\dot{\boldsymbol{\varepsilon}} - \dot{\boldsymbol{\varepsilon}}^{th} - \dot{\boldsymbol{\varepsilon}}^{visc}) + \dot{\boldsymbol{\sigma}}^s, \quad (2)$$

where

$$\dot{\boldsymbol{\varepsilon}}^{th} = \alpha T \mathbf{I}, \quad (3)$$

$$\dot{\boldsymbol{\varepsilon}}^{visc} = \frac{\boldsymbol{\sigma}'}{2\eta_s} + \frac{tr(\boldsymbol{\sigma}) - 3\sigma^s}{9\eta_b} \mathbf{I}, \quad (4)$$

$$\boldsymbol{\sigma}^s = \sigma^s \mathbf{I}, \quad (5)$$

$$\sigma^s = \frac{\beta \gamma_s \rho^2}{r_0}, \quad (6)$$

$$\rho = \hat{\rho} e^{-(\varepsilon_x + \varepsilon_y + \varepsilon_z)}, \quad (7)$$

where α is the thermal expansion coefficient, T is the temperature, $\gamma_s = 0.9 \text{ J m}^{-2}$ is the surface energy [36], r_0 is the particle radius at the reference temperature, η_s is the viscous shear modulus, η_b is the viscous bulk one, σ^s is the sintering stress module, β is a parameter related to the powder morphology, and $\hat{\rho}$ is the initial brown relative density - calculated to be averagely $\hat{\rho} = 69.17\%$ for the produced brown parts - all of which are strictly connected to microscopical properties and functions of porosity and temperature. Thus, Olevsky's model [37] is adopted for estimating the shear and the bulk viscosities after calculating the apparent viscosity η via an Arrhenius-type equation tailored to Al_2O_3 characteristic properties [38]:

$$\eta = \eta_0 e^{\frac{Q_v}{RT}}, \quad (8)$$

while in regard to grain growth, a cubic law was adopted [39] as reported below:

$$G^3 - G_0^3 = Kt, \quad (9)$$

$$K = K_0 e^{\frac{Q}{RT}} \quad (10)$$

where η_0 is a pre-exponential material-dependent constant, Q_v is the activation energy for the viscous flow [38], G_0 is the initial grain size assumed to be equal to the average particle size $G_0 = 800$ nm, t is time, K_0 is a pre-exponential material-dependent constant, $Q = 640$ kJ mol⁻¹ is the activation energy for grain growth for normal sintering conditions [39], R is the universal gas constant, and T is the temperature in Kelvin. The Arrhenius equation is deemed to be increasingly more accurate as the material approaches its liquidus temperature, such as at high sintering temperatures. The model evaluates the relative density at every increment as per the mass conservation Equation (7) based on the current values of the deformations calculated via the constitutive Equations from (1) to (6). Hence, the relative density value is updated and continuously changes through the simulation, changing the material properties and affecting the subsequent deformations that determine the new value of relative density for the following increment. As a result, the relative density evolution is estimated and, in the end, the final sintered relative density predicted.

The thermal expansion coefficient, specific heat, and thermal conductivity were inputted into the finite element model as a function of temperature, while Young's modulus and Poisson's coefficient were functions of both density and temperature defined via subroutine [40,41]. Therefore, the material properties modifications due to the temperature changes during the sintering cycles were taken into account. Gravity was considered and axial symmetry exploited to reduce the computational effort, while movements along the negative z-axis were impeded at the lower base of the cylinder and the sintering cycles were applied directly to the outer surface of the cylinder itself (Figure 3.3).

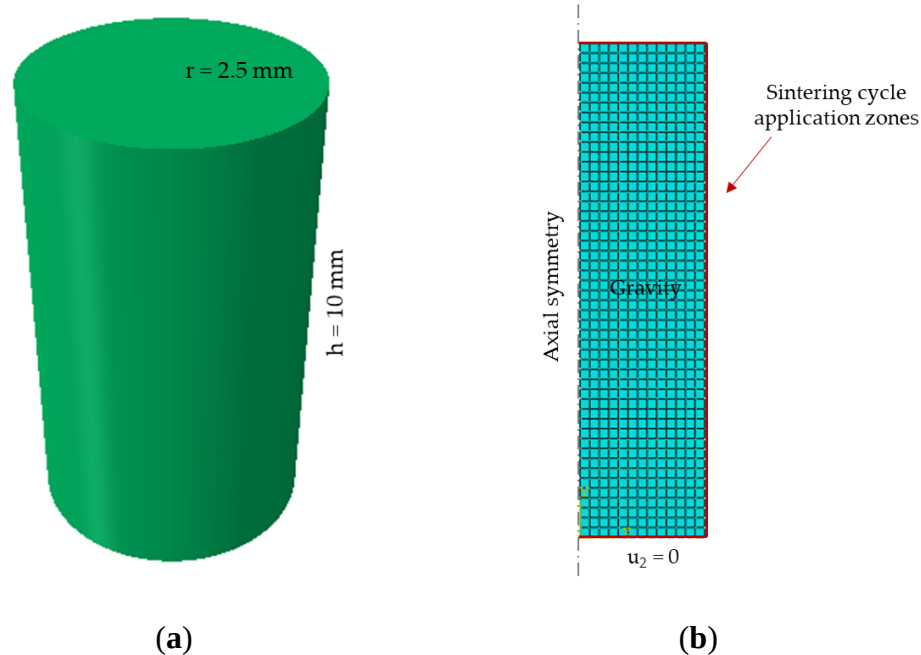


Figure 3.3 - (a) Geometry inputted in the FEM software. (b) Applied boundary conditions.

3.7 Results and discussion

3.7.1 Slurry Characterisation and Binder Removal

The properties of the alumina powder are shown in Table 3.3. The estimated mean particle size D_{50} is $0.80 \text{ }\mu\text{m}$, the theoretical density is 3.95 g/cm^3 , and the chemical impurities percentage is lower than 0.2% (Sympatec GmbH, Clausthal-Zellerfeld, Germany). The resulting powder distribution can be observed in Figure 3.4.

Table 3.3 - Properties of the Al_2O_3 powder.

Particle Size Distribution			
	$D_{10} \text{ (}\mu\text{m)}$	$D_{50} \text{ (}\mu\text{m)}$	$D_{90} \text{ (}\mu\text{m)}$
	0.23	0.80	2.31

Theoretical density		
3.95 g/cm ³		
Chemical composition ¹		
Al ₂ O ₃ (by difference)	99.8	
Na ₂ O	0.07	
Fe ₂ O ₃	0.02	
MgO	0.05	
SiO ₂	0.03	
CaO	0.02	
B ₂ O ₃	<0.005	
Surface area BET ¹		
8.9 m ² /g		

¹ Information provided by the supplier.

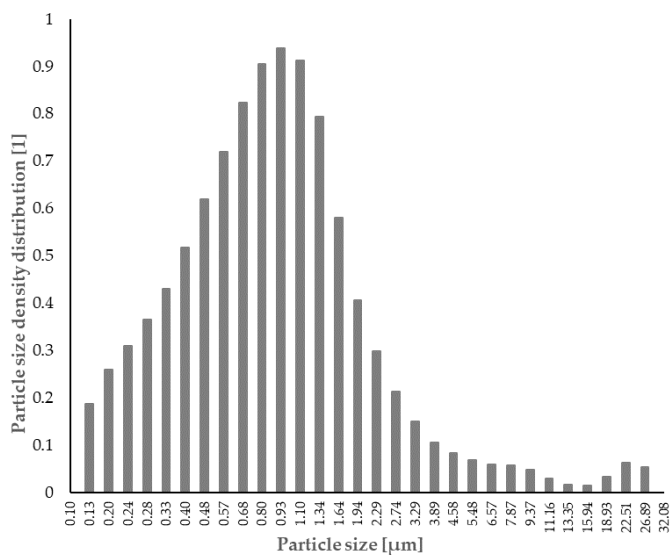


Figure 3.4 - Particle size distribution of the Al₂O₃ powder.

The rheology of the slurry is shown in Figure 3.5a. The prepared slurry shows a shear-thinning behaviour, in that a decreasing dynamic viscosity can be observed with the increase in the shear rates. Shear-thinning behaviour is highly desirable in stereolithography processes because it can allow the satisfactory spreading of thin layers; thus, a homogeneous green microstructure can be achieved. The shear rate working window for the adopted DLP machine ranges from 10 to 300 s^{-1} , where, in this range, the dynamic viscosity has a stable and constant value. The curing behaviour of the slurry, which is characterised by the cure depth, depth sensitivity and critical energy, was also investigated by exposing a single layer at various exposure energies to establish the critical exposure energy and depth of penetration. The slurry was degassed in a vacuum degasser for 10 min before measurement to eliminate air bubbles and decrease the inhibition of the polymerisation. A checkboard design was projected onto the photopolymerisable resin layer and, after removing the single layer from the foil, the thickness of the cured material was measured using a portable micrometre. The average cure depth was determined by performing a total of three measurements [34]. It can be noted that the cure depth increases linearly with the logarithm of incident energy, which is consistent with the Lambert-Beer model of the SL process for cure depth.

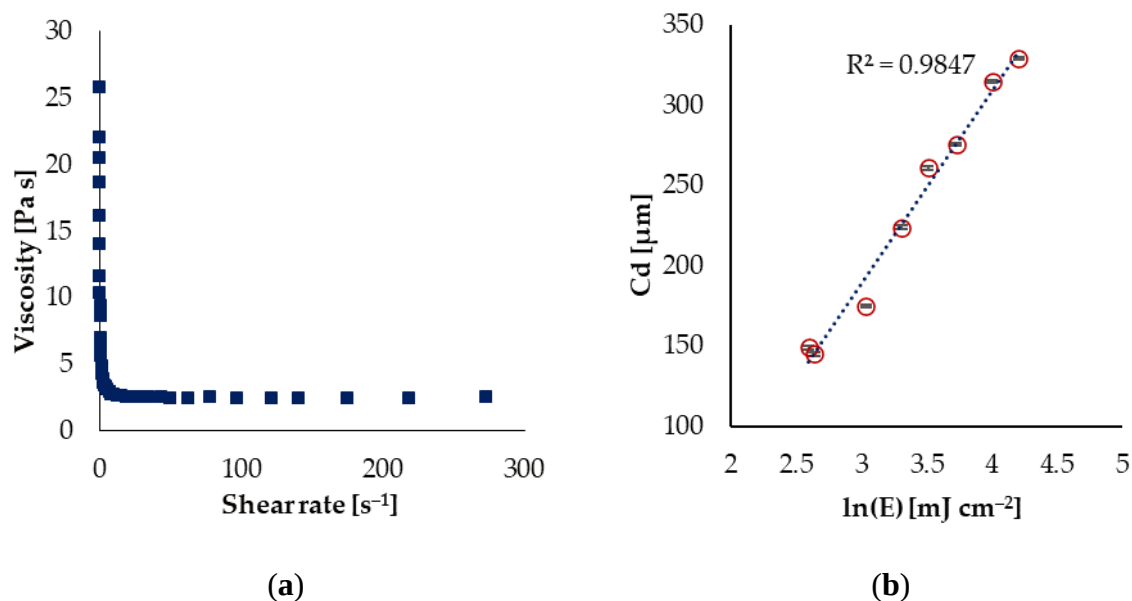


Figure 3.5 - (a) Measured viscosity of the ceramic slurry. (b) Cure depth vs. energy density [34].

The TGA-DSC analysis of the green body revealed information on the decomposition behaviour of the organic matter in line with the changing temperature (Figure 3.6a). Two substantial exothermic peaks were observed at around 375 °C and 480 °C. The major weight loss, as shown by the TG curve, is observed from 190–480 °C with a total mass loss of 19.18%. Based on these data, the debinding regime was determined. Detailed temperature settings of the debinding process are shown in Figure 3.6b. The temperature was raised from room temperature to 190 °C and the dwell time at this first temperature setpoint was 2 h. Following this, the temperature was increased to 375 °C and maintained for 3 h to decompose the organics slowly and, consequently, relieve the thermal stresses on the ceramic parts. Subsequently, the system was heated to 480 °C and held at this temperature for 2 h. Finally, the temperature was gradually brought to 650 °C to eliminate any organic residual, kept for 2 h and, in the end, cooled to room temperature. The heating rate of the whole debinding process was controlled and fixed at 0.2 °C/min.

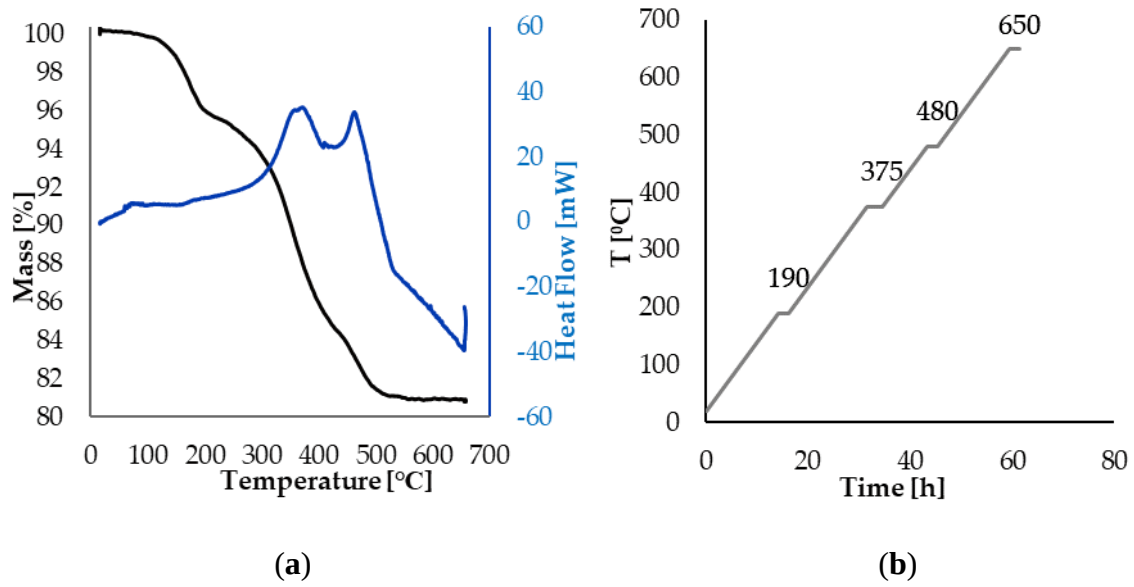
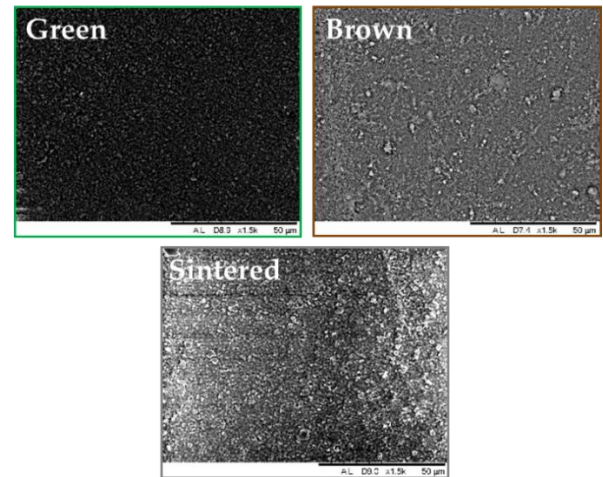
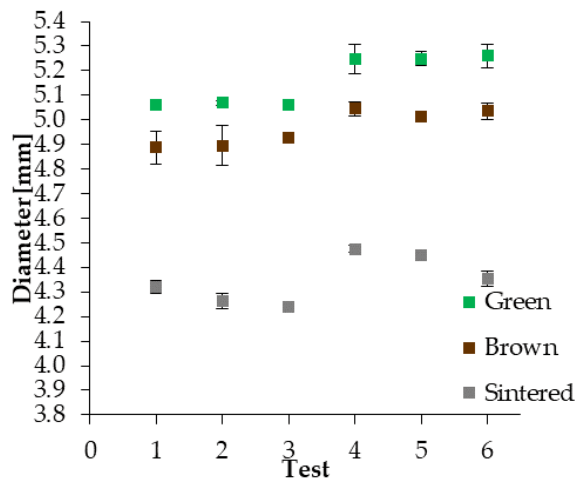


Figure 3.6 - (a) TGA-DSC curves of Al_2O_3 sample. (b) Details of the adopted debinding cycle.

3.7.2 Sintered Samples Characterisation and Numerical Model Validation

In Figure 3.7a, the average value for diameters with the corresponding standard deviations are plotted for each sintering trial. SEM pictures of the green, brown, and sintered stages were also taken, and, in Figure 3.7b, there is an example of the surface evolution detected by SEM for one of the trial T1 samples. In addition, the height change across the different processing steps can be seen in Figure 3.8. As can be observed, while both the geometrical features have similar modifications from the green stage to the brown one, the behaviour is different from the brown stage to the sintered one. In fact, the reduction in dimension is more relevant in terms of height rather than in terms of diameter, resulting in a slight difference in the aspect ratio of the cylinders.



(a)

(b)

Figure 3.7 - (a) Diameter dimension evolution. (b) SEM images of green, brown, and sintered T1 samples, respectively.

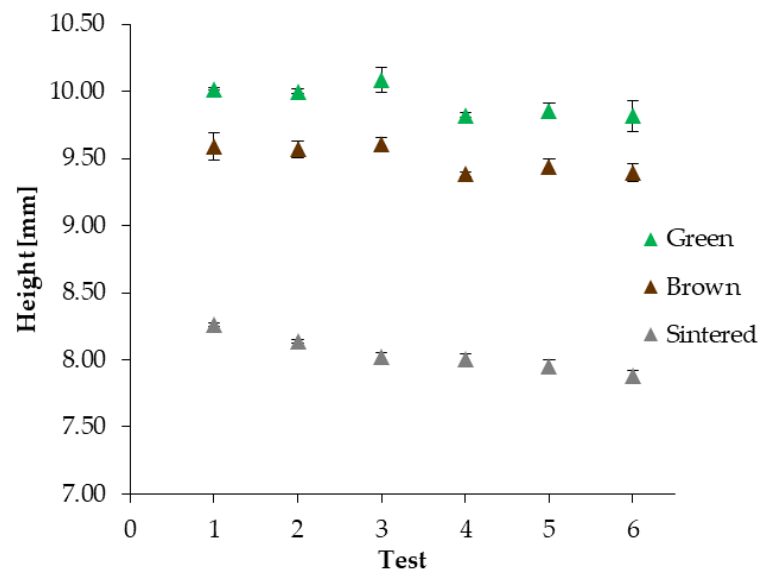


Figure 3.8 - Height dimension evolution.

This is made more evident when comparing the shrinkages (Figure 3.9). In fact, the shrinkage along the axial dimension is more pronounced than the one measured along the radial dimension. This is due to the nature of the DLP printing working principle itself [42,43]: while

on the layer plane, the material behaviour can be assumed to be isotropic if the used slurry had been thoroughly homogenised; along the building direction, more factors such as an optimal layer recovery influence the homogenisation of the material and, consequently, the material behaviour along it. Moreover, the final relative density obtained for the sintered samples, together with SEM images taken for trial 1 and trial 6, are shown in Figure 3.10 and categorised in terms of dwell time. As can be seen, longer holding times lead to a more pronounced grain growth. Additionally, when comparing tests conducted at the same temperature but different dwell times, it has been noticed that longer dwell times - as it could be possibly expected - corresponded with slightly higher grain dimensions. However, although trials T2 and T5 seem to behave slightly differently from the others, taking into consideration the error bars, it may be concluded that the effect of the dwell temperature is more relevant than the one of dwell time in terms of the final relative density of the sintered samples, in line with the literature findings [17–19].

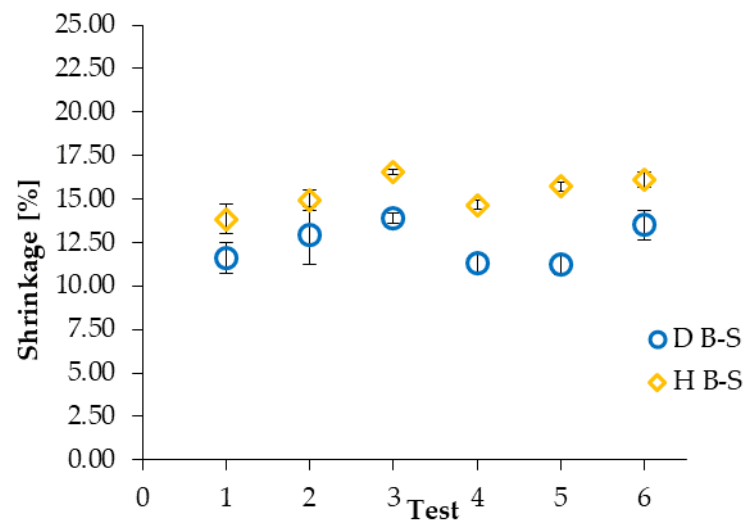


Figure 3.9 - Diameter and height shrinkage from brown to sintered bodies.

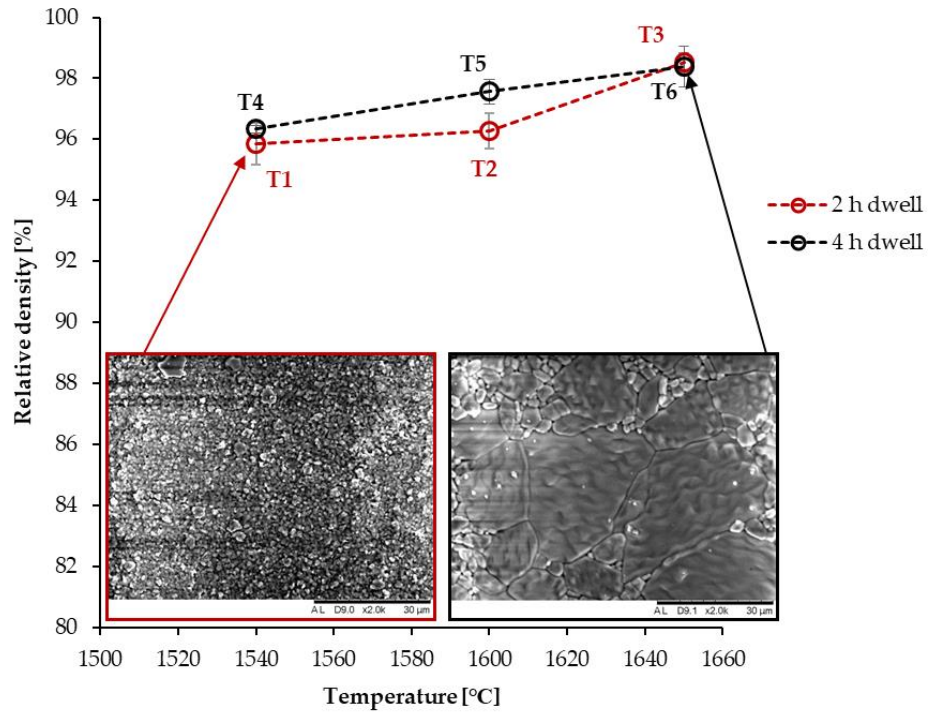


Figure 3.10 - Relative density evolution for 2 h and 4 h dwell at the end of cycles.

