

Slurry Jetting Printing of Ceramics with Nanoparticle Densifiers

A thesis presented to
the faculty of
the Russ College of Engineering and Technology of Ohio University

In partial fulfillment
of the requirements for the degree
Master of Science

Pragnya Kunchala

May 2018

© 2018 Pragnya Kunchala. All Rights Reserved.

This thesis titled
Slurry Jetting Printing of Ceramics with Nanoparticle Densifiers

by
PRAGNYA KUNCHALA

has been approved for
the Department of Mechanical Engineering
and the Russ College of Engineering and Technology by

Dr. Keerti Kappagantula
Assistant Professor of Mechanical Engineering

Dennis Irwin
Dean, Russ College of Engineering and Technology

ABSTRACT

KUNCHALA, PRAGNYA., M.S., May 2018, Mechanical Engineering

Slurry Jetting Printing of Ceramics with Nanoparticle Densifiers

Director of Thesis: Keerti Kappagantula

Additive manufacturing, though found to be an attractive alternative to make ceramics with complicated geometry, presents low mechanical properties due to high porosity. Literature showed introducing nanoparticle densifiers into the printed part as an effective way to improve its mechanical properties. However, focused investigation of the influence of variation in densifier content on the ceramic part properties is currently lacking in research pertaining to additive manufacturing. The current work addresses these issues in the additive manufacturing of ceramics by adding alumina nanoparticles (densifier) to the printing liquid.

The slurry-jetted samples were characterized for density, porosity and compressive strength with increasing densifier content in the printing slurry. The presence of the nanoparticle densifiers had a marked effect on the physical and mechanical properties of the slurry-jetted samples. Bulk density of slurry-jetted samples increased by about 29.6% while porosity of cured parts decreased by about 35.7% with increasing densifier concentration from 0 - 15 wt.%. Additionally, compressive strength of the samples improved from 76 kPa to 641 kPa. Surface tension of the printing slurry decreased from 43.7 mN/m to 22.6 mN/m as the densifier concentration was increased from 0 - 15 wt.%. It was evident that the concentration of densifiers is a limiting factor as it decreases the penetration depth of printing slurry in the filler particles with decreasing surface tension.

ACKNOWLEDGMENTS

I would like to thank my thesis advisor Dr. Keerti Kappagantula at Russ College of Engineering, Ohio University, who has travelled this journey and has always challenged and encouraged me on being professional and perfect not only on my research, but also on the way I think. I owe an enormous gratitude to my committee members Dr. John Cotton, Dr. Greg Kremer, and Dr. Katherine Cimat, Dean Dennis Irwin, and Chair Dr. Bayless for helping cross the obstacles. I owe a special thank you to Dr. Lawrence Witmer, Ridgely Ryan, Dr. Issam Khoury for helping me with the required concepts and software tools needed to complete my thesis. I have great pleasure to thank our lab coordinators Randy Mulford and Joey for their lab assistance. I also thank my office staff for helping me with administrative matters. I also would like to thank my mother, father, and my daughter for their never-ending support and encouragement. Finally, I would like to recognize my family, lab mates and friends with a vote of wholehearted thanks for supporting me during my tenure as a student of Ohio University.

TABLE OF CONTENTS

	Page
ABSTRACT.....	3
ACKNOWLEDGMENTS	4
LIST OF TABLES.....	7
LIST OF FIGURES	8
CHAPTER 1: INTRODUCTION.....	9
CHAPTER 2: OBJECTIVES.....	15
CHAPTER 3: LITERATURE REVIEW	16
3.1. Materials in BJP.....	16
3.2. Density and Porosity in BJP	17
3.3. Effect of Porosity on Mechanical Performance of Ceramics.....	19
3.4. Methods Adopted to Densify and/or Decrease Porosity of the Printed parts .	21
3.5. Effect of Nanoparticle Suspensions on the Powder-Binder Interaction	26
CHAPTER 4: EXPERIMENTAL SETUP	30
4.1. Materials	30
4.2. Sample Preparation	30
4.3. Characterization	32
4.3.1. Density and Porosity Testing	32
4.3.2. Compressive Strength Test	33
4.3.3. Printing Slurry Surface Tension.....	34
4.4. Statistical Analysis.....	35
CHAPTER 5: PROPOSED PLAN OF WORK.....	40
5.1. Objective 1	40
5.1.1. Objective 1 Plan of work.....	40
5.2. Objective 2	40
5.2.1. Objective 2 Plan of work.....	40
5.3. Objective 3	41