To further prove what was mentioned earlier regarding the intrinsic anisotropy of the process, two dilatometry tests were conducted following the sintering parameters of trial T1. The dilatometer could only measure the shrinkage along the axial dimension; so, in order to investigate the anisotropy of the process, two different printing patterns were adopted (Figure 3.11): in the first case, the shrinking behaviour of a vertically printed sample was tested and a value of 17% was obtained; in the second, however, the sample was printed horizontally, so that the dilatometer could test the shrinkage behaviour of the layer rather than across the layers. As expected, the latter showed a different shrinkage value of 12%, although it also has to be mentioned that the number of layers axially exposed to the dilatometry test in this configuration, closely correlated to the shrinkage along the z axis, is lower than that in the former one.

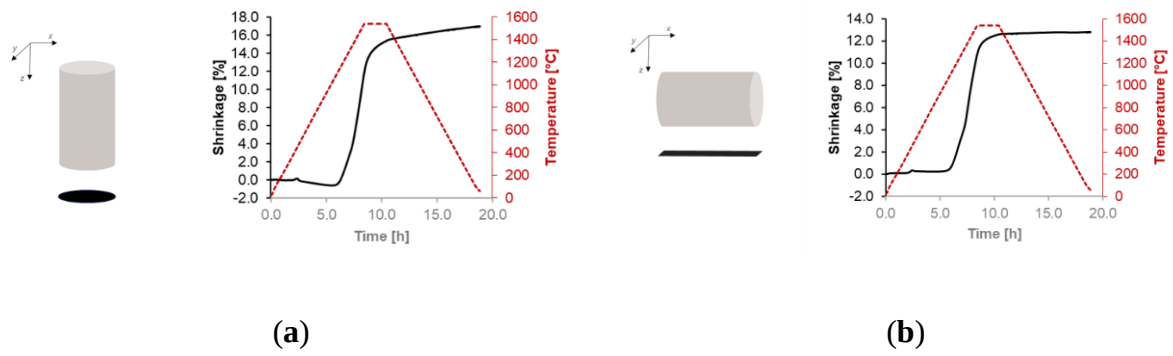


Figure 3.11 - (a) Dilatometry of the vertically printed sample. (b) Dilatometry of the horizontally printed sample.

In Figure 3.12, the predicted displacement and shrinkages along the radial dimension obtained from the FEM are shown for the 2 h dwell time trials and compared with the experimental results. Only radial shrinkages are considered at this time, since the model is not able to take into account anisotropic behaviours. Following a slight expansion in the initial stages of the heating curve, where the expansion effect is more relevant than the sintering one, the cylinder begins to shrink as the temperature increases, reaching maximum shrinkage at the end of the dwell time. The areas in red are meant to indicate the zones with the minimum displacement, while the blue ones indicate the maximum displacement. Figure 3.12b, instead, shows that there is a close match between the experimental and numerical data on the part of the finite element model, although further improvement may be achieved by the introduction of anisotropy into the model.

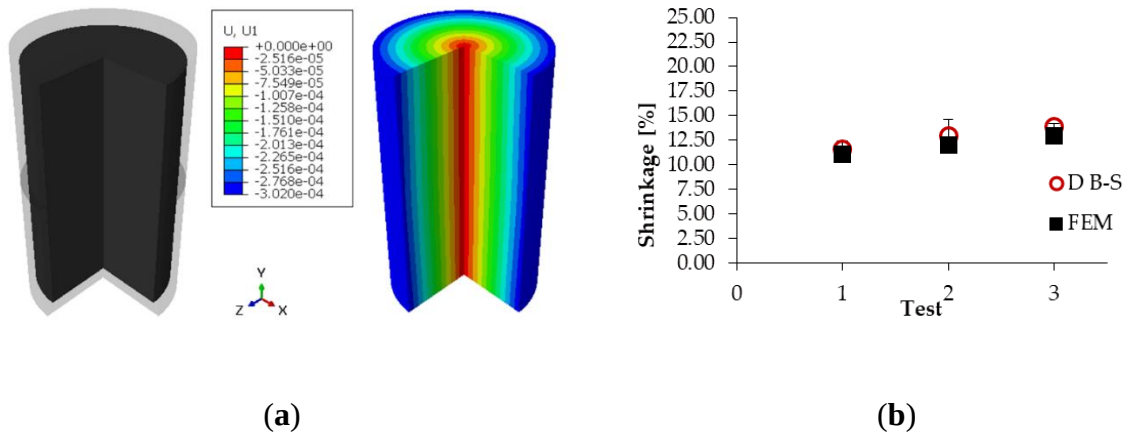


Figure 3.12 - (a) After sintering shape vs. translucent pre-sintered shape (left) and predicted radial displacement (right). (b) Experimental shrinkage vs. FEM simulations.

The final relative density was also estimated using the model. In Figure 3.13, the graph reports the comparison between the experimental results and the simulations. A good match between experiments and modelling can be observed: the model is able to predict the final relative density with a maximum of 2% error in either positive or negative directions. However, in the case of the relative density, the importance of taking into account a different shrinkage along the axial dimension tends to be of higher relevance as the dwell temperature increases; this is demonstrated by the fact that the FEM underestimates the final relative density at the highest dwell temperature according to the experimental results. In fact, by underestimating the axial shrinkage, the final volume of the simulated sample is higher and, consequently, the resulting estimation of the density is lower than the one obtained from the experimental trials.

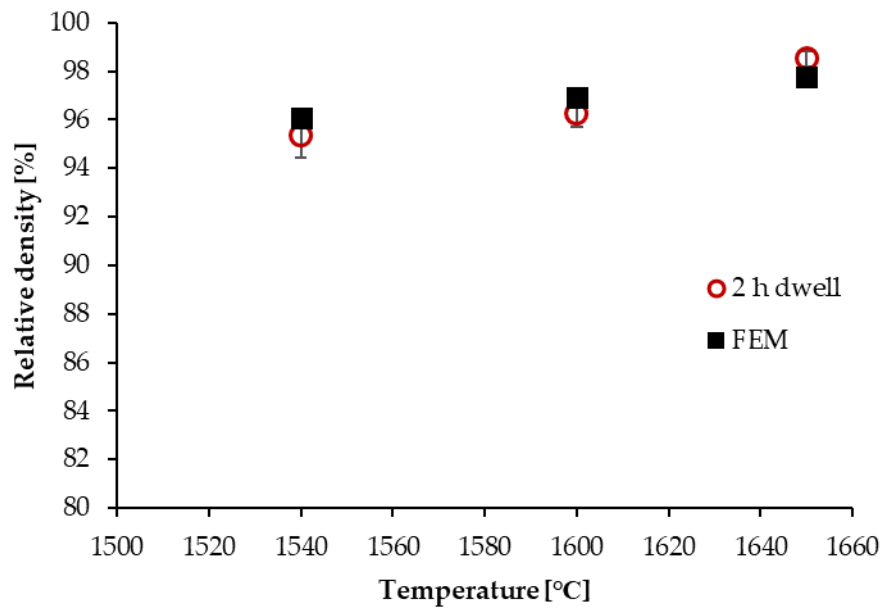


Figure 3.13 - Experimental relative density vs. FEM predictions.

3.8 Conclusions

A finite element model was developed exploiting a user-defined subroutine to simulate the thermomechanical behaviour of a simple cylindrical geometry undertaking specific sintering process schedules. A high-solid-loading, low-viscosity alumina slurry with suitable curing characteristics was prepared and cylindrical samples were additively manufactured using Digital Light processing. DSC/TGA measurements revealed the appropriate binder removal regime. Several different experimental trials involving sintering of the cylindrical samples were conducted and subsequent measurements and tests revealed that a certain degree of anisotropy could be detected in the DLPed samples. In fact, dilatometry tests suggested that anisotropic behaviour can be observed in the sintered samples, showing different shrinkage between the building direction and the layer plane. The FE model shows good agreement with the

experimental results. In particular, numerical data demonstrate a close match between the predicted shrinkage and the relative density, with less than a 2% mismatch between the experimental results and simulations, suggesting that the model can be used for further optimisation of the sintering processes of alumina. In general, the FEM is able to predict the relative density evolution; therefore, it can be used to optimise sintering processes. Employing the developed FEM to better understand the sintering mechanics of DLPed alumina parts can lead to the obtainment of tailored sintering cycles able to deliver fully dense parts (relative density >99.0%). In fact, starting from a highly dense green part and obtaining an almost fully dense component after sintering is crucial for a variety of applications, such as armours and transparent ceramics, where higher relative densities of alumina parts allow the material to exploit its full potential. However, the model is not able to take into account any anisotropy, something that is more evident as dwell temperatures increase. Consequently, future work should be directed to the integration of anisotropy in the evaluation of shrinkage and the relative density of the sintered bodies to predict the densification process even at high sintering temperatures.

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CHAPTER 4. DLP OF TRANSLUCENT ALUMINA: IN-DEPTH INVESTIGATION ON SLURRY DEVELOPMENT AND DEBINDING REGIMES

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DLP OF TRANSLUCENT ALUMINA: IN-DEPTH INVESTIGATION ON SLURRY DEVELOPMENT AND DEBINDING REGIMES

Abstract

Exploring the feasibility of producing near-net-shape components with advanced properties and geometrical features via 3D printing has incrementally become the research focus of various studies. Digital light processing (DLP) technology can manufacture complex-structured components for various technical applications. The aims of this research were to investigate Al_2O_3 ceramic slurry preparation procedures to identify the ideal components to add to an in-house-developed ceramic slurry, to determine the optimal DLP printing parameters and conditions while understanding their effect on the green part properties and to evaluate the appropriate debinding regime to achieve fully dense crack-free fired parts capable of exhibiting translucent behaviours. The slurry obtained from the ball-milled powder at 800 rpm for 1 h, together with 2 wt.% BYK-145 as a dispersant and the highest achievable solid loading of 85 wt.%, showed the desired rheological and photopolymerisation properties. Full-factorial design of experiments (DoE) was employed to study the impact of the printing parameters on the density and the dimensions of the samples. Different debinding regimes were investigated and it was proven that the lowest debinding heat rate ($0.2\text{ }^\circ\text{C}/\text{min}$) and longer holding times helped to reduce defects and promote densification ($>99.0\%$), providing optimal grounds to obtain translucent fired parts.

Keywords: additive manufacturing; DLP; ceramic slurries; debinding; DoE

4.1 Introduction

Additive manufacturing (AM) represents a possible alternative to conventional production. It is a technique for producing three-dimensional objects by adding individual layers based on a sliced computer-aided design (CAD) model. In terms of processed materials, plastics and metals are now the industry leaders, although ceramic additive manufacturing has lately garnered a great deal of attention [1–3]. Indirect and direct ceramic AM are the two most common classifications [4]: the former comprises, among other characteristics, selective laser sintering (SLS), selective laser melting (SLM) and direct inkjet printing (DIP), while the latter includes laminated object manufacturing (LOM) and stereolithography (SLA). SLA is one of the most popular kinds of ceramic additive manufacturing techniques and Digital Light Processing (DLP) is one of the most promising processes that originate from the SLA approach while improving it at the same time. The benefit of DLP technology is the more rapid and efficient fabrication of the part, as the projected light source solidifies one layer of slurry at a time [5] rather than a point or a single line.

A crucial objective of AM is the achievement of dimensional precision and reproducibility in the produced parts [6]. For AM of metals, it is common to find extensive research on the effect of printing settings on the part dimensions. For instance, in previous literature, it is possible to find examples of studies where laser powder bed fusion [7–9] and selective laser melting [10,11] were adopted to create complex metallic structures, and exhaustive research on the effect of the process parameters was conducted. However, on the other hand, the influence of AM processing parameters on the final properties of ceramic

components has begun to be investigated only more recently and, even though the conducted studies have been providing progressively more information, further investigations can strengthen the existing knowledge base. Regarding slurry-based methods, in particular, the effects of slurry preparation and printing settings of ceramic stereolithography-based methods on the dimensional accuracy and obtained density have not been thoroughly researched when linked to the final properties of the fired samples. Fu et al. [12] investigated the effect of laser power on the dimensional accuracy of the SLA of bulk items and concluded that the length and breadth increased with increasing laser power due to an increase in light scattering. In a separate investigation, the printing parameters were experimentally altered during the production of a gear shape using stereolithography and it was discovered that the horizontal resolution rose as the exposure energy decreased [13].

The slurries used for ceramic additive manufacturing via DLP generally comprise ceramic filler, binder, photoinitiator and other additives. The interactions between all of them must be taken into account when considering possible combinations. For instance, while dimensional error in ceramic-based stereolithography is usually due to the dispersion level of the added ceramic particles to UV resin [14,15], a high index of refraction mismatch between ceramic particles and photopolymerisable resins can reduce the cure depth and alter the resolution [15,16], affecting the achievable accuracy. In the existing literature, there are various examples of the selection process of starting slurry components and different methods for preparing ceramic suspensions are presented. The ceramic powder may be utilised as-is [17–21] or the surface of the ceramic particles may be pre-treated with a dispersant prior to the addition to the photopolymerisable resin [22–24]. There is a deficiency of information about the photopolymerisation behaviour and rheology, as well as a clear description of the optimal way of preparation and achievement of a solid loading greater than 40 vol%, which is a key

aspect in the development of ceramic slurries able to obtain successfully dense parts [17,25,26]. High solid loadings are desired, as they enhance mechanical characteristics while decreasing sintering shrinkages. However, the addition of hydrophilic ceramic particles to the hydrophobic resin dramatically increases viscosity, which directly affects the printing feasibility. To obtain a high solid loading and an excellent dispersion of ceramic particles in the resin, it is necessary to add a dispersant to create steric barriers between ceramic particles that compensate for the van der Waals attractive forces and avoid Brownian motion-induced particle collisions [17].

In addition to the preprocessing and printing parameters, the debinding and sintering processes need to be optimised and strict controls must be established to obtain samples free of cracks [27,28]. In fact, the 3D-printed ceramic green body is subjected to heat treatment methods in order to produce sintered bodies with the required final qualities and low solid loadings can result in 70% shrinkage during the thermal postprocessing. During the debinding procedure, the ceramic slurry's binder must be pyrolysed away. As the binder diffuses through the ceramic green body, microcracks are caused by high heating rates and unsuitable holding temperatures and holding durations [29]. When microcracks are not eliminated, their presence during sintering degrades the mechanical characteristics. Therefore, the heating rate and the dwelling temperatures within the temperature range where the binder decomposes must be accurately calculated prior to thermally stabilising the ceramic green body for an appropriate holding period [27]. In addition, a sufficient sintering temperature is necessary, as the ceramic densification process is incompletely attained when an improper heating temperature is used in the sintering process, resulting in a degradation of the material's physical properties. Therefore, optimal sintering temperatures should be investigated appropriately in advance to fully exploit the potentialities of ceramic materials [30].

Recently, several intriguing experiments have been devoted to the fabrication via AM of ceramic components for special applications in micro-electro-mechanical-system [31] or catalyst-substrate manufacturing [32–34]. However, due to the great optical transparency and characteristic ceramic features of transparent ceramics, they are equally suitable for a wide variety of high-performance applications, such as lasers, armours and lighting. There is a pressing need to simultaneously lower the weight of transparent armour systems and boost their ballistic protective qualities. When both mechanical strength and abrasion resistance are essential performance characteristics, material options are frequently restricted to a few materials [35–37], such as aluminium oxynitride (AlON) [38–40], sapphire (Al_2O_3) [41] and magnesium aluminate spinel (MgAl_2O_4) [42,43]. Due to their great strength and hardness, these three materials have been investigated as possible replacements for ballistic glasses in transparent armour applications for quite some time and ballistic tests have demonstrated that spinel, AlON and sapphire exhibit comparable performance. Payne and colleagues [44,45] claimed that transparent yttrium aluminium garnet (YAG) ceramics may be created via a direct ink writing (DIW) approach, but that the subsequent CIP and HIP processes are still required. Wu et al. [46] continued to use the extrusion-based AM method employing copolymer-assisted slurry so that complex-shaped transparent YAG ceramics could be immediately produced. Hostaša et al. [47] manufactured YAG laser ceramics by SLA to demonstrate the benefit of lithography-based techniques in terms of spatial resolution and product form. Two-photon printing was used to create small transparent YAG objects with nanometric precision in the nanometre and micrometre ranges (TPP) [48]. However, studies on the DLP of translucent alumina starting from an in-house systematically developed slurry and its consecutive post-processing have yet to be explored.

In conclusion, complex interactions between process settings, printer resolution and composition of the photopolymerisable slurry determine the precision of DLPed components. Although numerous studies have focused on the effects of printing parameters on the performance of manufactured parts, a systematic examination of the effects of slurry preparation and printing parameters on the geometrical properties of DLPed advanced alumina ceramics is necessary. The impact of different ball-milling pre-treatments, diverse slurry components and, hence, curing behaviours and debinding regimes has to be evaluated by analysing the evolution of the density and the geometrical accuracy at various layer thicknesses and energy dosages. This research aims to analyse the ceramic slurry preparation steps and establish optimal printing and debinding settings for achieving translucency in alumina-based structures even in air-sintering conditions. In this study, the influence of the pre-treatment of ceramic particles relative to the as-received powder was investigated, as well as the additions in the ceramic slurry of different components in various proportions. A full-factorial Design of Experiment (DoE) was used to explore the influence of layer thickness, exposure dose and exposure time on dimensional accuracy. On the basis of a comparison of the printing dimensional correctness and on the estimation of the density, the optimal printing parameters were determined. Different debinding regimes were then analysed and, finally, samples were sintered. In the end, the entire process was repeated following the now-established optimal route and adding MgO as a sintering aid in a minimal quantity (1000 ppm) without altering the slurry printability, in order to obtain even a slightly translucent sample.

4.2 Materials and Methods

4.2.1 Ceramic Powder Pretreatment

Alumina was used as the ceramic powder (CT 3000 LS SG, Almatis GmbH, Ludwigshafen, Germany) for the photopolymerisable slurry. The as-received aluminium oxide powder (D50 = 0.92 μm) was ball milled together with 0.8 mm of aluminium oxide grinding media (Industrie Bitossi S.p.A., Spicchio-Sovigliana, Italy) in a 1:1 ball-to-powder ratio (BPR) at different rotating speeds and holding times in a planetary ball milling (HMK-1901, Dandong HMKTest Instrument Co., Ltd., Dandong, Liaoning, China) in order to see if, within a limited window of investigation, any changes in the pretreated powders could be appreciated. Table 4.1 illustrates the various values of speed and time tested.

Table 4.1 - Ball-milling parameter combinations investigated.

Run	Milling Speed [rpm]	Milling Time [h]
1	400	1
2	400	2
3	400	3
4	600	1
5	600	2
6	600	3
7	800	1
8	800	2
9	800	3

The set of parameters producing the best results was adopted and finally sieved via a 250 μm mesh screen. The particle size distribution of the ceramic powder was measured by laser diffraction particle size analysis (Sympatec GmbH, Clausthal-Zellerfeld, Germany), which was performed in a liquid dispersion consisting of water and two drops of tetrasodium pyrophosphate as a dispersant. Additionally, SEM images were obtained to analyse the shape of the powder (JEOL JSM-6060LV, Tokyo, Japan).

4.2.2 Slurry Preparation

The resin was prepared by mixing polyfunctional and monofunctional monomers in different proportions together with a dispersant and a plasticizer (20 wt.% to the resin content) to prevent delamination. Diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (Sigma Aldrich, Gillingham, UK) was added to the resin mixture as a photoinitiator (1.0 wt.% of the photoreactive resin components). A difunctional and a monofunctional polymer were chosen in a proportion of 6:5 and a ceramic loading of 85 wt.% was selected to be implemented. The processes for preparing ceramic slurry were derived from the literature [49].

The first step consisted of blending the resin components using an overhead mixer at room temperature for 30 minutes, followed by the addition of the dispersant and another 30 minutes of stirring. Then, the ceramic powder was gradually added until a solid loading of 85 wt.% was reached. The photoinitiator was subsequently added to the combination, which was then mixed for further 30 min with the mechanical mixer and, finally, the slurry was placed in a turbula mixer for at least 12 h along with 6 mm spherical alumina grinding media (Industrie Bitossi S.p.A., Spicchio-Sovigliana, Italy) with a BPR = 1. Before the printing, the produced

slurry was processed for 10 min in a vacuum degasser to eliminate air bubbles and minimise polymerisation inhibition.

Different dispersants, various percentages of dispersants and diverse solid loadings were explored. Table 4.2 shows the components and parameters investigated.

Table 4.2 - Investigated slurry preparation parameters.

Parameter				
Dispersant	BYK-111	BYK-145	BYK-9076	
Dispersant content	1 wt.%	2 wt.%	3 wt.%	5 wt.%
Solid loading	75 wt.%	80 wt.%	85 wt.%	90 wt.%

Firstly, the dispersant influence was investigated by trying three different dispersants at the same weight content percentage to the ceramic powder content and the optimal dispersant was then selected. Secondly, the effect of the chosen dispersant weight content was studied by varying the weight content between 1% and 5% and the dispersant showing the ideal rheology behaviour was selected. Finally, the solid content workability range was explored by considering four different ceramic solid loadings and the optimal one was chosen. To comprehend the rheological properties of the prepared suspension, the rheology of the ceramic suspensions was examined with AR 500 (TA Instruments, New Castle, DE, USA) using a 40 mm parallel plate geometry in the shear rate window ranging from 0.1 to 300 s⁻¹ at a constant temperature of 20.0 °C, in accordance with DLP printing conditions.

4.2.3 DLP

With a light source operating at a wavelength of $\lambda = 405$ nm, the Admaflex 130 (Admatec Europe BV, Alkmaar, The Netherlands) was employed as a 3D printing machine capable of achieving a resolution of $40\text{ }\mu\text{m}$ on the layer plane. The actual forming tool of the machine is composed of thousands of mirrors that move in accordance with pixels to imprint the picture on the slurry. The Admaflex 130 utilises a rotating foil system for transporting the slurry from the reservoir to the 3D construction area and, subsequently, to the collecting zone, where a pump mechanism returns the unneeded slurry to the reservoir. The light-reactive slurry is exposed to light at the machine's operating wavelength and, as a result, the entire layer is cured at once due to the presence of multiple mirrors. Gradually, the green body is printed in its totality after being repeatedly cured, layer by layer (Figure 4.1b).



(a)

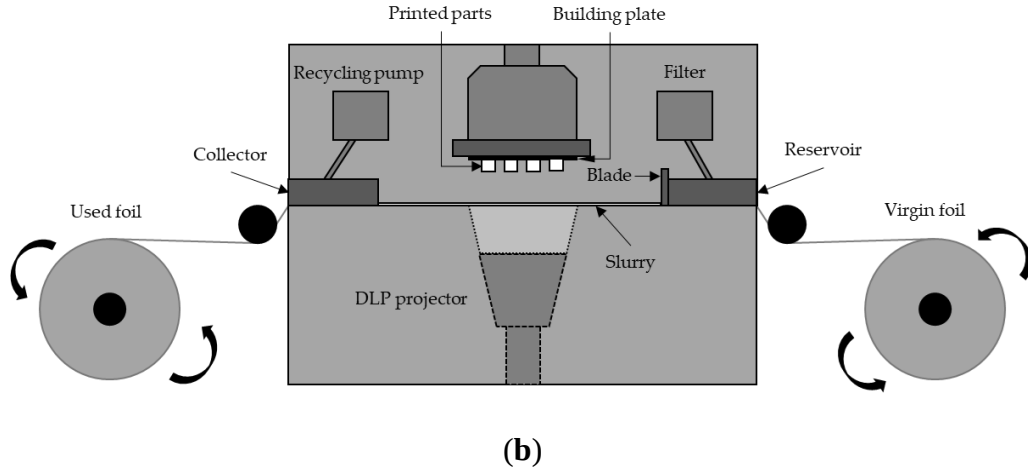


Figure 4.1 - (a) Admaflex 130; (b) schematic of the Admaflex 130 DLP process.

A single-layer curing approach was utilised to assess the critical exposure energy and depth of penetration by measuring the cure depth at various exposure energies. The working curve of the ceramic slurry depicts the slurry's curing depth as a function of the light dosage for a particular light source. The vertical polymerisation depth, C_d , may be experimentally stated with Jacob's equation:

$$C_d = D_p \ln \left(\frac{E}{E_c} \right), \quad (1)$$

where D_p is the penetration depth - i.e., the distance at which light intensity decreases by e^{-1} [22], E is the surface exposure energy density and E_c is the critical surface exposure energy density for the slurry [17], which specifies the minimal energy density necessary for the photopolymerisation of the slurry [50]. Therefore, for higher values of D_p and smaller values of E_c , a lower amount of energy density is required to obtain a certain cure depth C_d . E_c and D_p are believed to be resin-specific metrics that are unaffected by exposure factors [51].

On a layer of photopolymerisable resin, a checkerboard picture was projected at different exposure surface powers for various exposure times. Table 4.3 illustrates the exposure times and exposure surface powers studied for understanding the curing behaviour.

Table 4.3 - Curing parameters investigated.

Exposure Time [s]			Exposure Dose [mW/cm ²]				
1	2	3	3.52	6.69	10.21	13.93	17.24

The cured layers were peeled away from the foil and the thickness of the cured material was measured using a portable micrometre (Mitutoyo Digimatic Micrometer, MDC-25PX, Kawasaki, Japan). Five consecutive measurements were collected and the average cure depth was determined, together with its standard deviation.

Following the single-layer curing tests, full-factorial design of experiments (DoE) was employed to design an experimental plan and determine the impact of printing settings on the dimensional accuracy. The analysis of variance was utilised to determine the relevant printing factors and their interactions with the process outputs [6]. Exposure dose, exposure time and sliced layer thickness were chosen as the experimental variables. The first variable represents the surface energy density delivered to the slurry for every second of exposure to the light source; the second variable expresses the period of time during which the photopolymerisable slurry is continuously cured under the light source for each layer; the third variable is the height of each individual slice of the model. Three levels were chosen for exposure duration, exposure dose and layer thickness. The exposure dose is represented as a fraction of the DLP light source intensity, resulting in irradiance values of 3.52 mW/cm² for 50%, 6.69 mW/cm² for 100%, and 10.21 mW/cm² for 150%. The experimental matrix for the complete factorial experiment is presented in Table 4.4.

Table 4.4 - DoE factors, levels, and experimental matrix of the DLP experimental campaign.

Factors		Levels	
Exposure dose [mW/cm ²]	3.52	6.69	10.21
Exposure time [s]	1	2	3
Layer thickness [μm]	25	50	100
Experiment	[mW/cm²]	[s]	[μm]
1	3.52	1	25
2	3.52	1	50
3	3.52	1	100
4	3.52	2	25
5	3.52	2	50
6	3.52	2	100
7	3.52	3	25
8	3.52	3	50
9	3.52	3	100
10	6.69	1	25
11	6.69	1	50
12	6.69	1	100
13	6.69	2	25
14	6.69	2	50
15	6.69	2	100
16	6.69	3	25
17	6.69	3	50
18	6.69	3	100

19	10.21	1	25
20	10.21	1	50
21	10.21	1	100
22	10.21	2	25
23	10.21	2	50
24	10.21	2	100
25	10.21	3	25
26	10.21	3	50
27	10.21	3	100

For each set of conditions, the printing of a total of 5 discs (CAD dimensions: diameter = 20 mm; thickness = 1.5 mm) and 5 squared plates (CAD dimensions: side = 15 mm; thickness = 1.5 mm) was attempted. The designed CAD parts were converted to .STL files and sliced to the corresponding layer thickness using the machine's internal slicing software. In order to adopt a systematic and time-efficient approach, firstly the batch of samples with 25 μm as layer thickness was printed, investigating all the selected exposure dose and exposure time levels, followed by the 50 μm batch and, finally, by the 100 μm one. This approach was chosen to minimise the total printing time of the experimental campaign since multiple samples with different exposure doses and exposure times can be printed in one single run but not with different layer thicknesses. For each layer, the delay before exposure was set to 15 s to allow the slurry to spread homogeneously on the layer, while the delay after exposure was set to 3 s to allow the layer to stabilise. In addition, the building platform was lifted and lowered each time by 6 mm at a speed of 2.5 mm/s to ensure a complete detachment of the cured layer from the foil and permit safe passage to the sliding foil. Finally, successful or acceptable samples

were detached from the building platform and cleaned by using ethanol and compressed air. Minitab 21 statistical software was used to conduct an analysis of variance to determine the statistical relevance of each parameter.

The dimensions of the samples, as well as the geometrical accuracy and the shrinkage, were determined using a combination of a Vernier calliper and an optical microscope Alicona InfiniteFocusG5 plus (Bruker Alicona, Leicestershire, UK). The density of the samples was deducted adopting Archimedes' principle and the optimal printing parameters were selected.

4.2.4 Thermal Post-Processing

Removing the photopolymerisable resin from the region between the ceramic particles is a vital step in post-processing 3D-printed components. During the debinding process, the organic components of the green body disintegrate into gas molecules, which disperse or pierce the surface of the green body and ultimately escape, creating interspaces between particles inside the brown body. Thermogravimetric analysis (TGA) and a differential scanning calorimetry (DSC) test were performed on an SDT NETZSCH STA with a heating rate of 5 °C/min to determine the mass loss of the DLP-printed green body and the crucial temperature for the binder removal. After printing more samples for the optimal printing parameters, 6 different debinding regimes were explored by varying the heating rate and the holding times, while keeping constant the 3 dwelling temperatures previously set according to the TGA/DSC test. Moreover, a pre-sintering step at 1000 °C was added to promote densification and facilitate the post-debinding sample handling. The debinding cycles were then carried out in a tube furnace (TSH/15/75/450, Elite Thermal Systems Ltd., Market Harborough, UK).

The dimensions and density of the samples were again tested and measured. Finally, the brown parts with the optimal properties were sintered according to the available facilities at 1700 °C for 12 h in a sintering furnace (HTF 17/27, Carbolite Gero, Sheffield, UK) with a heating rate of 10.0 °C/min in an air atmosphere in order to achieve fully dense alumina parts. A schematic summary of the entire experimental campaign is reported in Figure 4.2.

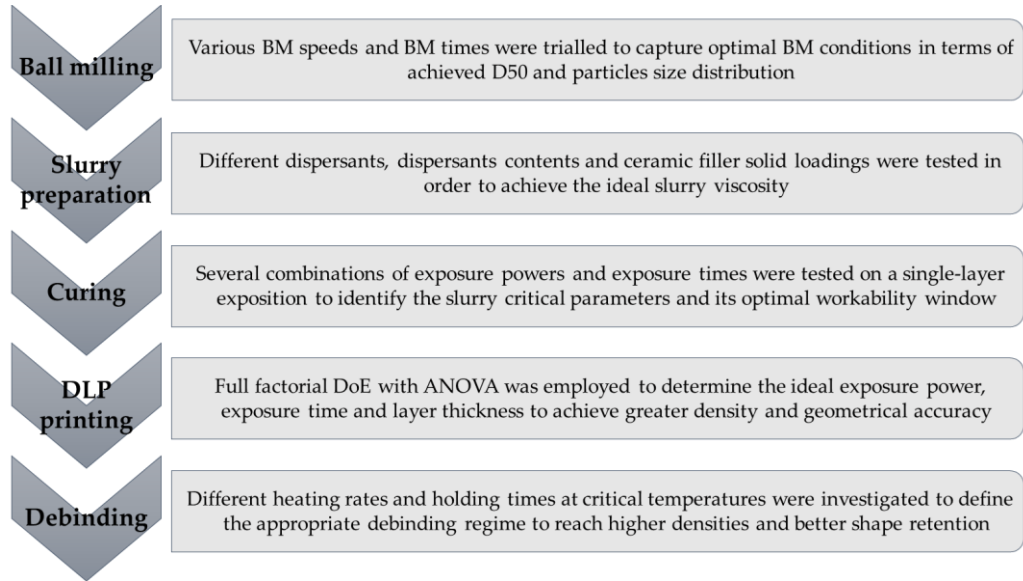


Figure 4.2 - Schematics of the whole experimental campaign.

4.3 Results and Discussion

4.3.1 Ball Milling

The various ball-milling (BM) trials resulted in similar results, as the window explored in terms of milling time was chosen according to the existing literature and was quite restricted, as, in this process chain, the ball milling is a preprocessing step that aims to break the agglomerates in the as-received powder rather than significantly changing the powder-size distribution. In addition, longer ball-milling times would increase the slurry preparation time

and, therefore, increase the total time duration of the process chain, the completion of which, in the case of additive manufacturing processes, is already relatively time-expensive. Hence, a tight range for ball-milling time was chosen while the ball-milling speed was allowed to change in a wider range, as reported previously in Table 4.1. Nevertheless, some of the trials, slightly more than other trials, managed to shift the distribution toward a lower average particle size, while breaking the agglomerates in the micron scale and leaving behind mostly sub-micron particles. For brevity, only the most successful trials are reported in Figure 4.3.

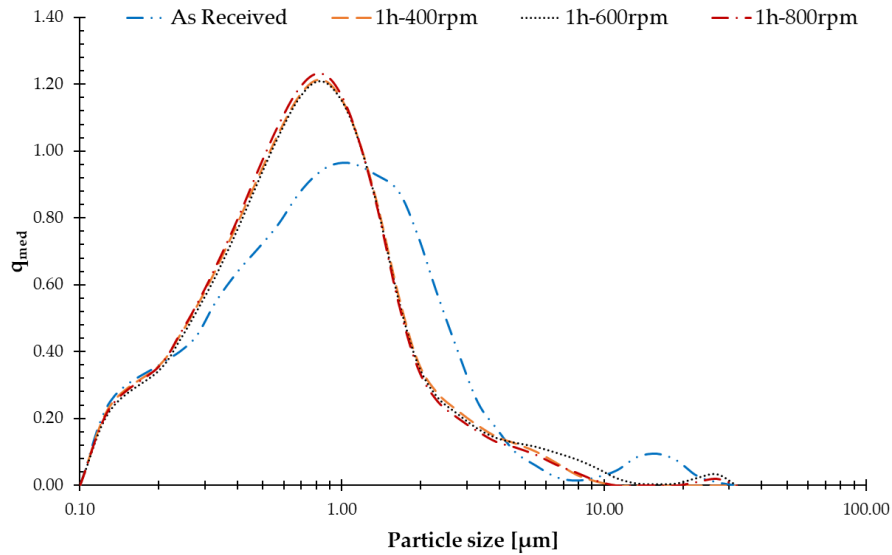


Figure 4.3 - Particle size distribution of the as-received and the most successful BMed powders.

Even though all the results across all the trials conducted were similar, the results corresponding to the lowest level of BM time succeeded in deagglomerating the as-received powder and shifting the D50 $0.92 \pm 0.02 \mu\text{m}$ to $\sim 0.75 \mu\text{m}$. However, the run with the highest BM speed and, hence, the highest kinetic energy input, managed to achieve a D50 of $0.71 \pm 0.01 \mu\text{m}$, while also performing better than the other trials, with the same BM time, at reducing

the presence of agglomerates. Furthermore, the samples were analysed under the SEM (Figure 4.4).

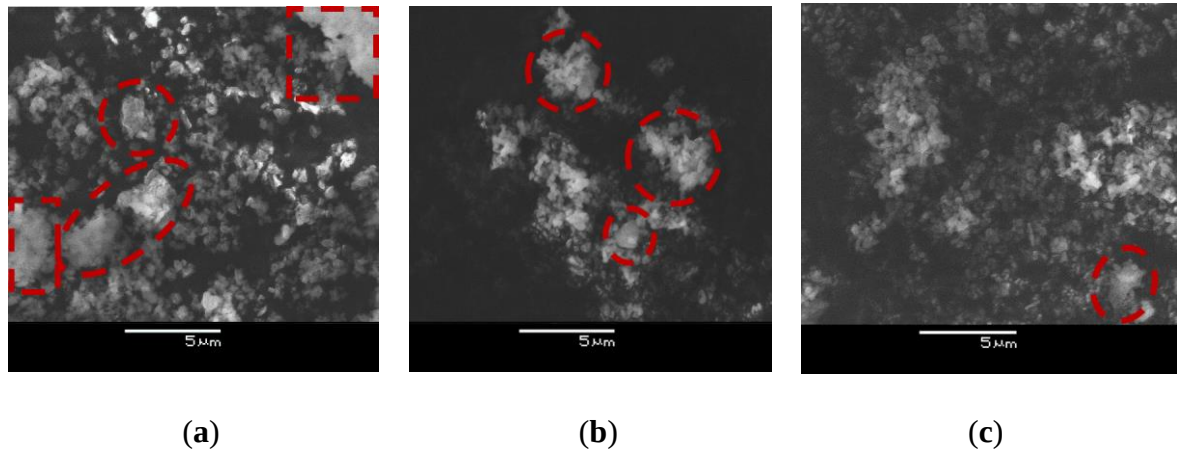


Figure 4.4 - SEM images of BM powders: (a) 1 h 400 rpm; (b) 1 h 600 rpm; (c) 1 h 800 rpm. Visible agglomerates are circled in dashed lines.

Although it is not easy at these magnifications to obtain high resolution, it can be seen that particles seem more deagglomerated as the BM speed is increased, suggesting that at lower BM times it is preferable to have a high kinetic input to thin out the ceramic powders. As a consequence, combining the results obtained from both PSAs and SEM images, the BM speed of 800 rpm and the BM time of 1 h were chosen to continue the investigation.

4.3.2 Slurries Characterisation

First, the rheology of the slurries with the chosen different dispersants was tested; the results are reported in Figure 4.5. It can be noticed that the viscosity of all the prepared slurries decreases at increasing shear rates and their viscosity does not change relevantly from shear rates higher than 20 s^{-1} , which is the suggested behaviour for slurries that have to be used with Admaflex 130. However, they should have a shear-thinning behaviour with a dynamic viscosity below $10 \text{ Pa}\cdot\text{s}$ for shear rates between 10 and 300 s^{-1} [49]. When utilising a doctor blade gap

of 120 μm , typical shear rates throughout the process can reach up to 200 s^{-1} on average. As a matter of fact, the BYK-9076 is not within the workability window previously defined. The slurry with the optimal performance is the one containing BYK-145 as a dispersant, as it possesses the rheology requirements needed to be DLP-printed with Admaflex 130, and both its stability and its lower viscosity, compared to the slurry with BYK-111 allow a better recovering of each layer during the printing process.

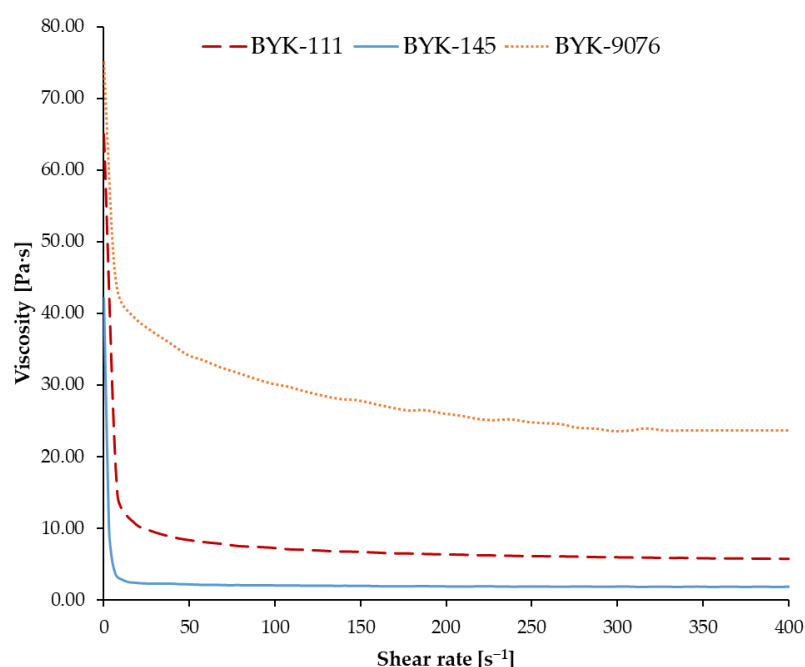


Figure 4.5 - Viscosity vs. shear rate of slurries with different dispersants.

After choosing the optimal dispersant, its weight percentage content was varied to understand the different outcomes in terms of viscosity and to comprehend if there was a saturation value beyond which the dispersant is actually agglomerating rather than dispersing. Viscosity tests were then carried out and the results are plotted in Figure 4.6.

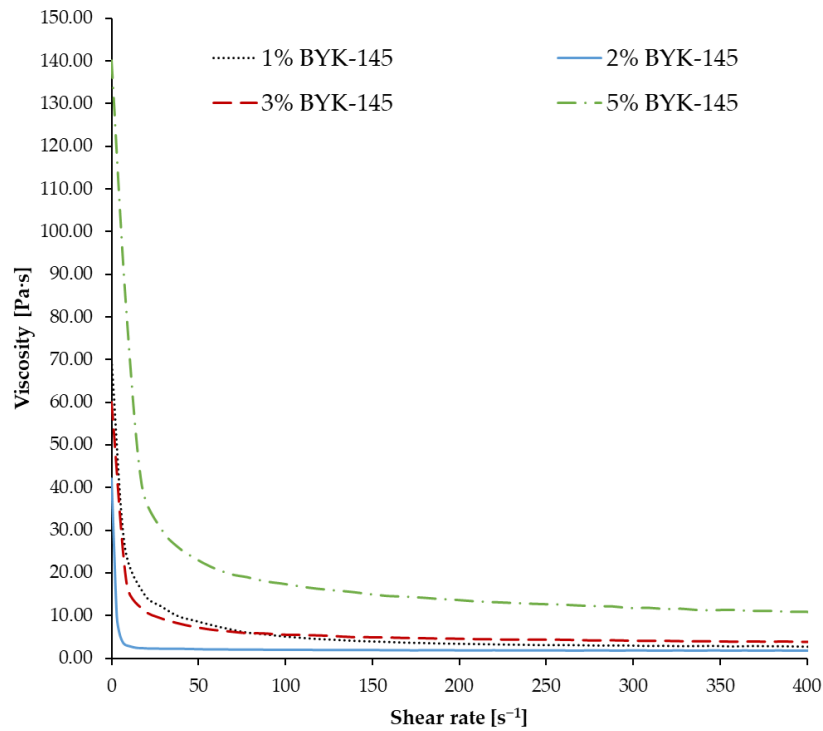


Figure 4.6 - Viscosity vs. shear rate of slurries with BYK-145 at different weight contents.

As can be observed, initially the viscosity of the slurry slightly decreased when increasing the dispersant content from 1 wt.% to 2 wt.% and it reached a stable value at smaller shear rates, which is the desired behaviour. However, if the content was increased to 3 wt.% or 5 wt.%, the viscosity values in the workability window of Admaflex130 increased. Therefore, the stability of the slurry is degraded if the dispersant concentration is too high [21]. Al_2O_3 particles are not efficiently modified by the dispersant when the concentration is extremely low; however, when its concentration was appropriately raised to 2 wt.%, the particles' surface covering is more efficient, resulting in a more stable network of particles [52]. However, at higher concentrations, there is a surplus of dispersant, which promotes flocculation and, hence, increases the viscosity.

Afterwards, the role of the solid loading was examined; the rheology of the various slurries is reported in Figure 4.7. As expected, the 70 wt.% solid-loaded slurry exhibited a less viscous behaviour, which resulted in a more liquid slurry being unable to remain within the reservoir during the DLP printing and be moved via the tape-casting foil system of Admaflex130 without spilling out. This was due to the extremely low viscosity ($<1 \text{ Pa}\cdot\text{s}$ in the window of interest). On the contrary, the 80 wt.% loading resulted in a more viscous slurry than the 85 wt.% loaded slurry at lower shear rates and slightly less viscous at higher shear rates. It is possible that the quantity of the dispersant was not optimal for the former, so the particles were flocculating at lower shear rates; however, as higher percentages of solid loading facilitate the densification of the finished samples while reducing the shrinkage and, hence, the insurgence of cracks due to the geometrical modifications, the 85 wt.% was preferred as it also showed better properties without further studies. The 90 wt.% solid-loaded slurry was also prepared, even though it was expected that increasing the packing fraction would have rapidly increased the suspension viscosity [53]. In fact, its consistency was more similar to a powder rather than a slurry, even after long mixing and varying the percentage of dispersant. This was essentially due to the reduction of the average distance between the ceramic particles when the solid loading was increased; as a consequence, a relevant increase in the friction between them resulted in a higher viscosity [54]. Therefore, it was concluded that such a high solid loading was not viable and the 85 wt.% solid-loaded slurry was selected for the continuation of the study.

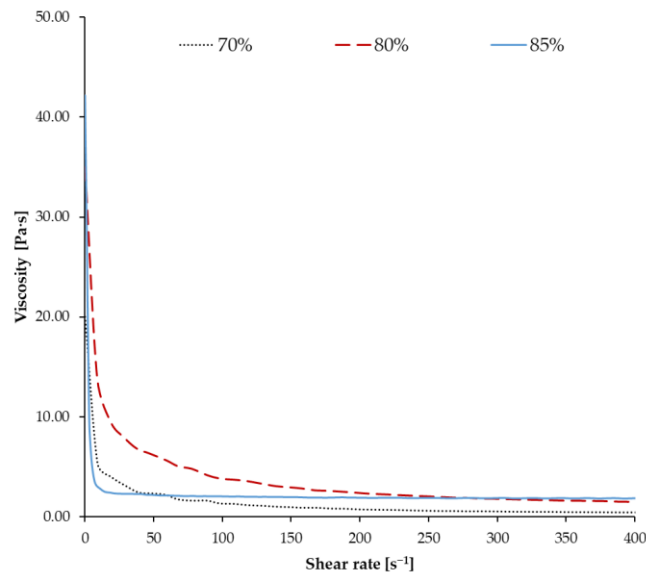


Figure 4.7 - Viscosity vs. shear rate of slurries with different solid loadings.

4.3.3 Curing Behaviour and DLP printing

The curing behaviour of the selected slurry was analysed by registering several cure depth values at different exposure times and powers, which are reported in Figure 4.8.