5.3.1. Objective 3 Plan of Work.....	41
CHAPTER 6: RESULTS AND DISCUSSION.....	42
6.1. Objective 1: Density and Porosity of Slurry-Jetted Alumina Samples.....	42
6.2. Objective 2: Compressive Strength of Slurry-Jetted Alumina Parts	46
6.3. Objective 3: Surface Tension of Printing Slurry with Nano-Densifiers	51
CHAPTER 7: CONCLUSION AND FUTURE WORK.....	57
REFERENCES	59
APPENDIX.....	70

LIST OF TABLES

	Page
Table 4.1. Experimental parameters considered for sample synthesis.....	31
Table 6.1. One-way ANOVA analysis of data sets in density test.....	43
Table 6.2. Post hoc analysis of data sets in density test.....	43
Table 6.3. One-way ANOVA analysis of data sets in compression test.....	48
Table 6.4. Post hoc analysis of data sets in compression test.....	48
Table 6.5. Density of printing slurry shown with respect to the composition of individual constituent components in wt.%......	51
Table 6.6. One-way ANOVA analysis of data sets in surface tension measurement.....	53
Table 6.7. Post hoc analysis of data sets in surface tension measurement.....	53
Table 9.1. Summary of the data from density measurements.....	74

LIST OF FIGURES

	Page
Figure 3.1. Variation in compressive strength with respect to porosity in ceramic parts fabricated using BJP (P-3DP), selective laser sintering (P-SLS), stereolithography (SL), direct ink writing (DIW) and conventional methods (non-AM processing).....	21
Figure 3.2. Printed green part of alumina (left), sintered alumina part (middle) and copper infiltrated alumina part (right)	23
Figure 3.3. SEM image of line formed by bimodal powder of 20 μm spherical and 5 μm equiaxial alumina powder (12.5 wt%).....	24
Figure 3.4. Substantial difference in the shrinkage of the sintered parts printed without (top) and with nanoparticles(bottom)	26
Figure 4.1. Experimental set up for compression strength using MTS machine and enlarged view of the sample on the right side of machine	33
Figure 4.2. Schematic of pendant droplet test set up	34
Figure 6.1. Bulk density of slurry jetted alumina samples as a function of varying nanoparticle densifier content in the printing slurry.....	42
Figure 6.2. Separation of pore phase (shown in red) from the solid phase (shown in grey) in the binder-jetted alumina samples. A. Alumina with 0 wt.% nanoparticle densifiers and 58.2% porosity (top); and B. Alumina with 15 wt.% nanoparticle densifiers and 37.4% porosity (bottom)	45
Figure 6.3. Compressive strength of alumina samples as a function of varying nanoparticle densifier content in the printing slurry	47
Figure 6.4. Compressive strength of alumina samples as a function of varying density of the slurry-jetted alumina samples.....	51
Figure 6.5. Surface tension of printing slurry as a function of varying nanoparticle densifier content.....	52

CHAPTER 1: INTRODUCTION

Advanced engineering ceramics are versatile materials, have excellent mechanical, thermal, chemical, and electrical properties [1] and are used in various applications such as cutting tools [2], [3], car clutches/brakes [4], dental crowns [5], capacitors [6], semiconductors [7], and piezoelectric materials [8]. Popular conventional methods used to manufacture ceramic parts include casting [9], CNC machining [10], and extrusion [11]. These processes are cost effective in the production of large-scale goods, but are inappropriate for producing small quantity parts like replacements or prototypes [12].

On the other hand, most small scale ceramic part production uses subtractive methods where the material is removed from a bulk block until the desired shape is obtained such as drilling [13], [14], grinding [15], [16], milling [17], [18], lathe cutting [2], [19], flame cutting [20], [21] and electric discharge machining [12]. However, this approach involves cost intensive issues of unwanted material wastage as well as tool wear [22]. Recent advances in additive manufacturing processes offer economically viable alternatives for small scale ceramic part synthesis with desired material properties [23].