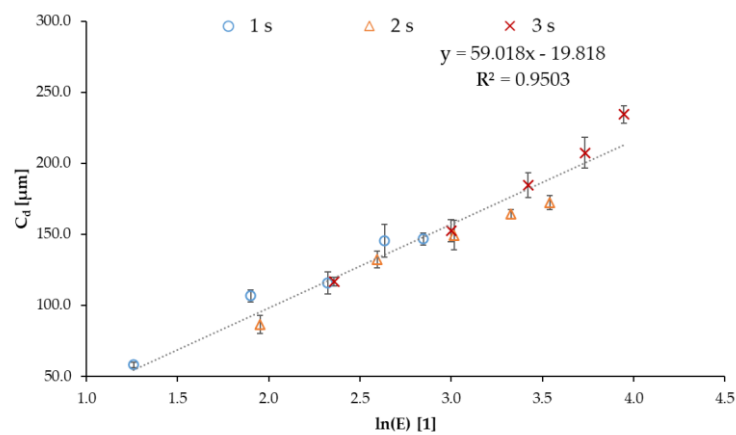
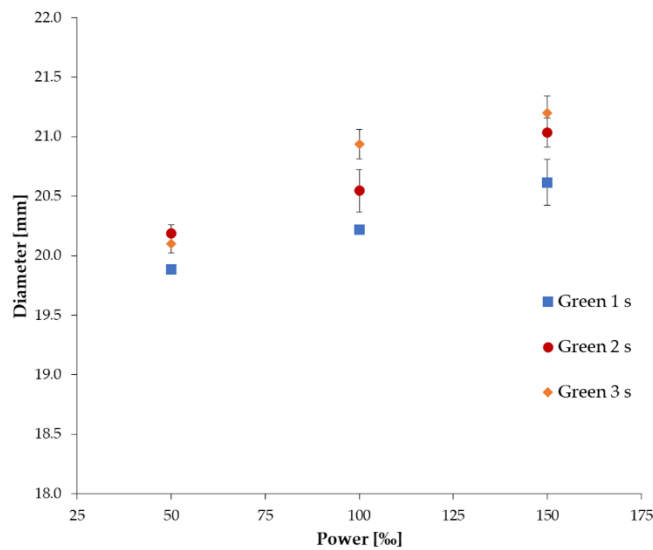


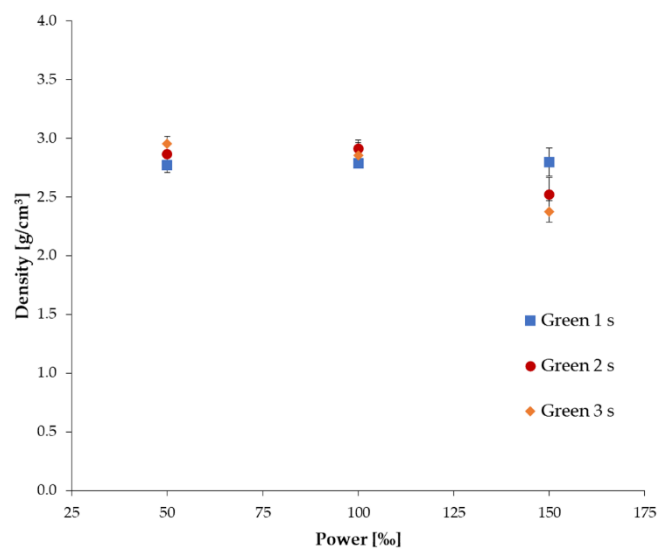
Figure 4.8 - Cure depth values of the slurry at different exposure doses and times.

The values of D_p and E_c can be deduced from the linear regression of the collected data and, in particular, $D_p = 59.018 \mu m$ and $E_c = 1.399 mJ \cdot cm^{-2}$. While the latter is compatible with a highly reactive slurry, the former describes a slurry that permits better control of lateral definition, as smaller values of D_p promote higher resolution [55]. In addition, even though all the values were registered while using different exposure parameters, all the collected data points lay acceptably around the trend line obtained from the linear regression with a good correlation coefficient, demonstrating that D_p and E_c are independent of the exposure conditions [51].

Afterwards, the printing trials were started following the schedule established through the DoE. Among all the trials undertaken, the 25 μm layer thickness samples were the most successful in terms of the density achieved and the fidelity of the dimensions to the starting CAD design (CAD diameter = 20 mm; CAD plate side = 15 mm) and, in particular, the ones corresponding to the lowest level of exposure dose were the most outstanding, as can be seen in Figure 4.9 for discs and Figure 4.10 for plates.

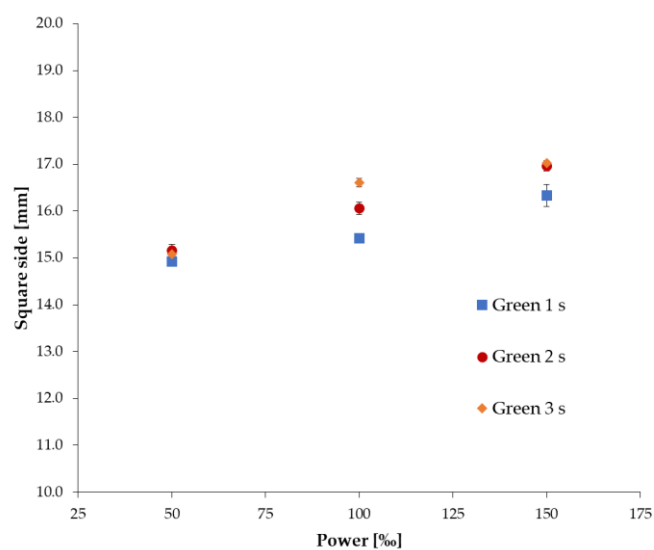


(a)

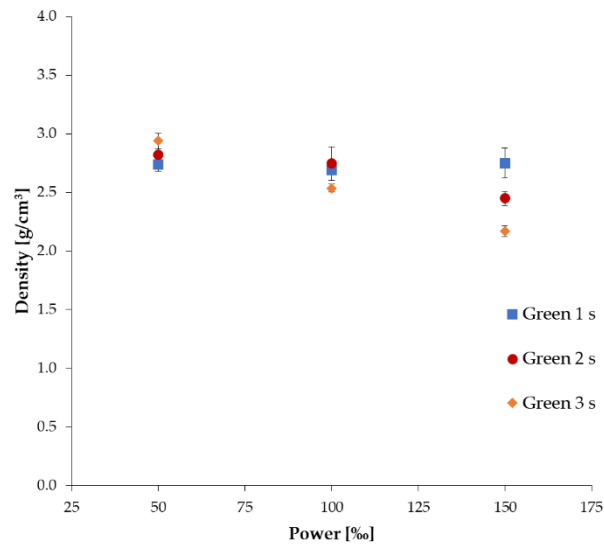


(b)

Figure 4.9 - Diameter dimension (a) and measured density (b) of the DLPEd discs with 25 µm layer thickness.



(a)



(b)

Figure 4.10 - Side dimension (a) and measured density (b) of the DLPed plates with 25 μm layer thickness.

The highest setting of power produced inaccurate parts with a high deviation from the corresponding dimension modelled via CAD and, also, a significant standard deviation, as the results were less predictable due to the light scattering phenomenon. Since the energy input was too high, the respective cure depth was the equivalent of a few layers which, hence, were irradiated many times repeatedly. In the case of an exposure time of 3 s and an exposure dose of 150%, the same layer was irradiated almost 10 times, as can be deducted from Figure 4.8; naturally, this caused relevant overcuring, dimensional inaccuracies, and higher standard deviations (Figure 4.11). Therefore, parts produced with the lowest exposure dose among the samples printed with a layer thickness of 25 μm were considered the best ones (Figure 4.12) and, specifically, the parts that were exposed for 2 s and 3 s were labelled as the optimal ones, due to their good geometrical accuracy and final green density.

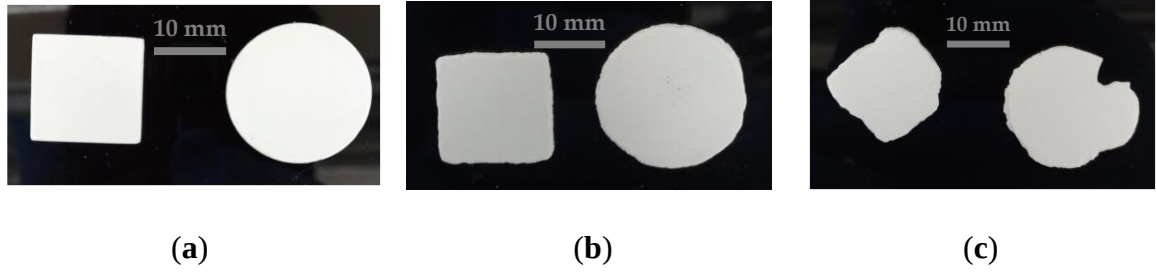


Figure 4.11 - DLP printed part with 25 μm as layer thickness, 3 s exposure time, and exposure dose of (a) 50%; (b) 100%; (c) 150%.

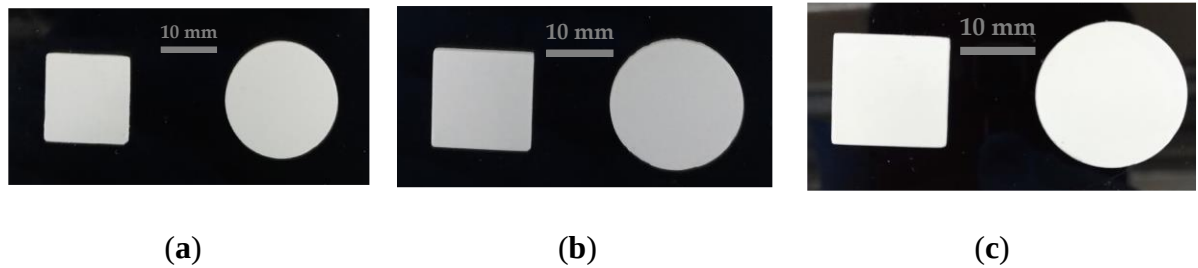


Figure 4.12 - DLP printed part with 25 μm as layer thickness, 50% exposure time, and exposure time of (a) 1 s; (b) 2 s; (c) 3 s, same as Figure 4.11a.

For the discs and plates with layer thicknesses of 50 μm and 100 μm , the samples that were tried to be produced at the lowest level of power and exposure time failed, as the energy input was probably not sufficient for guaranteeing enough light penetration to stick two consecutive layers in a stable way. Other conditions were all printed with different outcomes. Since the energy delivered to the layer in the same printing conditions, in terms of exposure time and power, was the same but the volume to which it was delivered was different, the samples with higher layer thickness failed or were mechanically weaker at lower energy input conditions, but survived successfully without heavy distortions or deviations at higher energetic conditions. However, due to the fact that for a specified thickness, the number of layers diminishes with the increase of the layer thickness, the 50 μm and, in particular, the 100 μm samples lacked a good interlayer cohesion, resulting in samples that had to be handled carefully and were slightly bendable. On the other hand, the 25 μm samples were more compacted and

rigid and, thus, achieved a greater density, which was the main objective for producing, in the end, translucent parts. It was interesting to notice that, in general, across all the samples, an increase in the exposure time level, rather than an increase in the exposure dose level when the same energy dose was delivered, led to better results, suggesting that the management of the exposure time is more significant than the management of exposure dose. In fact, the slower energy delivery to the slurry when longer exposure times and lower exposure doses are adopted allows the layers of the green parts to be cured more gradually from the uncured slurry surface directly exposed to the DLP projector up to the previously cured layers within the curing depth, ensuring a more stable printing, better interlayer bonding, and increasing geometric accuracy. On the contrary, conveying the same energy dose by utilising higher exposure dose levels and lower exposure times is more similar to an impulsive input of energy, which is less controllable and less accurate, resulting in a horizontal overcuring on the layer plane. Therefore, combinations of lower exposure doses and longer exposure times should be preferred when the optimal energy dose is already determined. It is very important to select the optimal set of parameters, as final sintered parts properties are dependent on the curing process during DLP printing, since the polymerisation grade of the green parts directly affects the bonded geometry of the unsintered alumina [56]. In addition, the high solid loading of small-sized ceramic particles ensures that the achievable final density is higher, as the capability to reach a greater sustainable packing factor allows a better densification [57].

Table 4.5 reports the significance values for the parameters investigated and their interactions, as obtained from Minitab 21, when density is imposed as the response to analyse, while Figures 4.13 and 4.14 illustrate the factorial plots for the density.

Table 4.5 - *p*-values of analysed factors and their interactions.

Factor	<i>p</i> -Value
Exposure dose	0.109
Exposure time	0.027
Layer thickness	0.066
Exposure dose – Exposure time	0.023
Exposure dose – Layer thickness	0.269
Exposure time – Layer thickness	0.246

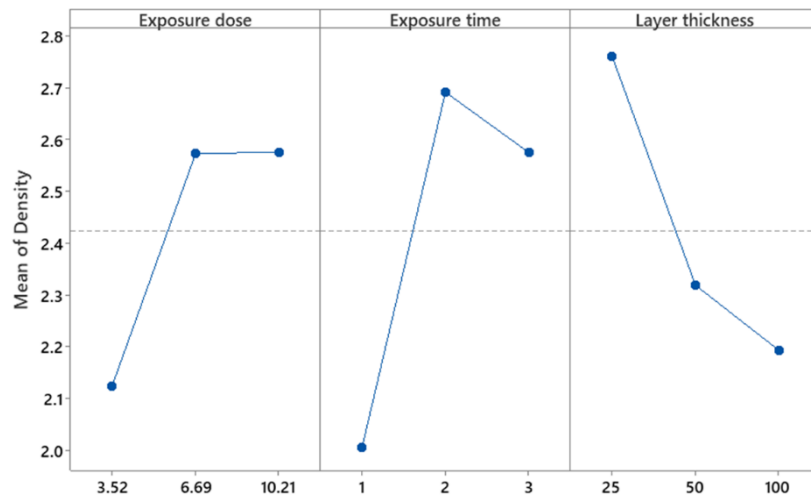


Figure 4.13 - Effect of the process parameters on the mean of the density.

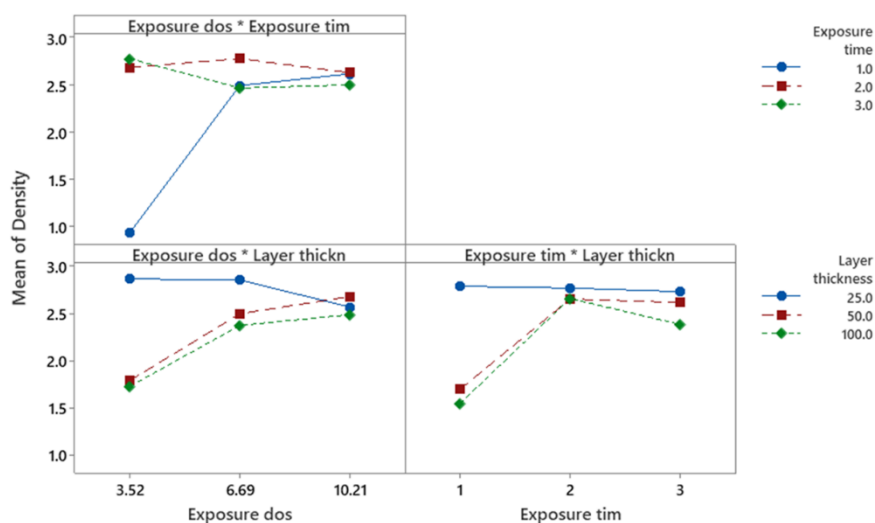


Figure 4.14 - Effect of the process parameters interactions on the mean of the density.

Following the previous findings that confirmed that the significant process parameters consisted of the exposure time and its interaction with the exposure dose, since their significance value was $p < 0.05$, the printing parameters of 25 μm as layer thickness, 2 s as exposure time, and 50% as exposure dose were considered the optimal parameters and were selected to print more discs for the following debinding experiments. It must be noted that the low values of mean density corresponding to the lowest levels of exposure dose and time were mainly due to the failed trials for the 50 μm and 100 μm layer thicknesses.

4.3.4 Thermal Post-Processing

The TGA–DSC study of the green body provided data on the breakdown behaviour of the organic materials in relation to the fluctuating temperature (Figure 4.15). At around 375 °C and 480 °C, two significant exothermic peaks were recorded and, as seen by the TG curve, the total mass loss was 15.29%, indicating the complete burnout of the organic components. The first

mass loss began to occur when the temperature was between 150 °C and 250 °C. This weight loss can be ascribed to the evaporation of adsorbed water and residual cleaning solution. The second mass loss took place between 270 °C and 380 °C, while the third and last significant loss occurred between 390 °C and 550 °C, beyond which the mass loss was negligible. Since the starting ceramic powder was α -Al₂O₃, from the DSC curve it can be deduced that the thermal debinding reaction was an exothermic process with two major peaks, the former attributed to the oxidative decomposition of polymer chains and the latter ascribed to the thermal decomposition of the crosslinked polymer network [58]. The debinding regime was established, based on these findings. Figure 4.16 illustrates the temperature settings for the debinding procedure in detail. The temperature was increased from room temperature to 175 degrees Celsius and allowed to dwell at this initial temperature setpoint. The temperature was then raised to 375 degrees Celsius and sustained for another dwelling-time period in order to degrade the organics slowly and, as a result, alleviate the thermal strains on the ceramic components. Afterwards, the system was heated to 480 degrees Celsius and kept at this temperature. Finally, the temperature was steadily increased to 1000 degrees Celsius to eradicate any organic residue and to pre-sinter the sample, which was held for another dwelling and, then, left to cool down to room temperature. Throughout the whole debinding procedure, the rate of heating was regulated according to the ongoing scheduled trial. Figure 4.16 illustrates the debinding regimes investigated.

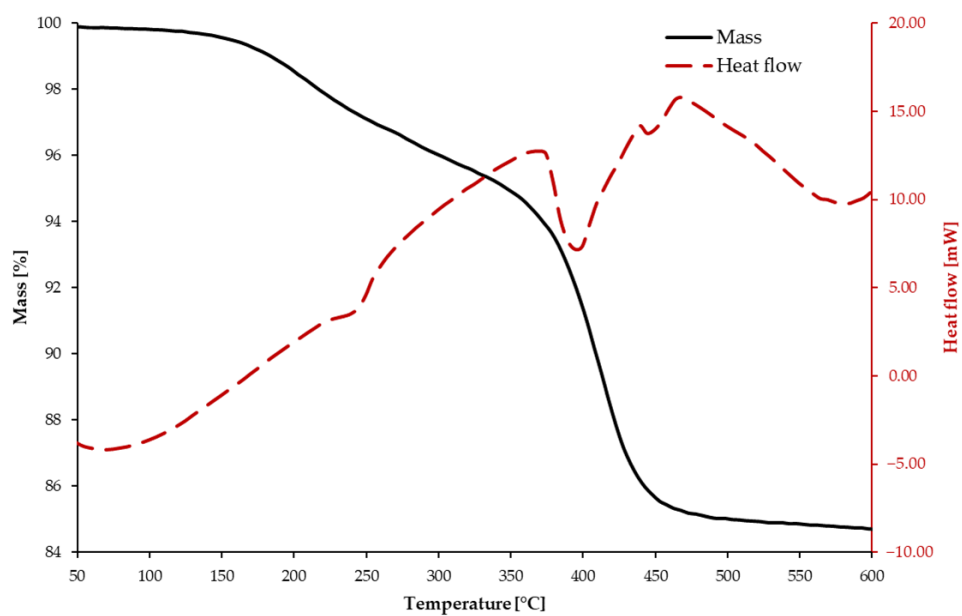


Figure 4.15 - TG-DSC curves of the DLPed Al_2O_3 sample.

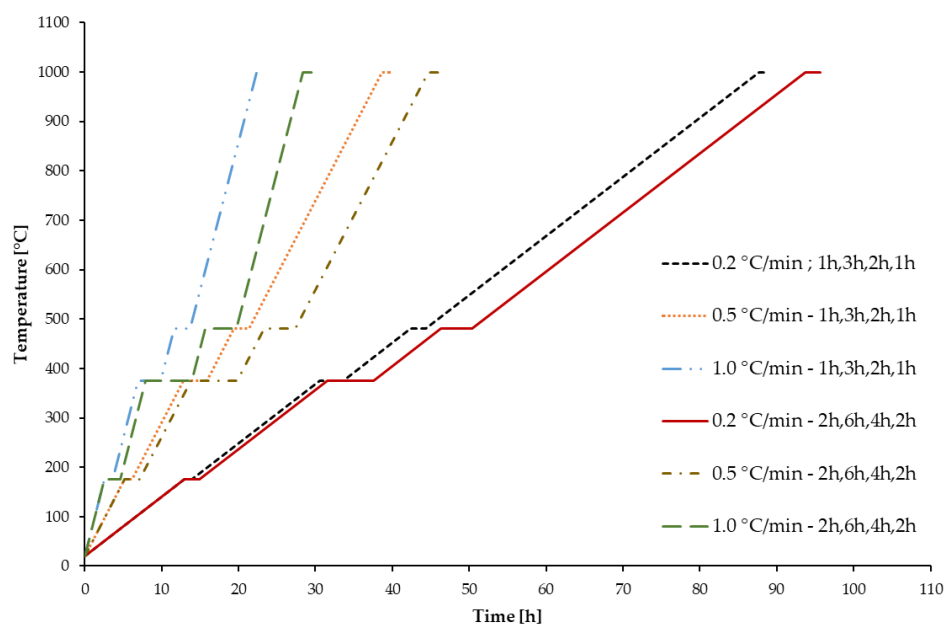
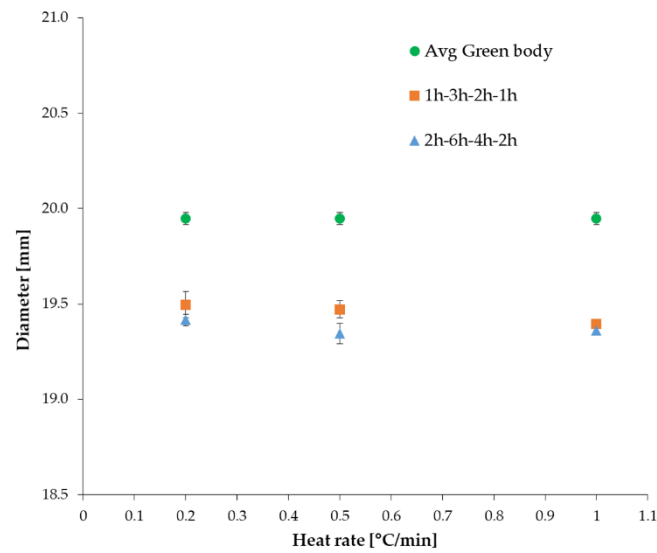
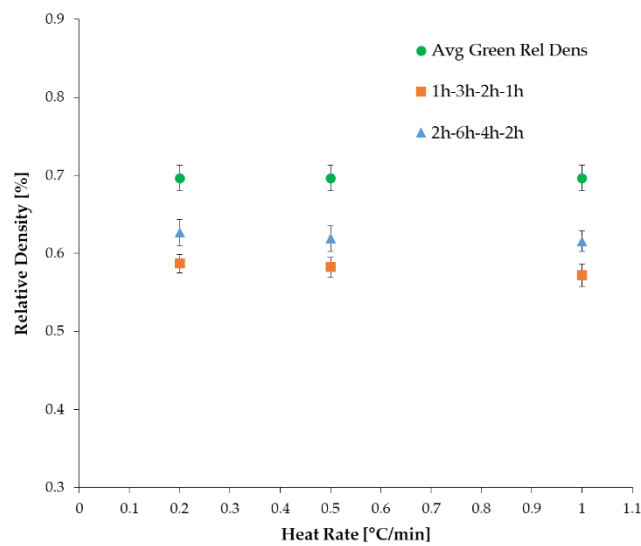


Figure 4.16 - Debinding regimes explored.

After undergoing debinding, the samples were again tested and measured to observe the geometrical dimensions and density evolution. The outcomes of these analyses are reported in Figure 4.17.



(a)



(b)

Figure 4.17 - Diameter dimension (a) and measured density (b) of the debound discs.

It was observed that at lower heating rates and longer dwelling times, the samples were able to reach higher densities, as the gradual removal of the binder over a longer time contributed to the reduction of residual pores [59] and, hence, to the reaching of higher brown densities. In fact, small heating rates when transitioning between peak dwelling temperatures provided more time for the organics to escape the ceramic structure, instead of being abruptly extracted and leaving behind cracks and defects. Moreover, longer holding times at significant dwelling temperatures ensured that all the corresponding organics exiting the sample were completely expelled. On the contrary, the highest heat rate of 1.0 °C/min, while allowing the samples to reach comparable densities to the ones obtained from the cycles at 0.2 °C/min, resulted in a lower diameter dimension, due to the rapid binder extraction, which caused loss of superficial debris and, hence, geometrical inaccuracy (Figure 4.18).

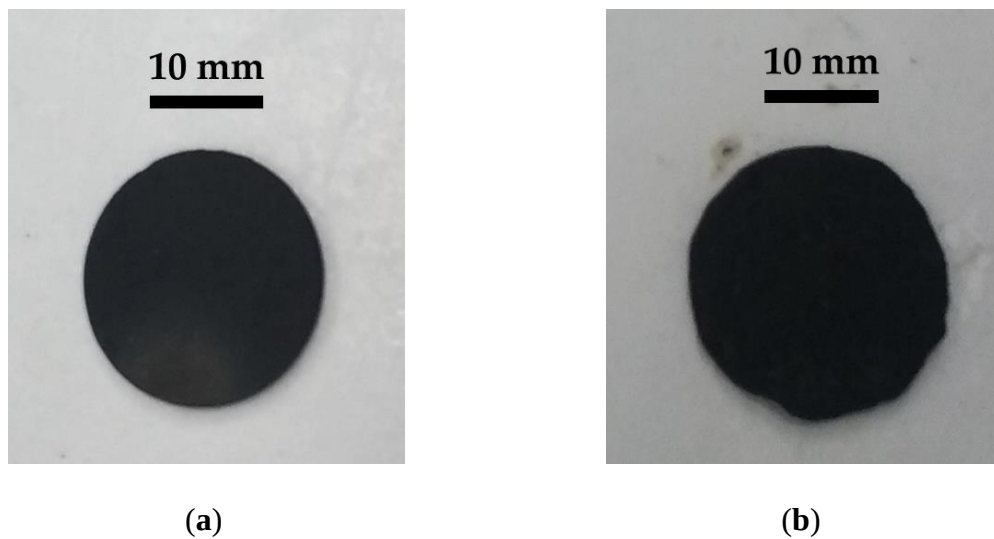


Figure 4.18 - (a) Sample debound at 0.2 °C/min for the longer set of holding times; (b) sample debound at 1.0 °C/min for the longer set of holding times.

Following the previous results, the debinding cycle with a heat rate of 0.2 °C/min and dwelling times of 2 h, 6 h, 4 h, and 2 h was chosen to conclude this investigation. The samples

were then prepared, following the process recipe established in this investigation, and finally heated up in an air sintering furnace at a heating rate of 10 °C/min until the temperature of 1700 °C was reached, then held in this condition for 12 h, after which they spontaneously cooled down inside the sintering furnace chamber. Another batch of samples was prepared following this process chain until the end, with the exception of adding MgO as a sintering aid in the starting slurry in a percentage of ~1000 ppm to promote densification and help with the management of the grain growth. Both samples exceeded the relative density of 98.5% and, in particular, the sample with MgO registered a relative density slightly higher than 99.0%, thereby starting to demonstrate a translucent behaviour (Figure 4.19).

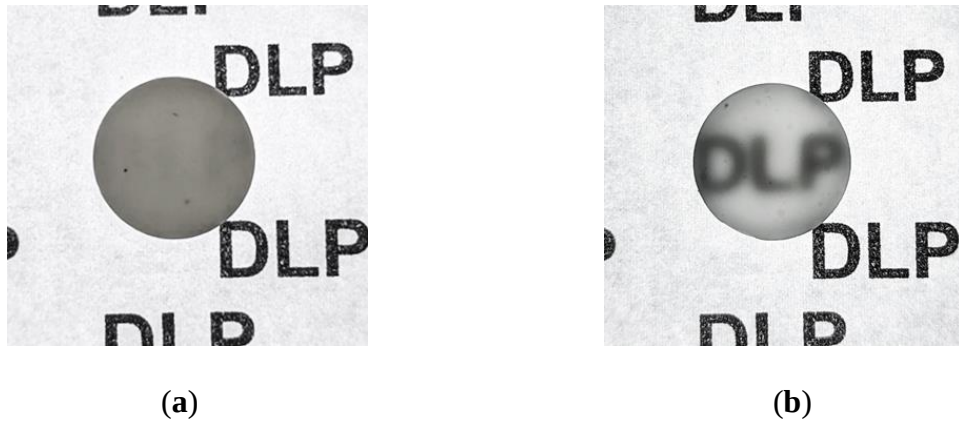


Figure 4.19 - (a) Sample prepared following the process recipe herein described; (b) sample prepared following the process recipe herein described with the addition of MgO as a sintering aid.

4.4 Conclusions

A systematic method for determining the optimal components and process parameters for developing an efficient slurry in-house from the ball-milling parameters selection down to the debinding regimes to follow was extensively presented. This method can be applied to tailor the slurry properties to the desired values and develop specific slurries for particular scopes,

such as, in this case, producing final parts that exhibit translucency, by working on constantly maintaining high values of relative densities. The main findings of this study can be summarised as follows.

- Within the workability window explored, dry ball milling with low milling time and high milling speed (1 h and 800 rpm) was the most effective in reducing agglomerates to sharpen the as-received powder size distribution.
- Among the investigated various dispersants and their concentrations, the most appropriate dispersant to use with the specific slurry prepared in this study was BYK-145 with a weight percentage content of 2% to the ceramic powder content.
- Different solid loadings were examined and ~85 wt.% of ceramic filler resulted in the optimal choice, reducing the risk of heavy distortions and excessive thermal stress while guaranteeing high densities at all stages.
- The curing behaviour of the prepared slurry was analysed and the conducted full-factorial DoE highlighted that exposure time and its interaction with the exposure dose were the most significant parameters in the DLP printing of the developed slurry. Optimal printing parameters were 2 s as exposure time and 50% as exposure dose when the layer thickness was set to 25 μm .
- Among all the debinding trials investigated, lower heating rates (0.2 $^{\circ}\text{C}/\text{min}$) and longer dwelling times delivered a more stable sample with higher relative density and geometrical dimensions retention.
- Finally, samples were manufactured according to the process schedule established and sintered at 1700 $^{\circ}\text{C}$ for 12 h. The ones with the addition of MgO (1000 ppm) as a sintering aid started to demonstrate a translucent behaviour.

Future development of this work should be aimed at achieving more dense and translucent samples by utilising a high-performance sintering furnace able to work under vacuum at high temperatures or a microwave sintering furnace. In addition, a study on the effect of sintering parameters, such as heating rate and dwelling time as well as dwelling temperature, may provide useful information on the optimal sintering cycle to follow and result in decreased light refraction. In fact, to obtain higher translucency, the final relative density of the parts must be increased further over 99.5% while controlling and tailoring the grain growth to maximise light transmittance. This could be achieved by sintering the parts under vacuum at high temperatures ($>1500\text{ }^{\circ}\text{C}$) in order to minimise air encapsulation and, hence, residual porosity, while improving the densification process.

Author Contributions: Conceptualization, methodology, investigation, formal analysis, data curation, and writing—original draft preparation, visualization, M.D.L.; investigation and writing—review and editing, C.S.; supervision and writing—review and editing, U.M.A. and K.E. All authors have read and agreed to the published version of the manuscript.

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CHAPTER 5. EFFECT OF DIFFERENT ADDITIVES AND SINTERING REGIMES ON THE OPTICAL PROPERTIES OF DLP PRINTED TRANSLUCENT ALUMINA

Authors Contributions:

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Michele De Lisi: Conceptualisation, methodology, formal analysis, investigation, data curation, writing – original draft preparation, visualisation, writing – review and editing

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Dr Usama M. Attia: Supervision, writing – review and editing

Prof Khamis Essa: Supervision, writing – review and editing

EFFECT OF DIFFERENT ADDITIVES AND SINTERING REGIMES ON THE OPTICAL PROPERTIES OF DLP PRINTED TRANSLUCENT ALUMINA

Abstract

Additive manufacturing of components with enhanced characteristics to combine the geometrical flexibility of layer-by-layer manufacturing and the remarkable thermomechanical and optical properties of advanced materials has become a focus for research in the last decades. In this investigation, in-house developed Al_2O_3 slurries mixed with either MgO or MgAl_2O_4 were digitally light processed and the resulting green parts underwent slow thermal debinding at low heating rates to produce dense and stable brown samples, which were subsequently subjected to different sintering regimes to obtain translucent samples. Air sintering trials were conducted at 1700 °C and the effect of different heating rates and holding times at the sintering temperature were investigated. In addition, vacuum sintering at 1600 °C was conducted for the best conditions to assess the effect of an oxygen-reduced atmosphere. Geometrical dimensions and density data were collected at the brown and fired stages to observe their evolution through the process with the help of high-magnification optical microscopy. Scanning electron microscope (SEM) images of the sintered samples were collected to observe and characterise the obtained microstructure. In addition, X-ray diffraction (XRD) was used to identify the

crystal structure and assess the insurgence of secondary phases. Finally, total transmittance and in-line transmittance were measured to evaluate the translucency level achieved by the produced sintered samples. Translucent alumina samples exhibiting a maximum total transmittance of 90.4% and a maximum real in-line transmittance (RIT) of 16.9% in the visible and near-infrared regions were fabricated.

Keywords: grain growth, porosity, optical properties, Al_2O_3 , additive manufacturing

5.1 Introduction

In recent decades, a potential substitute for conventional production has been proved to be Additive Manufacturing (AM). Plastics and metals currently dominate the processed materials sector and have been the main field of interest among researchers. In fact, previous literature has documented instances of adopting Fusion Deposition Modelling (FDM) to fabricate intricate PLA-based parts [1,2] or exploiting the benefits of selective laser melting [3,4] and laser powder bed fusion [5–7] to produce complex metallic structures. These investigations have extensively and systematically investigated the feasibility of achieving advanced material structures and the impact of the process factors on the mechanical and microstructural properties of the finished products. Nonetheless, ceramic additive manufacturing is increasingly emerging as a topic of significant interest in recent times [8–10]. While stereolithography (SL) has been widely recognised as a prominent additive manufacturing process, Digital Light Processing (DLP) has emerged as a particularly promising procedure that not only derives from the SLA approach but also enhances its capabilities. The main advantage of DLP technology over its parent process is its ability to expedite and enhance

the production of a component [11]. This is achieved by employing a projected light source that cures individual layers of slurry sequentially, as opposed to a single point or line.

Commonly, the slurries employed in ceramic additive manufacturing by DLP typically consist of ceramic fillers, binders and photoinitiators and may include other additives, such as dilutants, sintering aids and UV absorbers. When contemplating potential combinations, it is significantly important to evaluate the interplay among all entities involved as well as significant mismatches between the indexes of refraction of ceramic particles and photopolymerisable resins, which can lead to a reduction in cure depth and printing resolution [12], thereby influencing the final geometrical accuracy and density [13,14]. In addition to considering the preprocessing and printing settings, it is crucial to optimise the debinding and sintering processes and implement stringent controls in order to get crack-free samples [15,16]. The diffusion of the binder within the ceramic green body leads to the formation of microcracks, which can be attributed to elevated heating rates as well as inappropriate holding temperatures and durations [29]. If microcracks are formed at the debinding stage, the mechanical properties of a material are compromised during the sintering process. Hence, it is important to properly determine the optimal process parameters in order to efficiently produce defect-free brown bodies [14,16]. Nevertheless, it is also vital to utilise an appropriate sintering regime to ensure the complete attainment of the ceramic densification process to avoid a deterioration of the material microstructural properties. Therefore, it is imperative to conduct thorough investigations on suitable sintering temperatures in order to fully harness the potential of ceramic materials and achieve advanced properties, in particular translucency or transparency, which requires the component to have a relative density higher than 99.5%. In fact, even increasing the sintering dwell temperature of alumina samples from 1540 °C to 1650 °C as well as employing a sintering holding time of 2 or 4 h can lead to parts ~2% more dense [17].

Furthermore, the addition of sintering aids can significantly affect the diffusion and densification of the material. Oxides like SiO_2 , MgO and CaO are the most mentioned and commonly used sintering aids, even though La_2O_3 , B_2O_3 or Sc_2O_3 have also been employed as additives to facilitate the reduction of porosity and increase the relative density [18]. In particular, magnesium oxide has been found to be extremely beneficial for vacuum sintering processes of Al_2O_3 parts even at very small amounts (<0.25 wt%) [19], able to effectively prevent excessive grain growth [20,21]. Another efficient sintering additive for alumina components is La_2O_3 , particularly when used in combination with Y_2O_3 and MgO [22,23], as it has been proven that its addition via infiltration techniques facilitates the achievement of enhanced transmittance at wavelengths of 800 nm. Finally, another sintering aid adopted for significantly improving the densification process and the final optical properties of translucent alumina is MgAl_2O_4 by increasing the maximum relative density achieved [19,24]. To create transparent ceramics, it is required to remove all conceivable sources of light scattering, including residual holes inside the grains and at the grain borders, grain boundaries, second phases at the grain boundaries and birefringence for noncubic materials. Therefore, improving the densification process even with the addition of appropriate sintering aids is of invaluable importance to obtain the desired optical properties in the final part.

In recent times, a number of captivating investigations in the AM field have been undertaken to produce ceramic components specifically designed for the creation of catalytic substrates [25–27] or specialised uses in micro-electro-mechanical systems [28]. However, the optical capabilities of ceramic materials have not to be disregarded. Transparent ceramics provide distinctive thermomechanical properties, such as superior mechanical resistance, excellent resistance to thermal shock, the ability to include various dopants and excellent optical transparency that challenge single-crystal ceramics, rendering them highly appropriate for a

diverse range of high-performance applications, including but not limited to lasers, armours and lighting [29]. In fact, there exists an urgent requirement to concurrently reduce the mass of transparent armour systems while enhancing their ballistic protective properties. In this regard, ceramic materials like magnesium aluminate spinel, AlON and sapphire have displayed similar performance levels, optimal for the intended scopes. However, to this day, costly and advanced sintering techniques, such as spark plasma sintering (SPS) [30] and hot and cold isostatic pressing (HIP and CIP) [31,32] are commonly required to achieve a high density. Expensive machine assets, post-processing operations and high costs associated with these processes have relegated transparent ceramics mass production to a few prosperous industries.

As a consequence, research on the AM of transparent ceramics has been very prolific in the past decade. Two-photon printing (TPP), direct ink writing (DIW) extrusion-based copolymer-assisted AM processes were employed in the fabrication of tiny transparent and complexly shaped YAG parts, respectively, achieving precise dimensions in the nanometre and micrometre scales [33–35]. Nonetheless, it is important to note that, generally, the subsequent procedures of cold and hot isostatic pressing remained necessary. DLP has also been employed to produce transparent Nd: YAG ceramics and demonstrated its significant capabilities of achieving scalable massive fabrication of highly transparent Nd-doped YAG ceramics [36]. Recently, aluminium oxide has been additively manufactured via extrusion techniques [37] and digital light processing [14,24], despite its non-cubic lattice structure. By systematically optimising all the steps of the entire production chain, particularly focusing on the slurry development and the printing parameters, translucent alumina samples in the centimetre scale have been fabricated without recurring to conventional processing methods, such as CIP and HIP, thus drastically reducing the production costs and widening the audience spectrum.

However, while the influence of slurry preparations and printing parameters have been investigated to assess the process feasibility and optimise the final properties, the effect of different sintering regimes, diverse atmospheres and different additives on the densification and the optical properties of the additively manufactured samples has not been explored. In fact, only MgO and single-step or two-step vacuum sintering were employed to fabricate the aforementioned translucent components while optimised air sintering has not been explored. Since sintering aids and sintering parameters can significantly affect the densification process and the final microstructure, which is fundamental for achieving translucency, in this study the results obtained from the addition of MgO or MgAl_2O_4 as well as the use of different heating rates and dwell times have been analysed and investigated. By understanding the trends and the impact of each factor on the residual porosity and the microstructure of the part, improved density packing and enhanced optical properties can be achieved by revealing the optimal firing strategy.

5.2 Materials and Methods

5.2.1 Polymerisable slurry preparation

The methodology for preparing the alumina powder can be referenced in a prior publication authored by the present research team [14]. The ceramic powder utilised for the photopolymerisable slurry was alfa alumina (99.8%, CT 3000 LS SG, Almatix GmbH, Ludwigshafen, Germany). The initial aluminium oxide powder, with a median particle size of $0.92\text{ }\mu\text{m}$, was subjected to ball milling in the presence of 0.8 mm aluminium oxide grinding media (Industrie Bitossi S.p.A., Spicchio-Sovigliana, Italy) to obtain a starting D50 of

0.71±0.01 μm . The ball-to-powder ratio (BPR) used was 1:1 and the milling process was carried out using a planetary ball mill (model HMK-1901, Dandong HMKTest Instrument Co. Ltd., Dandong, Liaoning, China). The alumina powder was ball milled at 800 rpm for 1 h and subsequently sieved using a 250 μm mesh screen. When studying the effect of magnesium oxide (MgO) or magnesium aluminate (MgAl_2O_4) as additives, these were added before the ball milling in a content of 1000 ppm and, hence, were mixed with the as-received alumina powder. The ceramic powder particle size distribution was determined by laser diffraction particle size analysis (Sympatec GmbH, Clausthal-Zellerfeld, Germany) (Figure 5.1), performed in a liquid dispersion including water and a dispersant, namely two drops of tetrasodium pyrophosphate.

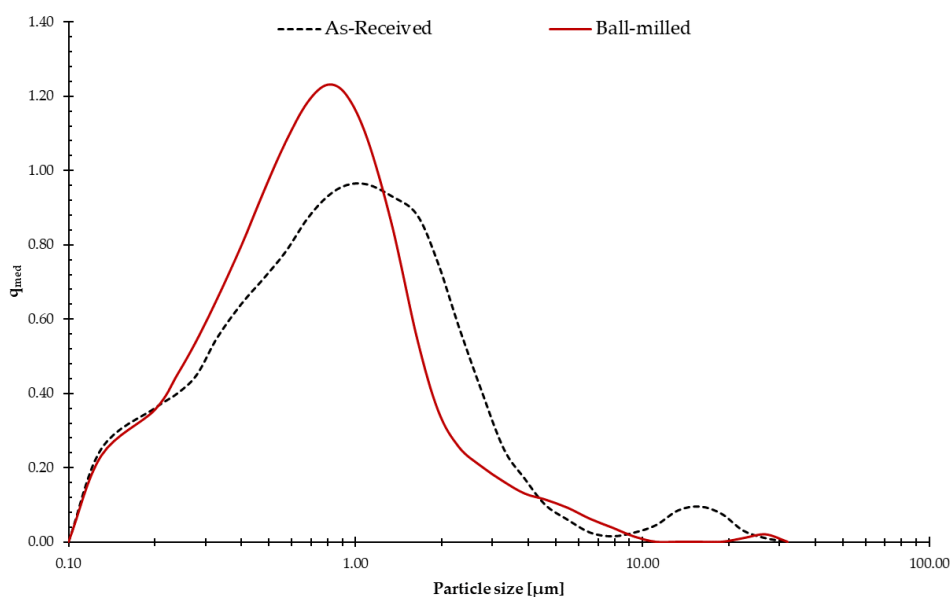


Figure 5.1 - Comparison of as-received alumina powder vs ball-milled powder particle size distributions.

The photocurable resin was synthesised in-house by the combination of polyfunctional and monofunctional monomers, along with the addition of BYK-145 as a dispersant (in a

quantity equal to 2 wt% of the ceramic powder content) and a plasticizer (constituting 20 wt% of the resin) to mitigate the occurrence of delamination. The photoinitiator used in this study was diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (TPO) (Sigma Aldrich, Gillingham, UK). It was added to the resin mixture at a concentration of 1.0 wt% relative to the total weight of the photoreactive resin components. Finally, a ratio of 6:5 was selected for a difunctional polymer and a monofunctional polymer, respectively, and a ceramic loading of 85 wt% was adopted (Table 5.1). The methodologies employed in the preparation of ceramic slurry were obtained from the existing literature [14,38].

Table 5.1 - Slurry composition.

Starting Materials	Resin–Photoinitiator Mixture	Powder
Composition	Monofunctional and difunctional	$\text{Al}_2\text{O}_3 + \text{MgO}$
	monomers, BYK-145, plasticizer,	or
	TPO	$\text{Al}_2\text{O}_3 + \text{MgAl}_2\text{O}_4$
Mass percentage	~15 wt% total	~85 wt% total

After efficiently amalgamating the resin constituents with an overhead mixer under ambient conditions and incrementally adding the ceramic powder till achieving the solid loading of 85 wt%, the photoinitiator was then added to the mixture, which was finally subjected to mechanical stirring for an additional 30 min. Afterwards, the resulting slurry was transferred to a turbula mixer and allowed to undergo agitation for a minimum period of 12 h. This process was carried out in the presence of 6 mm spherical alumina grinding media (Industrie Bitossi S.p.A., Spicchio-Sovigliana, Italy) at a BPR of 1. Prior to the printing procedure, the slurry underwent a 10 min treatment in a vacuum degasser in order to remove any air bubbles and reduce the possible occurrence of polymerisation inhibition [39,40].

5.2.2 Additive Manufacturing via Digital Light Processing

The 3D printing machine adopted in this research was the Admaflex 130, manufactured by Admatec Europe BV, Alkmaar, The Netherlands. This machine has the ability to achieve a layer plane resolution of 40 μm , with a light source with a wavelength of $\lambda=405\text{ nm}$. The Admaflex 130 utilises a rotating foil system to facilitate the transportation of the slurry from the reservoir to the designated 3D construction area and, finally, to the collector. During the actual 3D printing, several mirrors capable of moving in accordance with pixels enable the imprinting of intricate model slices into the viscous slurry work. Furthermore, to minimise waste, an integrated pump mechanism is employed to redirect any wasted slurry back to the reservoir. The light-reactive slurry is subjected to illumination at the operational wavelength of the apparatus, resulting in the simultaneous curing of the whole layer. The green body is cured iteratively, with each layer being printed and cured before proceeding to the next.

Several pure alumina and either MgO-doped or MgAl_2O_4 -doped samples, each having a diameter of 20 mm and a height of 1.5 mm, were fabricated. The fabrication process consisted of depositing consecutive layers with a layer thickness (LT) of 25 μm , cured at an exposure time (ET) of 2 s and an exposure power (EP) of 50% according to the machine settings, which corresponded to an irradiance value of 3.52 mW/cm^2 , until the complete part was produced. The printed components were then separated from the construction plate and subjected to a deep cleaning process, which consisted of debris removal via compressed air and ethanol baths (Figure 5.2).