Additive manufacturing (AM) is a component building technique through incremental material addition, typically layer by layer [23]. It was introduced by Charles Hull in the early 1980s [24]. Since AM is an automated process, it fabricates parts directly from solid modeling data. Manual calibration errors, part specific fixtures and tool requirements used in the traditional manufacturing process are eliminated in AM [25]. AM applications can be found in almost all the sectors like education, aerospace, defense, automobile industry, medical, sports and architectural fields [26], [27], [28], [29]. Different

types of additive manufacturing techniques used to fabricate intricate ceramic parts are stereolithography, poly jet, fused deposition modeling (FDM), selective laser sintering (SLS) and binder jetting printing (BJP) [30].

BJP is a powder based AM process developed in 1991 by Sanchs and Haggery at Massachusetts Institute of Technology [31]. In this process, structural material in the form of powder is connected with the help of binder deposited by a print head resembling that of an inkjet printer in selective regions which is then subjected to post processing to make the final part [32].

BJP can be used to manufacture parts made with a wide range of materials including, but not limited to, metals, ceramics, and polymers [24], [30], [33], [34]. In other AM processes, material melting point, electrical conductivity, thermal conductivity, optical reflectivity, and reactivity are limitations while selecting the materials. On the other hand, BJP works by binding particles with an adhesive without the involvement of any external heat or pressure on the filler particles [34]. Among all the methods, binder jetting is found to be more suitable for forming complex ceramic parts due to its faster manufacturing time with low operation cost and ability to print any ceramic powder [32].

Applications of BJP are found in almost all the sectors like teaching, architecture, industry and medical fields [24], [26]. BJP is used to produce prototypes for surgical reference, tissue engineering scaffolds, implants, dental crowns and prosthetics which involve complex ceramic structures [24], [35], [36]. BJP is used to synthesize production tools like patterns, fixtures, jigs, sand cast molds, and design prototypes [37]. All the parts printed using BJP need to be subjected to post processing methods to densify the parts.

Infiltration, and sintering are the regularly employed post processing methods in BJP [38], [39]. Sintering is the most common method of densifying cast or printed ceramic parts. When binder jetted green ceramic parts are sintered, powder particles adhered by the binder are welded locally by the application of heat below the melting point of the ceramic. Surface energy of the powder particles is minimized at the higher temperatures and they favor a lowered surface area configuration. Consequently, ceramic particles coalesce at their points of contact owing to solid state diffusion, reducing the total surface area of the particles and increase density [40]. The main disadvantage with sintering is that the final treated ceramic part demonstrates shrinkage leading to both dimensional inaccuracy and creep [41]. In addition, pores formed between the powder particles during the printing process (called inter-particulate pores) are not reduced, leaving the part with considerable amount of porosity [42].

Infiltration is a post processing technique used to densify binder jetted parts. It involves immersing the printed part in a solution containing a secondary material, called infiltrant, such that it “infiltrates” the pores of the printed part via capillary action. The infiltrant can be either a suspension with solid loadings or molten materials such as metal or polymer [43]. Usually ceramic and metal ceramic composites are subjected to infiltration to reduce the porosity, improve mechanical performance, and sometimes to synthesize cermets or alloys [44]. Infiltration can be performed for both sintered or green ceramic parts.

Though infiltration decreases porosity of the post-processed part and subsequently enhances its mechanical properties like compression strength and hardness [45], there are

a few disadvantages associated with the process. The first drawback is the insufficient penetration of the infiltrant into pores with size smaller than the average particle size of the solid loadings [46]. Similar problems are noticed when the viscosity of the infiltrant increases either with the increase in the solid loadings or with the use of a viscous liquid metal or polymer. Additionally, the effectiveness of infiltration depends on the connectivity of the pore network developed in the printed part. Those pore clusters that are not connected to the outer surface of the printed part via channels to allow proper infiltration typically to remain unfilled with the infiltrant. All of these issues lead to having areas of inhomogeneity due to pockets of pores resulting in localized stress concentrations [47] which is detrimental to part performance.