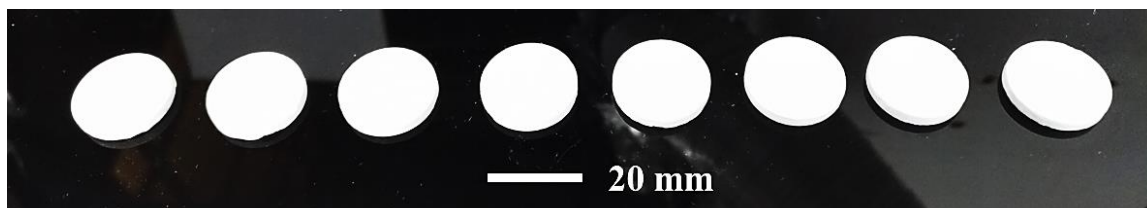
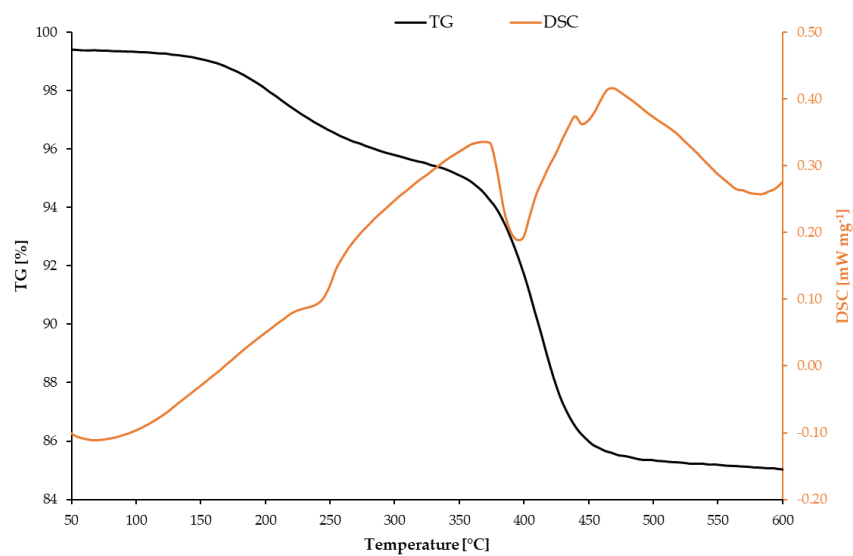


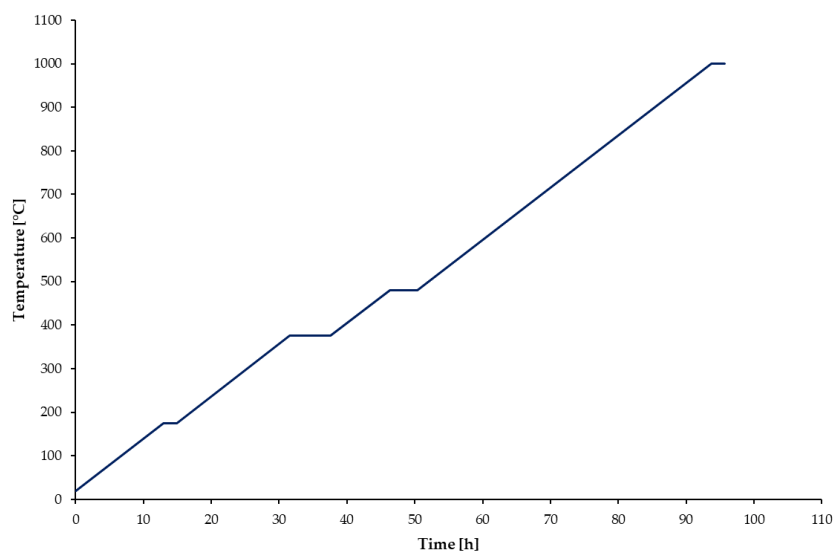
Figure 5.2 - DLPed green samples.

5.2.3 Post-processing binder removal

The extraction of the photopolymerisable resin from the interstitial spaces among the ceramic particles constitutes a crucial stage in the post-processing of 3D-printed components. During the debinding process, the organic constituents of the green body undergo decomposition, resulting in the formation of gaseous molecules. These molecules diffuse and penetrate the surface of the green body, finally being released and generating voids between particles inside the resulting brown body. In order to ascertain the mass loss of the DLP-printed green body and identify the critical temperature for binder removal, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) tests were conducted using an SDT NETZSCH STA instrument (Figure 5.3a). The adopted debinding regime for producing highly dense and pores-free samples possessed a very low heating rate of 0.2 °C/min to improve densification and facilitate binder removal [41] while the dwell temperatures were set at 175 °C, 375 °C and 480 °C, with holding times of 2 h, 6 h and 4 h, respectively. Additionally, a pre-sintering step was implemented at a temperature of 1000 °C for 2 h in order to enhance the compactness of the material and simplify the handling of the sample after debinding (Figure 5.3b). The debinding cycles were conducted in static air using a tube furnace (TSH/15/75/450, Elite Thermal Systems Ltd., Market Harborough, UK).



(a)



(b)

Figure 5.3 - (a) TGA/DSC curves of green Al_2O_3 samples; (b) adopted debinding cycle.

5.2.4 Sintering cycles

In order to investigate the density modification of the debound DLPed cylinders, firstly, sintering tests on the pure alumina samples were conducted in an air sintering furnace (HTF 17/27, Carbolite Gero, Sheffield, UK) at various heating rates and holding time durations at the sintering temperature, which was maintained fixed at 1700 °C, according to the maximum temperature safely reachable by the available furnace. A total of nine distinct sintering cycles were explored, as outlined in Table 5.2. Ultimately, three different heating rates, spanning from 1.0 °C/min to 10 °C/min, were chosen, along with three diverse holding periods, from 2 h to 12 h.

Table 5.2 - Sintering experiments investigated with pure alumina samples.

Sintering trial	Sintering temperature [°C]	Heating rate [°C/min]	Dwell time [h]
T1	1700	1	2
T2			4
T3			12
T4		5	2
T5			4
T6			12
T7		10	2
T8			4
T9			12

A total of four samples were produced for each sintering experiment and subsequently cooled in air in the furnace chamber. The mean values of the geometrical dimensions and densities, together with their respective standard deviations, were documented. The measurements of the samples' geometrical dimensions were conducted using a Vernier calliper in conjunction with an optical microscope, namely the Alicona InfiniteFocusG5 plus (Bruker Alicona, Leicestershire, UK), while the density of the samples was determined using Archimedes' method in deionised water with long settling times. Furthermore, scanning electron microscopy (SEM) images (TM3030 Tabletop SEM, Hitachi High-Technologies, Tokyo, Japan) were captured at the sintered stage in order to investigate grain microstructure changes.

Subsequently, the two sintering conditions resulting in the most promising samples were selected to investigate the effect of the sintering aids (magnesia and magnesium aluminate spinel) on the physical and optical properties of the fired samples. The same sintering conditions were also adopted to perform vacuum sintering trials in the presence of the additives, with the difference that, due to the limitations imposed by the available furnace capabilities, the sintering temperature was decreased to 1600 °C. Fired sample dimensions and densities data of four diverse samples for each studied condition were collected with the same methods previously described. Afterwards, the fabricated discs were polished on both circular surfaces and X-ray diffraction (XRD) analysis (Cu-K α cathode, AXRD Benchtop Powder Diffraction System, Proto Manufacturing, Michigan, USA) was conducted while rotating the thin disc samples (<1 mm) to identify the crystallographic structure of the parts and assess if any secondary phase had emerged to hinder the translucency of the samples. In addition, the optical properties of the samples were tested on a UV-3600i Plus Shimadzu UV-VIS-NIR Spectrophotometer (Shimadzu Corporation, Kyoto, Japan) and total transmittance and in-line transmittance data

were collected. Lastly, after thermally etching the alumina discs at 100 °C below their corresponding sintering temperature [42–44], SEM images (JCM-6000, JEOL Ltd., Tokyo, Japan) were also collected to analyse the grain distribution and size.

5.3 Results and Discussion

5.3.1 XRD analysis

The XRD patterns of the samples sintered for 12h are reported in Figure 5.4. The obtained diffraction data are in optimal agreement with the ones of the entry 96-100-0033 in the Crystallography Open Database (COD) [45].

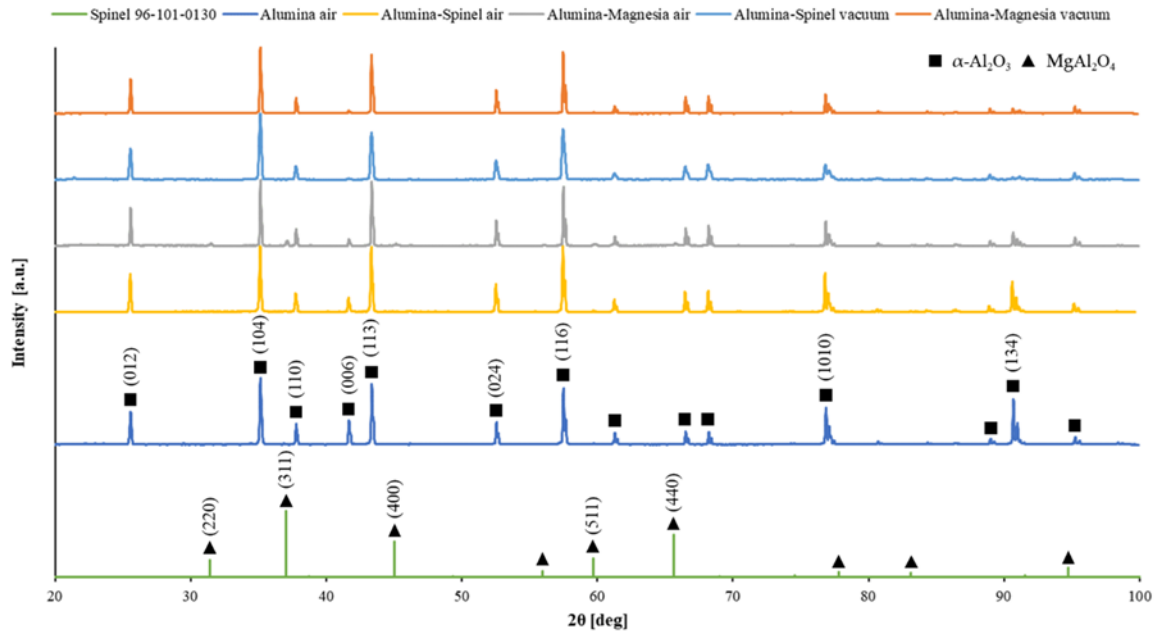


Figure 5.4 - XRD patterns of the samples sintered at the dwell temperature for 12 h

XRD data revealed a hexagonal crystal structure and intensity peaks at the 2θ values of 25.6° , 35.2° , 37.8° , 41.7° , 43.4° , 52.6° , 57.5° , 76.9° and 90.7° could be observed, with corresponding indices of Miller of (012), (104), (110), (006), (113), (024), (116), (1010) and (134) for the favourite crystallographic directions. It can be noticed that all the diffraction peaks that appeared in the pure alumina sample were generally maintained across all the analysed sintered parts in similar proportions, with the exception of the ones corresponding to the Miller indices of (006) and (134), which decreased in intensity in the air sintered samples and nearly completely disappeared in the vacuum ones to negligible values. Conversely, the air-sintered MgO-doped sample exhibited smaller peaks at the 2θ values of 31.5° , 37.1° , 45.1° , 59.8° and 65.7° , approximately matching the 2θ positions of the most intense diffraction peaks of a slightly compressed magnesium aluminate diffraction pattern with Miller indices of (220), (311), (400), (511) and (440), respectively. These findings may suggest the in situ formation of extremely small amounts of alumina-rich magnesium aluminate spinel at the alumina grain borders as the MgO and Al_2O_3 initiate an interdiffusion process which is further promoted by longer sintering holding times [46]. In fact, according to the MgO- Al_2O_3 phase diagram [46], alumina-rich spinel, which has better corrosion resistance than equal mole magnesium aluminate [47], can be produced at the sintering temperature of 1700°C , especially if cooling rates are restrained as in the case of air cooling inside the sintering chamber.

5.3.2 Sintered Al_2O_3 samples characterisation

In Figure 5.5, the average values of diameter and related standard deviations for each sintering trial are illustrated. As can be noticed, the differences between the explored sintering conditions in terms of diameter evolution are minimal.

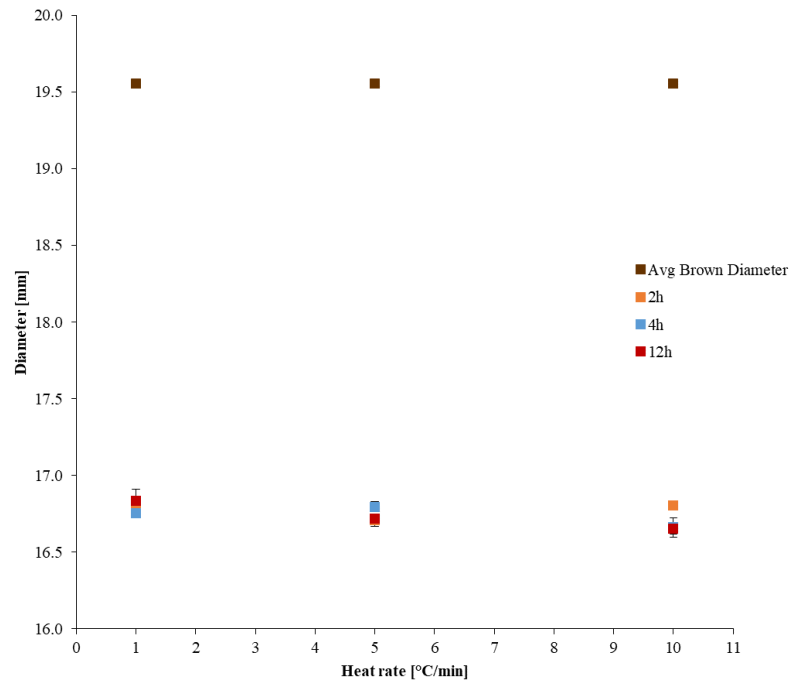


Figure 5.5 - Diameter dimension evolution at different sintering conditions.

Nonetheless, even though all the trials exhibited a similar trend when the standard deviation was considered, the samples held at the sintering temperature for 12 h, in particular, showed a noticeable increase in the shrinkage in the radial dimension when the heating rate increased. In fact, when lower heating rates are applied, the samples are maintained for a longer time at lower temperatures, where thermal expansion is the predominant phenomenon over the sintering effect, leading temporarily to coarser grains and wider diameters [17] that result in reduced final shrinkages. However, at higher heating rates, grain densification is promoted and the synergy of this effect and grain growth at high temperatures rather than low ones facilitates the increase in shrinkage. Besides, when the dwell time is increased, the interlayer spacing decreases enhancing the hardness and compactness of the sample due to the robust interfacial connection between alumina particles [48]. This is also proven by the relative density evolution of the alumina discs, reported in Figure 5.6.

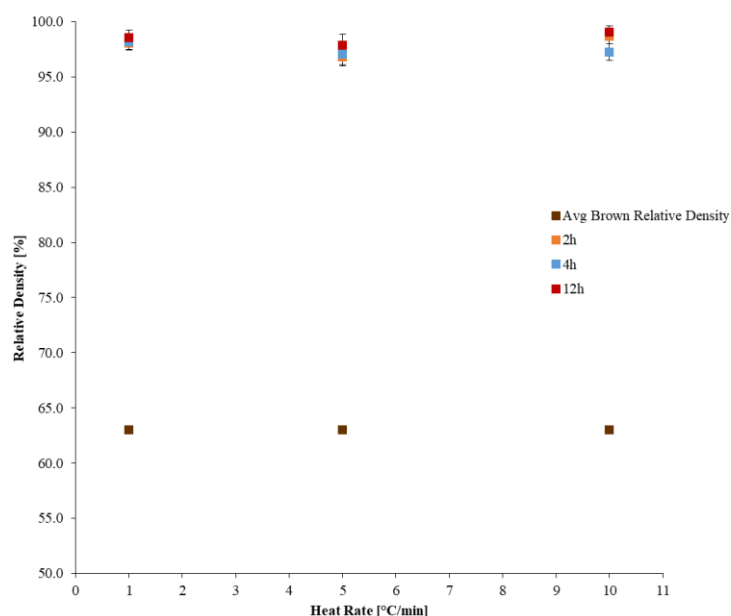
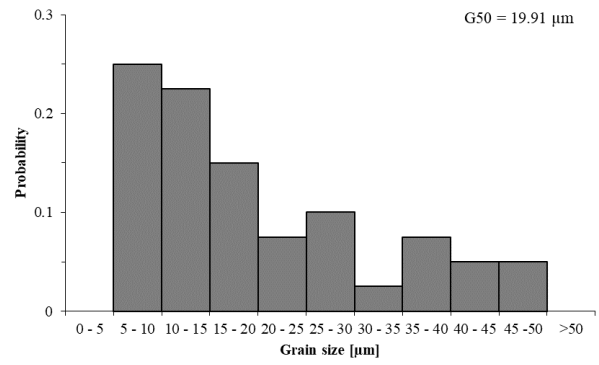
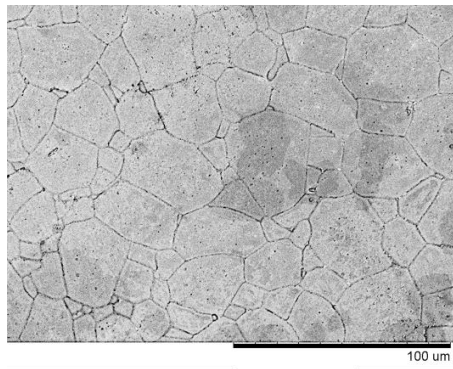
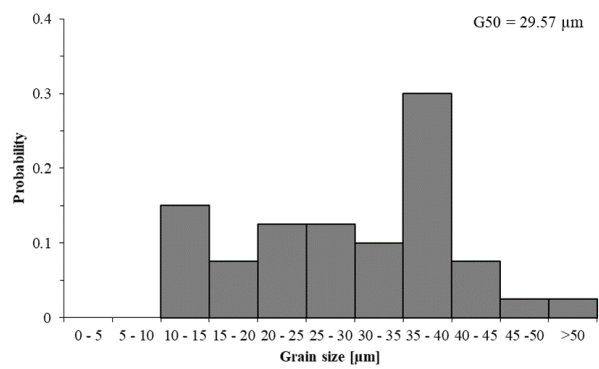
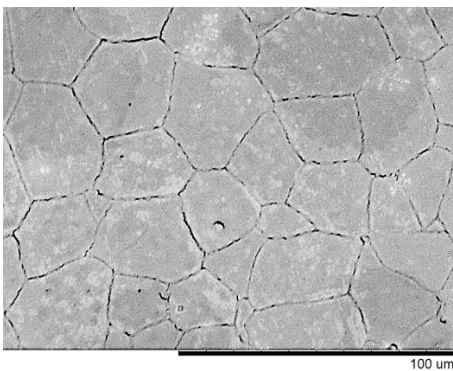


Figure 5.6 – Relative density evolution at different sintering conditions.

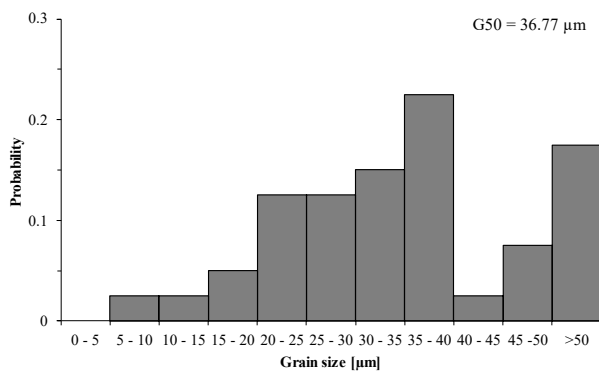
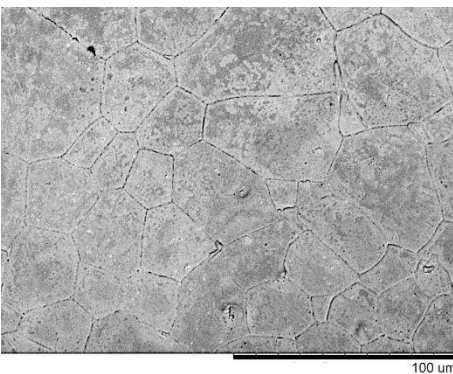
The T9 alumina parts, sintered at 1700 °C for 12 h at 10 °C/min, possessed the highest observed relative density (99.0 ± 0.4 %), followed by the T7 ones (98.7 ± 0.5 %), proving that rapid heating improves the densification and long holding times at high temperatures further enhance the packing of alumina particles. In fact, when comparing SEM images of the investigated sintering trials (Figure 5.7), it can be rapidly noticed that, even though T9 samples have more enlarged grains compared to T7 and T8 ones due to the longest holding time, they possessed a noticeably dense microstructure that doesn't leave almost any space to intergranular porosity. On the other hand, while T8 samples exhibited a similar average grain dimension without presenting the same cohesion level of T9 ones as intergranular porosity could be detected, the T7 microstructure was still well-organised and consisted of grains with an average dimension of around half the one of T9 alumina discs.



a)



b)



c)

Figure 5.7 - SEM images and grain analysis of the microstructure of the samples: a) T7; b) T8; c) T9.

For the well-organised microstructure and for achieving higher densities, hence possessing the needed requirements for exhibiting translucency, T7 and T9 sintering conditions

were selected to continue the experimental research for studying the effect of including the sintering aids in the formulation on the fabrication of fully dense alumina discs.

5.3.3 Sintered MgO-doped and MgAl₂O₄-doped Al₂O₃ discs characterisation

After debinding all the disc samples in static air following the prescribed heating cycle, T7 and T9 sintering conditions were applied to MgO-doped and MgAl₂O₄-doped alumina discs in both air and vacuum atmospheres. It must be mentioned that, while it was possible to fire the air-sintered samples relatively shortly after the binder removal, vacuum-sintered ones remained for an extensive period of time in the debound stage before being fired, which facilitated the accumulation of moisture. The extended permanence in the debound state, overall in an environment with substantial fluctuations in temperature and humidity, should be avoided at any cost to impede the build-up of moisture and the worsening of the pre-sintering conditions of the samples. Moreover, the alumina discs were removed from the debinding furnace covered in layers of carbon powder, since the binder removal is conducted in static air, and were not properly flushed. Whereas carbon deposits do not pose a substantial risk during air sintering, in the case of vacuum sintering they represent a relevant obstacle to surface densification, a serious source of sample contamination and a discolouring agent that darkens the parts [49,50]. In fact, the phenomenon of carbon diffusion into alumina is influenced by the reduction in partial pressure of air that occurs during the process of vacuum sintering, promoting a pinning effect on the alumina samples and resulting in the suppression of the grain growth and reduction of the densification rate at the poorly densified surfaces of the parts [50]. Even though the contained grain growth may be considered a positive effect to obtain a finer microstructure and

the reduced densification is constrained to a few superficial microns, these conditions lead to samples that were overall less dense and darkened in colour, hindering the insurgence of the desired optical properties and impeding the development of translucency or transparency in the samples. In the presented research, the samples designated for vacuum sintering were unintentionally contaminated from the debinding carbon residues and the extensive permanence in thermally uncontrolled environments at the debound stage promoted the build-up of moisture, which further fostered the adhesion of carbon powder to the alumina discs, leading after vacuum sintering to black-coloured alumina parts throughout their whole body unable to demonstrate significant transmittance (Figure 5.8).