In the recent years, BJP gained recognition for producing low volume ceramic parts and achieved significant market penetration [48]. Though BJP is successful in producing complex shapes irrespective of the size of the part, the applications of the end products are limited to prototypes due to the inability of the printed parts to meet performance certification standards. This is attributed to the presence of high volume of pores in the printed parts consequently resulting in low density of the ceramic green parts [49]. The cause for this porosity is the limited packing factor of the powder particles. Subsequently, high volume shrinkage is observed during post-processing resulting in dimensional inaccuracy and creep formation [34]. Also, the presence of porosity makes the printed parts brittle and leads to poor mechanical properties like compression strength, flexural strength, and bending strength [46], [50], [51]. There is a critical need to improve the BJP process such to overcome the disadvantage of porosity and improve the density of green ceramic

parts. The density of a part can be represented in three different ways- bulk density, theoretical density, and relative density. Theoretical density (TD) is the true density of the material given by the Equation 1.1. Bulk density is the measured density of the sample which is the measure of weight of solid material per unit volume. It considers both solid material and pore spaces in the sample. Relative density is the ratio of bulk density to the theoretical density. Unless specified as theoretical or relative density, the term density is always referred to bulk density of the part.

$$TD = \frac{(Molecular\ weight \times No.\ of\ molecules\ per\ unit\ cell)}{(Volume\ of\ unit\ cell \times Avogadro's\ number)} \quad \text{Equation (1.1)}$$

In this research project, it is hypothesized that addition of nanoparticles to the printing liquid will lead to their deposition in the inter-particulate pores in the BJP parts decreasing the porosity of the green part and enhancing their mechanical performance. Also addition of nanoparticles through the printing slurry overcomes the problem of improper penetration during infiltration and also acts as sintering aid with increased contact points lowering the sintering temperatures and improving dimensional accuracy [56], [57]. The printing liquid in the binder jetting process is proposed to be replaced with a slurry of ceramic nanoparticles to transform the manufacturing process to slurry jetting printing (SJP).

The effectiveness of the SJP process in synthesizing was tested in the present work by measuring the mechanical properties of the slurry jetted ceramic parts namely density, porosity and compressive strength. Adding nanoparticles to the printing liquid will affect its properties such as surface tension, viscosity, and wettability, and ultimately the SJP process. To ensure that the nanoparticle addition to the printing formulation will improve

mechanical properties of the printed part without compromising the effectiveness of AM process, their influence on surface tension of the printing slurry will be measured and correlated to the ability of the slurry to penetrate a powder layer.

CHAPTER 2: OBJECTIVES

The central objective of this project is to explore the use of nanoparticle densifiers to decrease the porosity of additively manufactured ceramic parts fabricated using powder printing techniques, and the effects this technique will have on the 3D printing process.

Objective 1:

The first objective of this research project is to determine the effect of nanoparticle densifiers on the density of slurry-jetted alumina parts. Samples made with alumina fillers containing nanoparticle densifiers with concentration varying from 0 – 15 wt.% will be evaluated.

Objective 2:

The second objective is to determine the effect of nanoparticle densifiers on the strength of a green slurry-jetted alumina part. Samples made with alumina fillers containing nanoparticle densifiers with concentration varying from 0 – 15 wt.% will be evaluated. Compressive strength will be determined for each sample concentration.

Objective 3:

The third objective of this work is to determine the effect of nanoparticle densifiers in the printing slurry on its surface tension. Printing slurry with alumina nanoparticle densifiers of average particle size less than 50 nm with concentration varying from 0 – 15 wt.% suspended in a solution of polyvinyl alcohol dissolved in deionized water will be evaluated.

CHAPTER 3: LITERATURE REVIEW

This chapter describes state-of-the-art literature available on the BJP process and the commonly used materials, sources of porosity during binder jetting and their remediation approaches.

3.1. Materials in BJP

Powder formulation is an important consideration when designing BJP process. In a printed part, on an average, the volumes occupied by printing powder and liquid binder before any post processing of the parts are 30% - 75%, and 10%, respectively, and the remaining spaces are void spaces (porosity) [54]. The powder material used for BJP typically consists of filler and adhesive or binder particles. The filler forms the structural material in the printed part providing mechanical and structural integrity, while the binder adheres the filler particles in a network. In addition, additives such as fiber particles and processing aid can be added to improve the mechanical and structural properties of the final specimen [55].