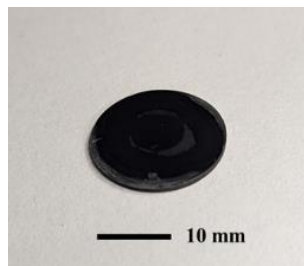


Figure 5.8 - Example of vacuum-sintered carbon-contaminated Al_2O_3 sample.

Nevertheless, the relative density and the microstructure of all the samples were investigated. Figure 5.9 illustrates the collected data on the relative density of the sintered alumina discs.

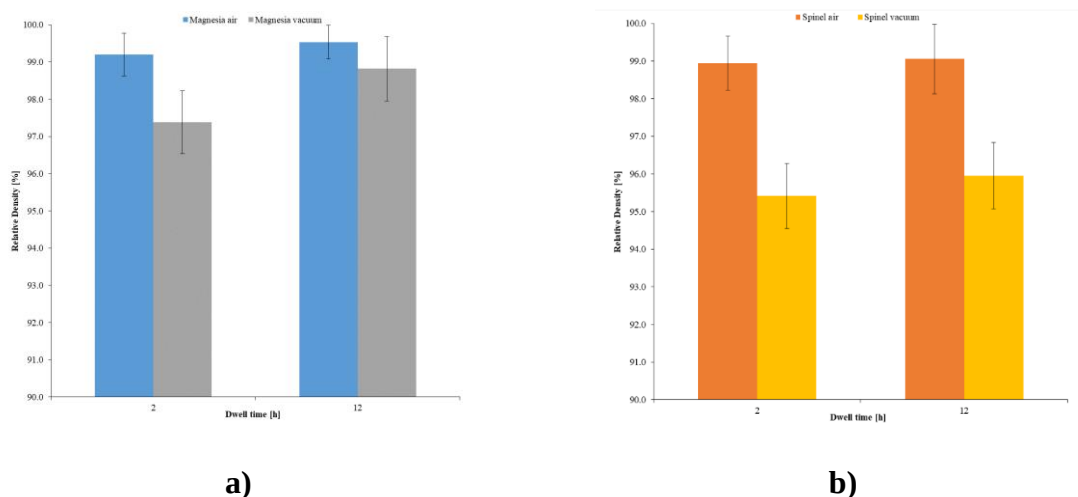
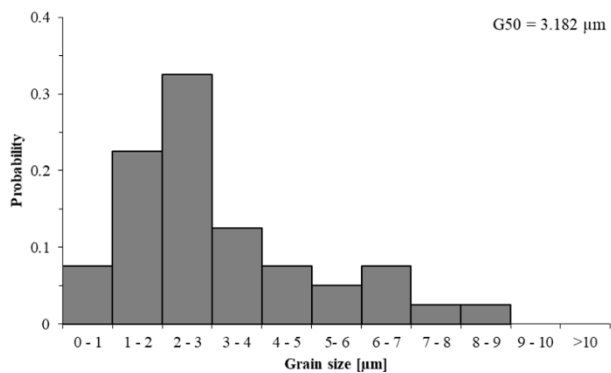
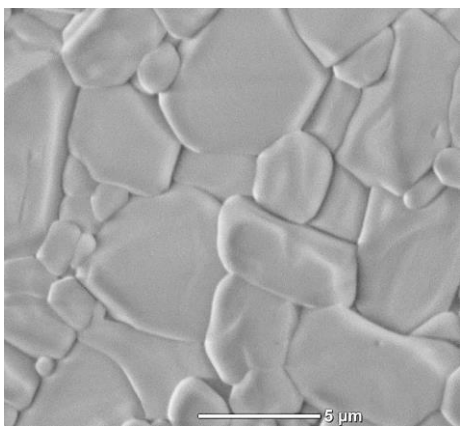


Figure 5.9 - Relative density data at different sintering conditions of: a) MgO-doped Al₂O₃; b) MgAl₂O₄-doped Al₂O₃

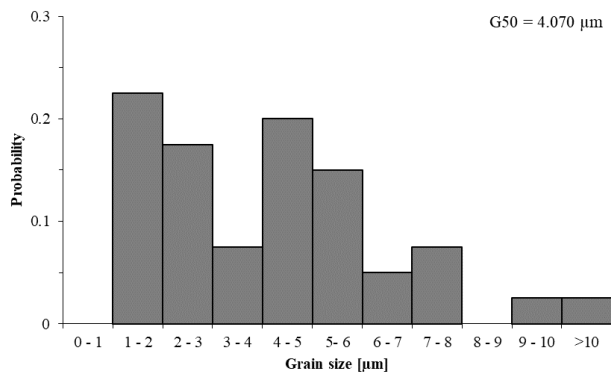
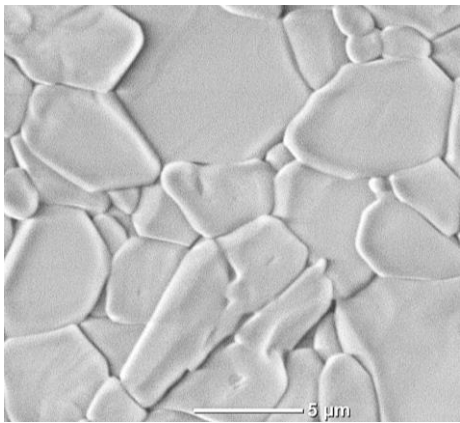
As can be observed, all the samples sintered in air performed noticeably better than their corresponding vacuum-sintered counterparts, mainly due to the significant carbon contamination, with differences of 1.8% and 0.7% when MgO was added and 3.5% and 3.1% when MgAl₂O₄ was used as a dopant, at 2 h and 12 h, respectively. In addition, it is noteworthy that longer dwelling times resulted in all cases in slightly higher relative densities in agreement with previous research [48], obtaining the maximum observed relative density (99.5±0.4%) when samples doped with magnesia were sintered at the dwell temperature for 12 h. However, none of the T7 and T9 trials conducted in vacuum achieved a relative density equal to or greater than 99.0%, with the exception of the MgO T9 experiment if the standard deviation is considered. In this case, the increased shrinkage and holding time contributed to reducing the overall volume of the sample and strengthening the alumina particles bonding at the interfaces. Conclusively, MgO was revealed as the better additive in terms of achieved relative density, outperforming the magnesium aluminate spinel across all the sintering trials.

5.3.4 Doped Al₂O₃ discs sintered microstructure analysis

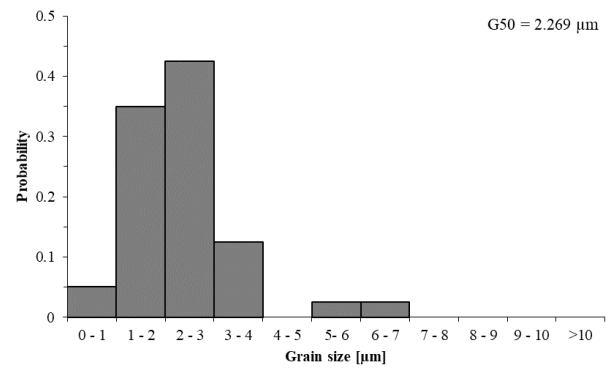
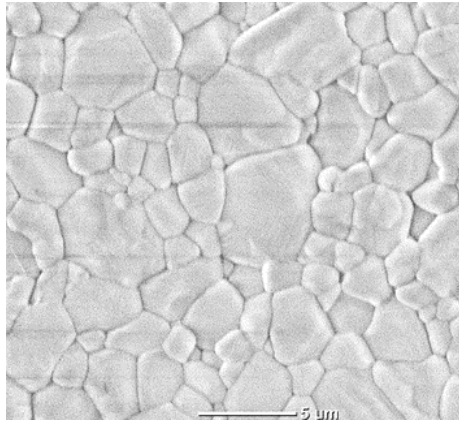
The resultant microstructure in the magnesia-doped and spinel-doped discs at different sintering conditions together with the associated grain distribution analysis after polishing both sides of the samples is illustrated in Figure 5.10 and Figure 5.11.



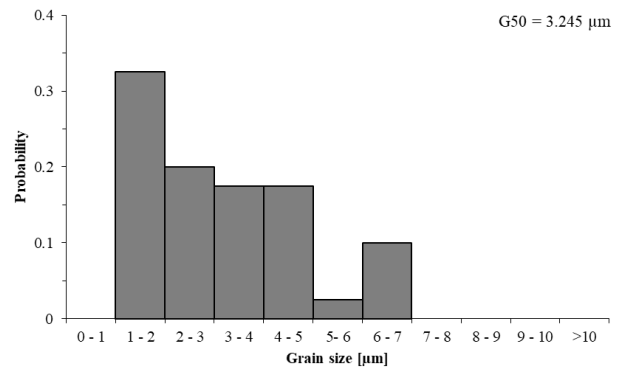
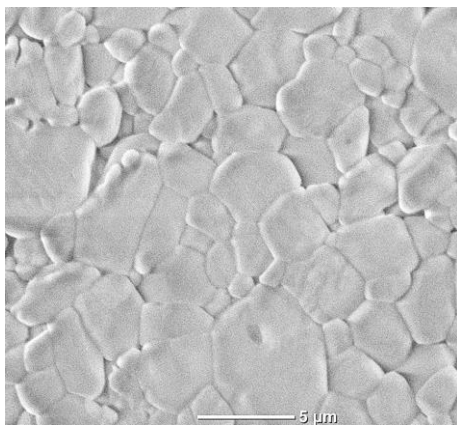
a)



b)

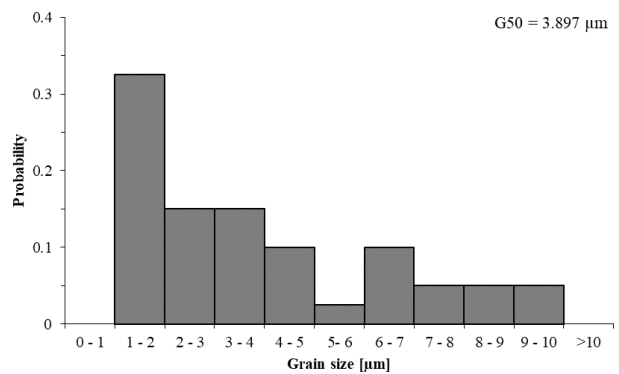
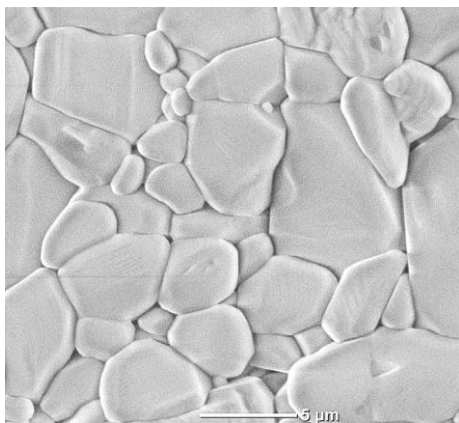


c)

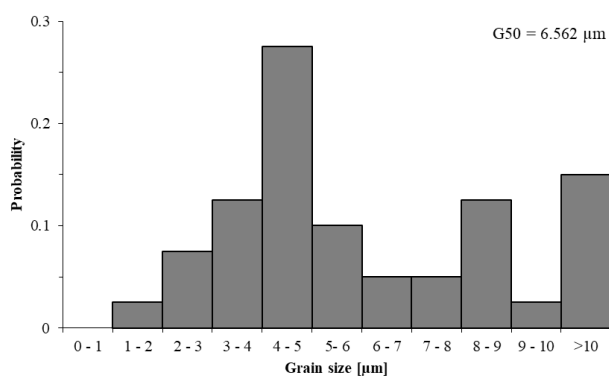
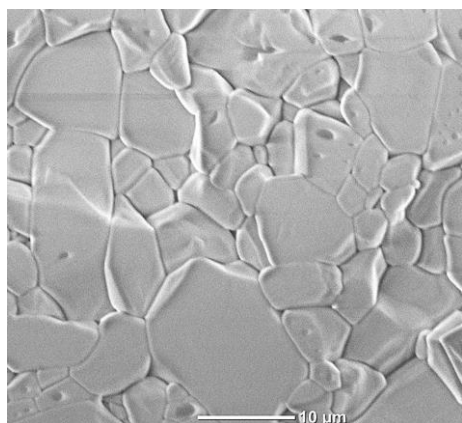


d)

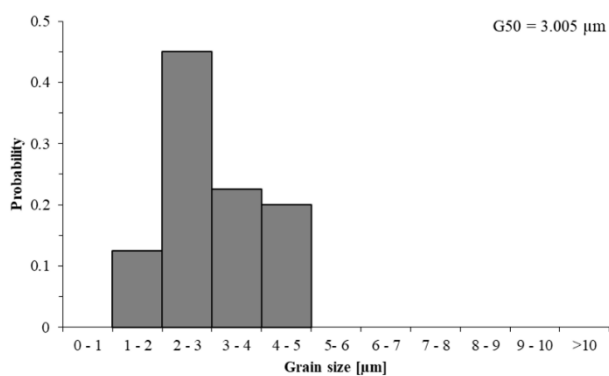
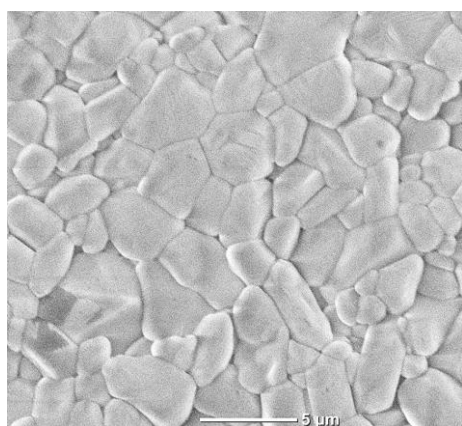
Figure 5.10 - SEM images of MgO-doped Al_2O_3 discs and corresponding grain size distribution after being sintered at: a) 2 h in air; b) 12 h in air; c) 2 h in vacuum; d) 12 h in vacuum.



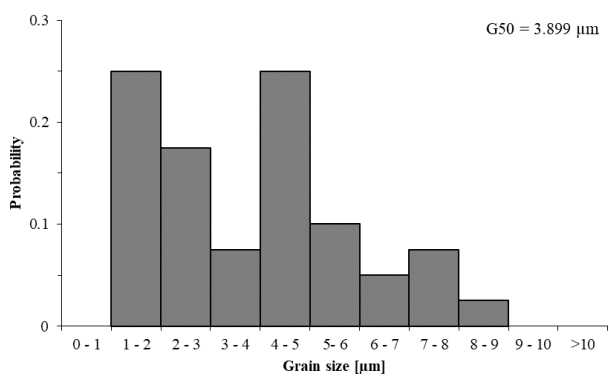
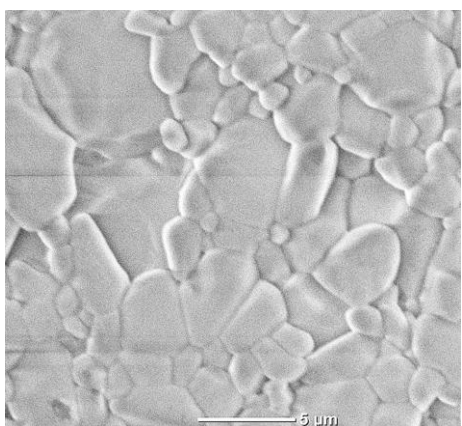
a)



b)



c)



d)

Figure 5.11 - SEM images of MgAl_2O_4 -doped Al_2O_3 discs and corresponding grain size distribution after being sintered at: a) 2 h in air; b) 12 h in air; c) 2 h in vacuum; d) 12 h in vacuum.

As it can be deduced in the above presented figures and graphs, in all the investigated sintering conditions, the alumina discs show an organised microstructure devoid of intragranular or intergranular porosity, which results in compacted solid bodies with high relative densities. In the case of vacuum-sintered samples, the polishing procedure removed around 20 μm on both sides of the samples, which is sufficient to observe the core microstructure and remove the portion of the discs where the carbon diffusion hindered the densification [50]. In the entirety of the experimental set, the sintering aids clearly demonstrated their effective action in containing the grain growth and ensuring the development of a finer microstructure compared to pure alumina samples, although bigger grains may occasionally be detected due to the relatively wide distribution of the starting particle size. The grain growth restriction is particularly evident in the vacuum-sintered samples, where the reduced surface diffusion contributes to the refinement of the microstructure and higher densification rates [51], even though the presence of carbon residue may have impacted its effectiveness. On the other hand, in the alumina parts sintered in air, the primary process for atomic transport can be attributed to grain boundary and volumetric diffusion at high temperatures and to surface diffusion at low temperatures [52], which results in a decrease in the surface area and, hence, in a decline in the densification process [53]. However, it also must be noted that the air-sintered parts were fired at a temperature 100 °C higher than vacuum ones due to the limitations of the available vacuum furnace.

In general, in this research, as could be possibly expected, the shorter sintering holding time led to smaller grain dimension averages, although the difference in grain sizes with samples sintered for 12 h is not quite pronounced, overall in the case of MgO-doped parts. The previous statement is even more in agreement with the collected data when considering the vacuum-sintered discs, in which the elongated dwelling time had an almost negligible effect.

The finest average grain dimension was detected in the MgO-Al₂O₃ sample sintered for 2 h in vacuum, while the coarsest average grain size was found in the MgAl₂O₄-Al₂O₃ disc fired for 12 h in air. In addition, less dispersed grain dimension data and sharper distributions were observed in the vacuum-sintered samples, demonstrating the higher potential of a vacuum atmosphere in obtaining a highly homogenous and finer microstructure. Overall, in this investigation, sintering conditions being equal, MgO-doped Al₂O₃ parts exhibited a smaller average grain size, revealing magnesia as a more effective sintering aid than spinel and a more suitable additive candidate for the preparation of translucent alumina components. In fact, while possessing a high relative density is crucial for ensuring the minimisation of pores and their consequent light scattering independently from the crystallographic nature of the material, finer grains can lead to transparency in optically anisotropic crystal structures such as the distorted hexagonal one of α -Al₂O₃ because smaller grains result in increasingly smaller pores size and, as a consequence, compared to coarser microstructures, more light beams are transmitted directly through the sample without being scattered at pores locations [54–56].

5.3.5 Transmittance characterisation

Figure 5.12 shows the aspect of the alumina samples with different thicknesses sintered at the various sintering conditions investigated during the course of this research. Upon visual examination, it can be clearly stated that the vacuum-sintered samples, although they possess a finer microstructure which could lead to improved transparency, do not even exhibit a translucent behaviour due to the darkened discolouration induced by the contamination of carbon diffused in their whole volume. Therefore, the total transmittance and real in-line transmittance (RIT) of the vacuum-sintered discs are negligible regardless of the adopted

sintering aid or conditions, confirming that removing possible carbon contaminations before sintering alumina is crucial for obtaining optical translucency or transparency.

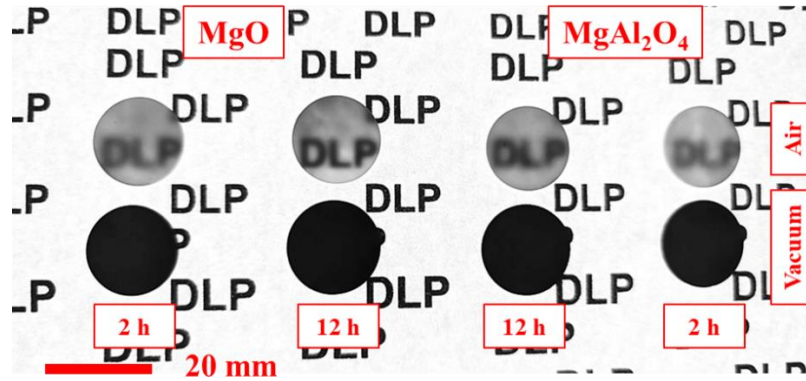


Figure 5.12 - Sample image of the sintered doped alumina discs presented in this investigation.

Nonetheless, the total transmittance of all the samples was analysed in the range of wavelength spanning from 200 nm to 1000 nm to determine the optical response of the samples to incident light in the ultraviolet (UV), visible (VIS) and near-infrared regions (NIR) (Figure 5.13). For the vacuum-sintered discs, only the obtained set of data of one of the samples per sintering aid was reported for simplicity as their transmittance values were practically identical.

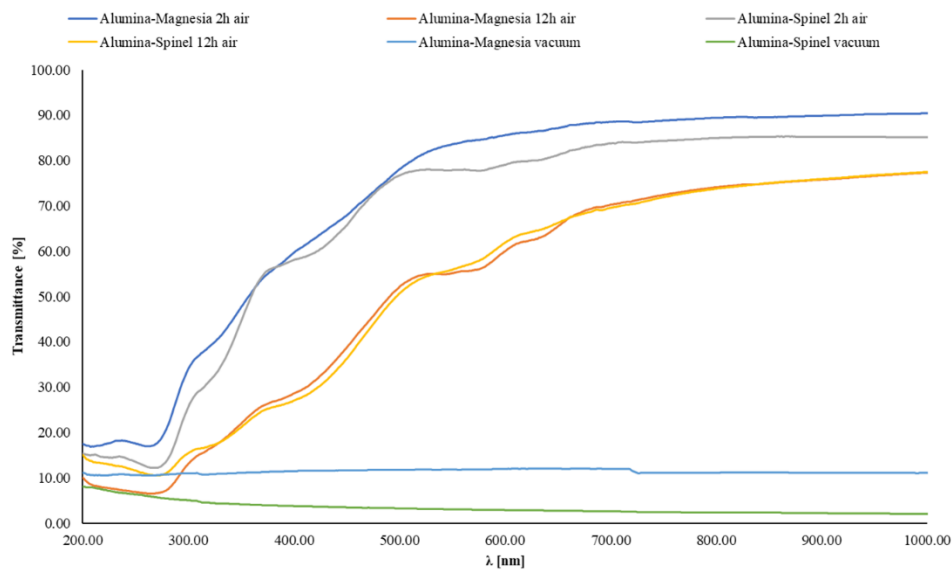


Figure 5.13 - Total transmittance vs wavelength of the sintered discs.

Firstly, the total transmittance of all the discs in the UVC region until the wavelength of 280 nm was below 20% and gradually increased in the UVB (280-315 nm) and UVA (315-400 nm) ranges to a maximum of 59.7% for the $\text{MgO-Al}_2\text{O}_3$ sample sintered for 2 h in air. With the exception of the vacuum-sintered discs, all the investigated sintering conditions led to a similar growth trend in the transmittance values across the VIS-NIR wavelength range, with the T7 data sets of both additives achieving the best results (maximum of: 88.5% at 696 nm in the VIS range and 90.4% at 994 nm in the NIR region for MgO; 83.7% at 697 nm in the VIS spectrum and 85.3% at 874 nm in the NIR one for MgAl_2O_4) and surpassing their corresponding T9 counterparts (maximum of: 70.1% at 696 nm in the VIS range and 77.3% at 994 nm in the NIR region for MgO; 69.4% at 697 nm in the VIS spectrum and 77.4% at 996 nm in the NIR one for MgAl_2O_4).