Filler particles are either adhesive in nature by themselves or are coated with adhesives. They bond with each other once the adhesive is cured. Depending on their composition, fillers are comparatively less soluble in a liquid binder than adhesive powder [56]. Reactive fillers chemically respond to liquid binder to form a hardened composition after being dried and impart mechanical structural integrity to the printed part. Binders are highly soluble in liquid binder; they form a solution of low viscosity that penetrates the void spaces in the powder bed and forms adhesive bridges between the filler particles [55], [57], [58]. It is preferred to use binders with high solid strength as the bridges between the

filler particles are the main contributors to green strength of the part before it is post processed.

Printing liquid is the vehicle carrying the binder and is deposited through the print head nozzle. Printing liquid should meet specific liquid rheology properties to be compatible with the print head of a BJP machine. Printing liquid viscosity depends on the pH and solid suspensions in the liquid medium; consequently it can be controlled by altering the solid loading or by adding dispersant [33]. Surface tension of the printing liquid is an important factor of consideration in BJP. Optimal printing liquid surface tension determines its penetration depth in a powder layer and prevents liquid from spreading readily from the print head nozzle. Surface tension of a printing liquid can be altered by adding a surfactant like sodium benzoate [59], [60].

3.2.Density and Porosity in BJP

BJP has gained popularity as preferred AM method for 3D printing ceramics owing to its versatility, economic viability, scalability, and ease of operation and maintenance. However, a major drawback of binder jetted ceramic parts is the lack of dense packing of particles in sample microstructure. This is frequently attributed to friction among the filler particles when they are rolled from the powder platform to fabrication platform preventing them from close arrangement as well as the absence of any external force to densely pack the filler particles in the powder bed.

As a direct result of the above mentioned reasons, poor powder packing in the powder feeding bed with density less than 25% of the theoretical density was developed resulting in highly porous structures with low density [61]. Several researchers have

documented the low-density and high-porosity properties of binder jetted parts. Yoo *et al.* observed that density of the 3D printed alumina samples prior to any post-processing methods was as low as 36% due to the presence of the pores in material microstructure [62]. For this study, spherical alumina (30 μm), coarse platelet alumina (30 μm) and spray-dried alumina (<53 μm) were used. It was observed that the specimen density varied from 36 to 58%, with spray-dried alumina parts showing the highest and coarse platelet alumina parts demonstrating the least density [62]. BJP is suitable to produce porous parts like scaffolds which are the elements/framework used to support cellular and tissue growth. Ceramics like calcium silicate, hydroxyapatite (HA) and plaster of Paris-based powders (calcium sulphate hemihydrate derivatives) are used to make bioimplants. Wu *et al.* printed calcium silicate scaffold with particle size 0.3-5 μm using aqueous solution of PVA with 15 wt.% of PVA. The porosity of the printed green parts was found to be 65% [63]. Suwanprateeb *et al.* studied different ways of powder bed packing in BJP and its effect on the green density and porosity of the printed hydroxyapatite parts using adhesive-coated filler particles with an average size of 70 μm . They successfully synthesized printed parts with the lowest porosity as high as $51 \pm 0.9\%$, with highest green density of 0.85 mg/m^3 . Although the parts are subjected to sintering at 1300 $^{\circ}\text{C}$ for 1 hour, the binder jetted parts achieved only about 50% of the theoretical density [64]. Gonzalez *et al.* observed that alumina parts (filler particle size 53 μm) produced from BJP have very low relative densities averaging 64% after sintering at 1600 $^{\circ}\text{C}$ for 16 hours [65]. Melcher *et al.* showed that alumina parts produced from BJP after sintering at 1600 $^{\circ}\text{C}$ for 4 hours have higher porosity values (36%) compared to cast alumina parts (28%) after sintering at 1600 $^{\circ}\text{C}$ for

1 hour, reinforcing that the porosity of the green parts produced from BJP have lower density even after post processing [42], [66]. Maleksaeedi *et al.* also measured the density of the sintered alumina parts (20 - 40 μm) produced from BJP to study the effect of infiltration. Relative sintered density of the printed parts before infiltration was found to be as low as 38.4% which they attributed to low packing density of the filler particles and subsequently and high volume of interparticle pores in the green parts [46]. It was also reported that alumina granules packed in the powder bed itself have a porosity of about 50% which results in parts with much lower porosity [46]. Compared to the high bulk densities (>99%) that could be achieved in ceramics manufactured by traditional processes like casting or forming, densities achieved in BJP is very less [46].