While the total transmittance provides information on the light passing through the samples and measured by an integrating sphere, the real in-line transmission determines the percentage of incident light that is transmitted from the light source through the sample on a

straight line to a detector located at the opposite side of it. Therefore, the latter value gives information on the amount of light that travels through an object without being deviated or scattered and, hence, results in clear and not distorted images. The RIT of the sintered samples is reported in Figure 5.14 and, as a reference, the RIT of pure alumina discs has been included. The steps in the graphs are caused by the change in sensitivity of the spectrophotometer due to the optimised adoption of three different light detectors in the different wavelength bands (UV, VIS and NIR).

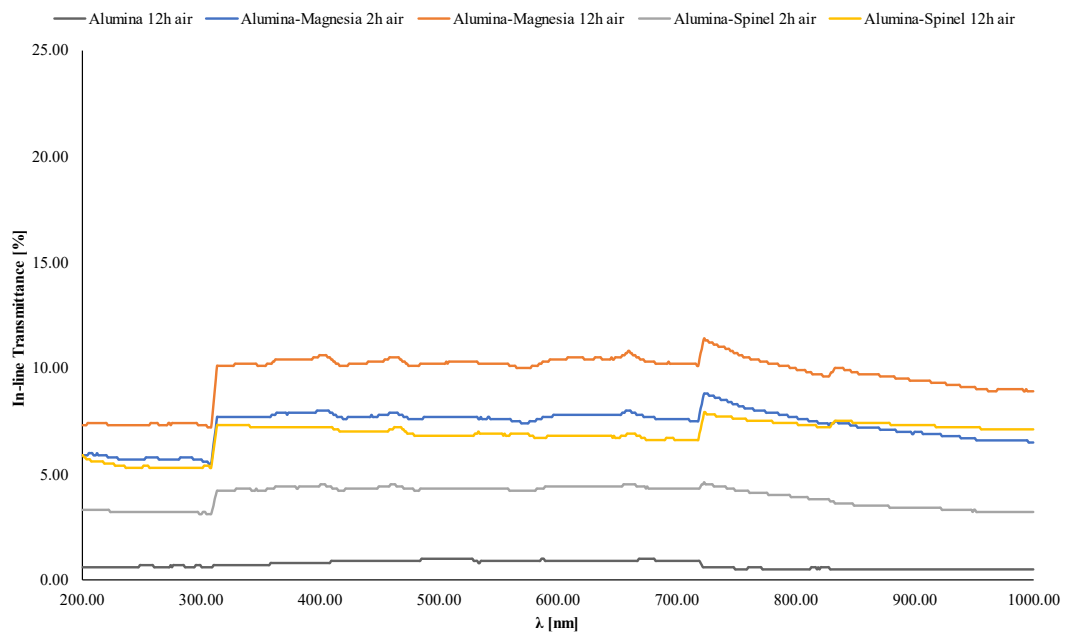


Figure 5.14 – Real in-line transmittance vs wavelength of the sintered discs.

The T9 disc with the MgO addition performed the best across all the wavelength regions, followed by the T9 spinel sample. However, both before and after polishing, the discs presented different thicknesses, which highly influences the transparency behaviour of an object since the thicker is the sample the higher is the possible number of defects introduced along the direction of the incident light. Therefore, being the grains average dimension small and assuming the

sample anisotropy low, the adjusted RIT values could be estimated for the specific thickness of each sample exploiting the Raleigh-Gans-Debye solution to the Mie problem [55]:

$$RIT_1 = (1 - R_s) \exp \left(- \frac{3\pi^2 r (\Delta n)^2 d_1}{\lambda_0^2} \right) \quad (1)$$

where RIT_1 is the decimal value of sample in-line transmittance, R_s is determined by the losses in reflection at the outer surfaces of the sample along their normal direction (~ 0.14) [55], r corresponds to half of the average grain dimension, Δn is, in the case of alumina, the difference in refractive indices due to birefringence and averaged over all grain orientations, d_1 represents the thickness of the sample and λ_0 is the wavelength in vacuum. Extrapolating the constant values when considering the same sample, it can be obtained that:

$$\exp \left(- \frac{3\pi^2 r (\Delta n)^2}{\lambda_0^2} \right) = \left(\frac{RIT_1}{1 - R_s} \right)^{\frac{1}{d_1}} \quad (2)$$

Thus, the real in-line transmission of the same sample at a different thickness can be estimated by introducing Equation (2) in Equation (1) with a different subscripted index as follows:

$$RIT_2 = (1 - R_s) \left(\frac{RIT_1}{1 - R_s} \right)^{\frac{d_2}{d_1}} \quad (3)$$

The thickness-corrected RIT curves normalised to a thickness value of 0.8 mm and expressed in percentages are illustrated in Figure 5.15.

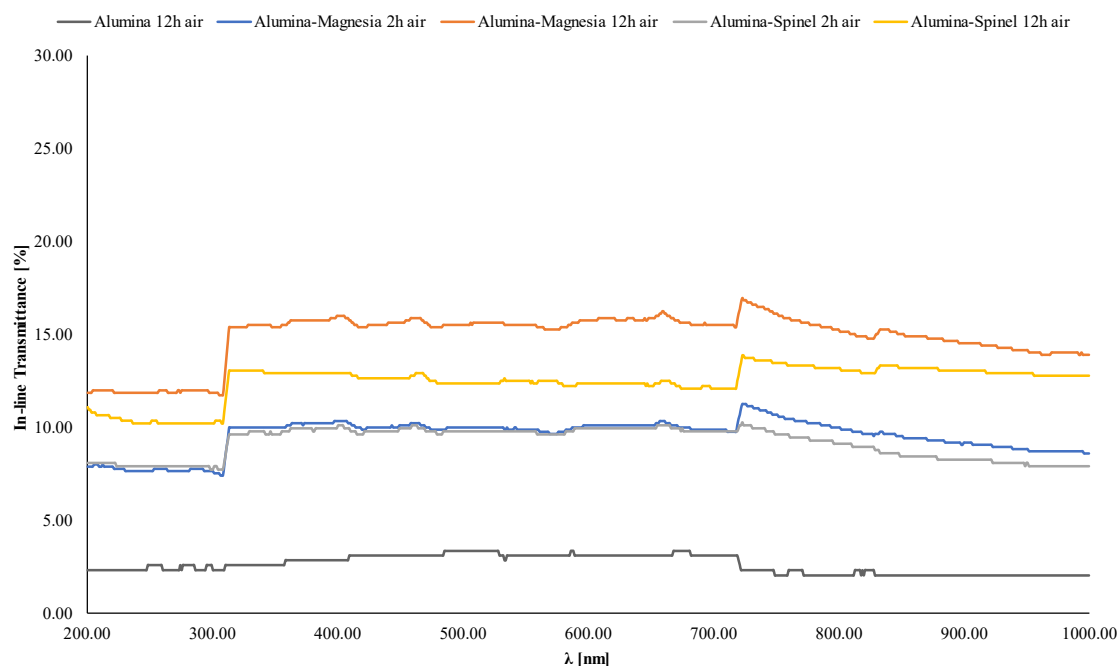


Figure 5.15 – Corrected real in-line transmittance vs wavelength of the sintered discs to a normalised thickness of 0.8 mm.

The updated RIT values generally respect the previously shown hierarchy and trends, with the exception of the 2 h sintered MgO-doped alumina sample, which is now still performing better than the respective spinel-doped disc but worse than the 12 h sintered spinel-alumina one. The T9 air-sintered alumina parts achieved the highest RITs with MgO- Al_2O_3 performing the best with an average in-line transmittance of 15.6% in the VIS range and a maximum overall value of 16.9% at 723 nm, followed by MgAl_2O_4 - Al_2O_3 with an average in-line transmittance of 12.4% in the VIS range and a maximum overall value of 13.9% at 724 nm.

5.4 Conclusions

In this research, the effect of diverse sintering conditions and additives on the light transmittance of sintered samples was studied. Firstly, various firing regimes were investigated for the sintering of DLPed pure alumina discs and different heating rates and holding times at the chosen sintering temperature of 1700 °C were explored. Subsequently, after selecting the two more promising sets of experiments based on the achieved relative densities and microstructures, MgO and MgAl₂O₄ were introduced in a proportion of 1000 ppm as sintering aids to further improve densification and restrict the grain growth and the selected sintering regimes were adopted for the sintering of these doped samples in air at 1700 °C and in vacuum at 1600 °C, due to the available furnace limitations. Relative densities, XRD, microstructure and optical transmittance data were then collected and the main highlights from the obtained results can be summarised as follows:

- XRD patterns were found in agreement with referenced pure alumina diffraction data. No significant trace of the insurgence of a secondary phase was detected in any of the investigated settings, although further increases in MgO content could lead to the in situ formation of small amounts of spinel, especially if longer dwelling times and slower cooling rates are adopted.
- Among all the sets of experiments investigated, the highest values in the relative densities of pure alumina samples were obtained when sintering was conducted at the highest explored heating rate (10 °C/min) for either 2 h or 12 h dwelling time at the maximum sintering temperature.
- Moisture, carbon sedimentation and contamination due to poor post-debinding cleaning of DLPed alumina samples resulted in superficially porous and volumetrically darkened

discs unable to reach the necessary values of relative density and optical prerequisites for translucency or transparency to appear. Careful sample handling, reducing the interaction with possible contaminants and the permanence time in the debound stage would help to solve these issues.

- The addition of MgO as a sintering aid led to values of densities closer to the theoretical limit (the highest relative density being $99.5 \pm 0.4\%$ for the sample sintered in air for 12 h) and a generally finer microstructure, if the vacuum-sintered samples are not considered, resulting in the better candidate as dopant compared to magnesium aluminate spinel.
- Finally, total transmittance data and RIT values confirmed that MgO-Al₂O₃ discs demonstrated the highest light transmission capabilities, with the magnesia-alumina sample sintered in air for 2 h exhibiting the highest total transmittance (90.4% at 994 nm) and the 12 h air-sintered MgO-Al₂O₃ disc possessing the most significant RIT (average of 15.6% in the VIS range and a maximum value of 16.9% at 723 nm).

CRedit authorship contribution statement

Michele De Lisi: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing – original draft preparation, Visualization, Writing – review & editing.

Francesco Careri: Investigation, Writing – review & editing. **Usama M. Attia:** Supervision, Writing – review and editing. **Khamis Essa:** Supervision, Writing – review and editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability statement

All data are provided within the article and the referenced sources.

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CHAPTER 6. CONCLUSION AND FUTURE WORK

6.1 Conclusions

Transparent ceramics are a class of advanced materials that possess the unique combination of optical transparency, similar to glass, and the thermomechanical properties typically associated with traditional ceramics. These materials have garnered significant attention due to their remarkable combination of properties. This convergence of transparency and robustness opens up new possibilities for applications in various industries and technologies since transparent ceramics exhibit excellent optical transparency in specific wavelength ranges, enabling the transmission of light with minimal absorption and scattering. Such characteristic makes them suitable for optical and photonics applications. Unlike traditional glasses, transparent ceramics are crystalline materials with strong atomic bonding, resulting in superior mechanical properties such as hardness, fracture toughness and resistance to wear and abrasion. In addition, they can withstand high temperatures without significant degradation in their optical and mechanical properties while often being chemically inert and corrosion-resistant. Their thermal stability and chemical resistance are crucial for applications in high-energy and harsh environments as well as laser systems. The diverse range of applications underscores the multidisciplinary nature and significance of transparent ceramics in advancing technology across various industries, as outlined in Chapter 2. The utilisation of additive manufacturing technologies in the context of transparent ceramics applications enables the creation and production of distinctive product designs that are unattainable using conventional manufacturing approaches. In accordance with the intended aim, the research

hereby reported was focused on the in-house development of a photopolymerisable ceramic slurry and its consecutive additive manufacturing for the fabrication of translucent alumina parts to assess the process feasibility and pave the way to further investigations to fully optimise and establish an in-house manufacturing route to achieve transparent ceramic parts.

Digital Light Processing widely demonstrated in the literature the potential to manufacture intricate components and, therefore, was selected as the researched additive manufacturing process for its effectiveness and suitability for a wide range of technological applications. In Chapter 3, since the postprocessing of ceramic components produced by AM has been demonstrated to be a crucial stage in defining the ultimate resolution and mechanical properties of the finished product, especially in terms of distortions and resulting densities, the various parameters of the sintering process were investigated via an experimentally validated FEM in order to achieve the production of defect-free and fully dense ceramic components.

The investigation of the practicality of manufacturing near-net-shape components with enhanced characteristics and geometric features through the use of 3D printing has progressively emerged as the primary area of interest in several research endeavours, as highlighted in Chapter 4. Various process parameters and preparation strategies as well as debinding procedures were examined. The most suitable components to incorporate into an alumina slurry developed in-house, the optimal parameters and conditions for DLP printing were investigated while comprehending their impact on the properties of the green parts and assessing the appropriate debinding regimen for achieving fully dense and crack-free fired parts that exhibit translucent characteristics.

The developed slurry and the optimal debinding cycle were then used to manufacture the brown alumina discs utilised for the research presented in Chapter 5 on additives and optimal sintering cycles to achieve translucency. The in-house developed Al_2O_3 slurries mixed with

either MgO or MgAl₂O₄ were digitally light processed, the obtained green samples debound and subsequently subjected to different sintering regimes to obtain translucent samples. The conducted experiments focused on examining the impact of various heating rates and holding durations during sintering as well as the impact of different additives and reduced oxygen environments on the parts final properties.

The main conclusions of the whole research can be summarised as follows:

- The additive manufacturing technique of DLP makes it possible to create highly dense translucent alumina ceramics.
- The methodology for optimum removal of the binder from a high solid loading and low viscosity slurry was determined through the use of differential scanning calorimetry and thermogravimetric analysis measurements. After conducting independent experimental trials, measurements and testing revealed the presence of a certain level of anisotropy in the fabricated parts. While it is already well known that anisotropy is an intrinsic property conveyed by layer-by-layer manufacturing, the findings obtained from dilatometry tests demonstrated the presence of anisotropic characteristics in the sintered samples is also dependent on the building orientation or the plane of the layers, resulting in different levels of shrinkage (~16% when built along the cylinder axis and ~12% when across).
- A finite element model with an integrated custom subroutine was developed to replicate the thermomechanical characteristics of a cylindrical structure under specific sintering process schedules. It exhibited a significant level of congruence with the results obtained from the conducted tests. Specifically, the numerical data indicated a strong correlation between the predicted shrinkage and the relative density, with a discrepancy of less than 2% between the empirical results and the simulated outcomes.

- The FE model was capable of predicting the progression of relative density changes and taking them into account for the evaluation of the mechanical properties of the final part. Consequently, it was employed to optimise the sintering cycle to achieve the maximum density. Higher dwell temperatures rather than longer holding times resulted in denser and almost defect-free samples.
- A systematic approach to determine the ideal components and process parameters for generating an efficient slurry in-house was developed. This approach covers the selection of ball-milling parameters and extends to the debinding regimes to be followed. This technique may be utilised to customise the characteristics of the slurry in order to achieve desired outcomes and create customised slurries for certain purposes, such as the production of translucent components. In the mentioned case, translucency was achieved by consistently maintaining elevated levels of relative densities.
- In the investigated range of operating conditions, it was found that dry ball milling with a short milling duration and high velocity (1 hour and 800 revolutions per minute) yielded the most favourable results in terms of minimising agglomerates and achieving a more refined size distribution for the initial powder.
- After conducting a thorough investigation into several dispersants and their concentrations, it was determined that the most suitable dispersant for the particular slurry created in this study was BYK-145, with a weight percentage of 2% relative to the ceramic powder content.
- Various solid loadings were also investigated and it was found that an approximate weight percentage of 85% of ceramic filler was the most favourable option. This decision mitigates the potential for significant distortions and severe thermal stress while ensuring high densities across all phases.

- The analysis of the curing behaviour of the created slurry was undertaken and a full-factorial design of experiments was performed. The results of the DoE indicated that the exposure duration and its interaction with the exposure power were the most critical parameters in the Digital Light Processing printing of the generated slurry. The optimal printing parameters for achieving desirable results were determined to be an exposure period of 2 seconds and an exposure power of 50% when the layer thickness was set to 25 micrometres.
- In the various debinding experiments that were examined, it was shown that employing lower heating rates (0.2 °C/min) and longer living durations resulted in a more stable sample with increased relative density and better retention of geometrical dimensions.
- The samples doped with MgO in a concentration of 1000 ppm and produced in accordance with the optimised process chain and subjected to sintering at a temperature of 1700 °C for a duration of 12 hours exhibited the onset of translucency.
- The potential creation of spinel in tiny quantities may occur with the increase in MgO concentration, particularly when longer holding times and slower cooling rates are employed.
- The presence of moisture, carbon sedimentation and contamination caused by inadequate post-debinding cleaning of DLPed alumina samples led to the formation of vacuum-sintered discs that exhibited superficial porosity and volumetric darkening. Consequently, these discs failed to achieve the required levels of relative density and optical properties necessary for the manifestation of translucency or transparency. Implementing meticulous sample handling techniques, minimising contact with potential contaminants and minimising the permanence in the debound step are recommended strategies for addressing these challenges.

- The inclusion of MgO as a sintering aid resulted in densities that approached the theoretical maximum, with the highest obtained relative density being $99.5 \pm 0.4\%$ after sintering in air for 12 hours. Additionally, in the case of MgO-doped alumina samples, the microstructure exhibited finer characteristics overall, proving that magnesia is a more favourable dopant compared to magnesium aluminate spinel in order to achieve translucency.
- In conclusion, the collected data on total transmittance and RIT values provide confirmation that MgO-Al₂O₃ discs exhibit superior light transmission capabilities. Specifically, the MgO-Al₂O₃ sample sintered in air for 2 hours demonstrated the highest total transmittance at 994 nm (90.4%), while the MgO-Al₂O₃ disc sintered in air for 12 hours exhibited the most significant RIT, with values averaging 15.6% in the visible range and possessing a maximum value of 16.9% at 723 nm.

6.2 Future work

The future progression of this study should focus on attaining denser and more transparent specimens by the use of a high-capacity sintering furnace capable of operating under vacuum conditions at elevated temperatures, or alternatively, a microwave sintering furnace. Furthermore, conducting further studies that investigate the impact of various sintering parameters, including heating rate, dwelling duration and dwelling temperature, might yield valuable insights into determining the most effective sintering cycle to adopt, ultimately leading to a reduction in light refraction. To achieve enhanced translucency, it is necessary to further increase the ultimate relative density of the components above 99.5%. Simultaneously, it is

important to carefully manage and customise grain development in order to optimise light transmission. The desired outcome can be attained by the process of sintering the components in a vacuum environment at elevated temperatures exceeding 1500 °C. This approach serves to decrease the entrapment of air and hence reduce residual porosity, while simultaneously enhancing the densification process.

This study has demonstrated the possibility of using DLP and in-house developed slurries for the production of transparent alumina parts that can be adopted in several fields of application, from optics and electronics to military and medical imaging. The AM technique proposed allows for enhanced control and further customisation of slurry formulation as well as post-processing parameters to optimise the optical and mechanical properties of finished parts. Based on the research conducted in this study, it is advised that additional advancements should be pursued in the following areas:

- A detailed study on the influence of the starting ceramic powder properties on the translucency and microstructural properties of the final parts may reveal more accurately the significance of the grain count and dimensions. For instance, smaller D50s could lead to increased grain counts and decreased average grain dimensions, hence resulting in a stronger microstructural configuration with enhanced mechanical properties. On the other hand, higher grain counts would lead to higher amounts of grain boundaries, which would probably cause a worsening of the optical translucency. Further analysing this delicate balance could extensively improve the final outcomes of the entire process chain.
- The hereby developed finite element model does not include anisotropic constants among the inputted material properties. It has been actually developed assuming that the brown part is homogeneous and isotropic, which is within the acceptability window for an optimised process adopting optimal slurries. In the case of a research environment where

very high accuracy (<2% mismatch is constantly needed), this anisotropy has to be studied and taken into account for predicting final relative densities, distortions and finished parts shapes. Therefore, even though anisotropic constants are dependent on the manufacturing process and the utilised material, hence needing specific analyses for each case study, developing a VUMAT subroutine capable of including anisotropic behaviours while considering density variations and related mechanical properties changes during the entire sintering cycle could result in a very accurate FEM for forecasting geometrical properties of fired parts.

- In addition to the aforementioned point, although preliminary studies on the development of a numerical simulation of the debinding process were started, a model capable of reproducing the phenomena happening during the debinding cycle has not been developed. Being able to accurately and consistently simulate the binder removal process without actually experimentally doing it would be an inestimable capability that would allow researchers to evaluate the brown density and the porosity configuration beforehand. Consequently, it would remove the most time-consuming step from the entire process chain, since, as can be seen in this research, the optimal debinding cycle can last the equivalent of five days or more, while reducing the experimental load on the available furnaces. Furthermore, linking both the debinding and the sintering numerical models by inputting the results of the former as inputs in the latter would result in a complete simulation of the whole postprocessing able to heavily cut off experimental trial runs.
- Further research on the influence of DLP printing parameters may lead to even more optimised slurry behaviours and final accuracy. Even though several parameters have been explored in this research, the effect of the energy density, longer exposure times, film speed and acceleration as well as delay times during printing and part orientation

should be explored. Furthermore, as also stated in the first point of this list, slurry formulations still have huge potential to deliver interesting results when considering the variation of the starting powder properties or the inclusion of other additives to reduce photosensitivity. Exploring other workability windows and the effect of the abovementioned parameters is highly advisable.

- The type of research hereby conducted can be applied to the study of other ceramics that have the capability of being translucent or transparent. Therefore, developing the same process for other materials would increase the flexibility of the manufacturing process while contributing to the widening of its range of applications.
- Following the previous point, the extension of this investigation to other advanced or smart materials could be of high scientific interest. In fact, although preliminary studies on other advanced materials were conducted, in particular self-healing ceramics, after a few experimental trials, it was concluded that a separate research project would be needed to establish a stable and consistent manufacturing route to fabricate other smart materials. It would certainly represent an interesting research with significant industrial attractiveness to conduct.
- Continuing to explore the influence of debinding and sintering process parameters on the final properties of the part could be highly beneficial in providing an in-depth knowledge of the involved thermodynamics and tailoring the postprocessing to achieve the desired mechanical and microstructural characteristics. For instance, in regard to the debinding regimes, the addition of intermediate holding stages, increasing the pre-sintering dwell temperature or even further lowering the debinding heating rate to 0.1 °C/min should be explored. On the subject of sintering cycles, instead, a multistep sintering approach with

different dwell zones could be investigated as well as higher dwelling temperatures and holding times.

- Moreover, observing the different results that can be obtained in terms of translucency from various sintering techniques, such as microwave sintering, spark plasma sintering and hot isostatic pressing, could improve the outcome of the whole process chain. Even though a few attempts at microwave sintering were conducted, it was deemed that more efforts should be directed toward it to fully exploit this advanced firing process.
- In conclusion, it would be advantageous to ascertain the economic viability of the DLP method by expanding its implementation to an industrial scale. Additionally, conducting trials on full-scale geometrically intricate transparent alumina components would be valuable in evaluating the suitability of this technique for manufacturing lenses and domes. As a consequence, it is advisable to utilise a DLP printer that possesses an expanded build capacity.