3.3.Effect of Porosity on Mechanical Performance of Ceramics

Porosity has adverse effects on the strength of the high strength ceramics [67], [68], [69]. Coble *et al.* investigated the variation in the flexural strength of the alumina casting slip samples as their porosity varied from 35% to 50% and observed that the flexural strength decreased exponentially from 193 - 35 MPa with increasing porosity [70]. Kawai *et al.* also investigated the effect of porosity on flexural strength of the Si_3N_4 ceramics with different grain morphology in the microstructure, namely spherical, columnar and combination of the columnar and spherical. Independent of the microstructure of the powder grains, highest flexural strength (530 MPa) was observed in samples with least porosity (12.1%) while the lowest flexural strength (50 MPa) was observed in samples with high porosity 49% [67].

Parts printed from BJP generally have high porosity levels in green parts which result in high residual porosity when subjected to post processing methods which in turn limits the mechanical properties of the printed parts. Chumnanklang *et al.* observed an increase in green 3-point bending strength from 0.18 MPa to 0.7 MPa in printed hydroxyapatite parts with decreasing porosity. On increasing the size of spray dried hydroxyapatite particles from 38 μm to 83 μm , a decrease in porosity of the sintered sample was observed, from 63.66% to 59.43% [71]. Suwanprateeb *et al.* observed a very low green flexural strength of the hydroxyapatite parts of less than 0.5 MPa; post-sintering, flexural strength increased to about 12 MPa as a result of 20% reduction in the porosity [64]. In another study by Klammert *et al.*, cylindrical samples with brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) and monetite (CaHPO_4) powders were printed. Green parts of brushite were observed to have a compressive strength of 23.4 MPa with porosity of 38.8 vol% while green parts of monetite were observed to have a compressive strength of 15.3 MPa and microporosity of 43.8 vol% [72]. Castilho *et al.* also observed a low compressive strength in calcium phosphate cylindrical parts equal to 23.8 MPa, for a porosity of 43.1% [73]. Wu *et al.* showed that calcium silicate scaffolds with pore size of $1 \times 1 \text{ mm}$ had a total porosity of 65% resulting in a very low compressive strength of 3.6 MPa [63]. Results from Tarafder *et al.* demonstrated that reduction in porosity enhances the compressive strength of the tricalcium phosphate (TCP) scaffolds. Cylindrical scaffolds with varying pore sizes of 500, 750 and 1000 μm were printed in this study, to identify differences in compressive strengths of pure TCP and TCP doped with strontium oxide and magnesium oxide. Porosities (37.01 - 50.19%) of the sintered samples corresponding to the three different

interconnecting pore sizes was found to increase with increasing pore size. Highest compressive strength (12.01 MPa) was observed in doped TCP scaffolds having lowest porosity (37.01%) [74]. Liu *et al.* observed the effect of porosity varying from 33% to 78% on the compressive strength of the hydroxyapatite ceramics, typically used in bone implants. It was noted that the compressive strength varied exponentially with porosity in case of smaller pore diameters (~ 0.093 mm) and linearly for larger pores (diameters ~ 0.42 mm) [75]. Figure 3.1 shows the results from several studies, compiled by Zocca *et al.*, correlating the compressive strength of additively manufactured parts on their porosity.

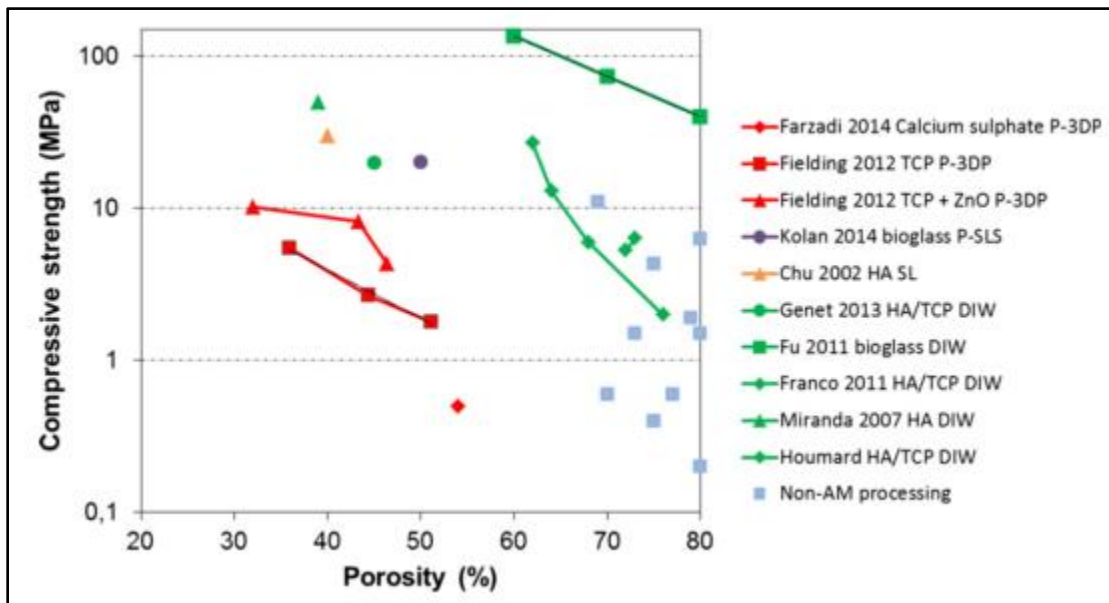


Figure 3.1: Variation in compressive strength with respect to porosity in ceramic parts fabricated using BJP (P-3DP), selective laser sintering (P-SLS), stereolithography (SL), direct ink writing (DIW) and conventional methods (non-AM processing) [61].

3.4.Methods Adopted to Densify and/or Decrease Porosity of the Printed Parts

Common post processing methods adopted to reduce porosity and improve the density of the green printed samples are infiltration, sintering, and hot isostatic pressing

(HIP) [46]. Gaytan *et al.* studied the effect of sintering temperature on binder jetted barium titanate samples on density and porosity. Sintering temperature was varied from 1260 - 1400 °C at constant binder saturation level of 60% and porosity was observed to decrease from 31% to 7% while part shrinkage increased from 20.12% to 29.45% [76]. In the work of Tarafder *et al.*, two different types of sintering methods were tested on doped TCP scaffolds. Raw filler powder for printing was prepared by adding strontium oxide (1 wt.%) and magnesium oxide (1 wt.%) to the TCP powder. It was observed that microwave sintering achieved higher bulk density (52.84% vs. 45.06%) and lower porosity (37.01% vs. 41.63%) compared to conventional sintering. Shrinkage measured in microwave sintering (33.2%) was higher compared to conventional sintering (29.8%) [74]. Sintering processes demonstrated high linear shrinkage which results in dimensional inaccuracy and creep formation during post processing which is undesirable for industrial applications [34], [41] and needs to be overcome. Melcher *et al.* binder jetted alumina samples infiltrated with molten copper to make a cermet, which was sintered at 1600 °C for 4 hours. This decreased the porosity in the sintered alumina part post binder jetting to 36%, and then infiltrated with Cu/Cu₂O after sintering [77]. The alumina-copper parts before and after sintering and infiltration was shown in Figure 3.2 demonstrating dimensional changes in the binder jetted part during post-processing.



Figure 3.2: Printed green part of alumina (left), sintered alumina part (middle) and copper infiltrated alumina part (right) [77].

Maleksaeedi *et al* investigated the effect of infiltrating binder jetted samples with ceramic slurries during post-processing [46]. In this study, binder-jetted alumina parts were infiltrated with slurry containing alumina powder with average particle size of $0.32\ \mu\text{m}$. As the alumina content in slurry was increased from 0 to 50% by volume, relative green density of infiltrated samples increased from 25% to 50% while sintered sample density increased from 38.4% to 85% of theoretical density. Micro-computed tomography (micro-CT) imaging showed that samples infiltrated with slurries containing >40 vol.% alumina particles showed inhomogeneous porosity due to limited penetration of highly viscous infiltrant [46]. Kerman *et al.* and Kumar *et al.* used a combination of sintering with hot isostatic pressing for post-processing their binder-jetted samples and almost achieved theoretical density for tungsten carbide-cobalt and alumina parts respectively [78], [79]. However, they noted that though HIP is successful in improving density effectively albeit with high shrinkage, it is very expensive compared to other post processing methods.

Another approach to improving green part density during binder jetting is to use multimodal powders. Filler powder particles with an average particle size greater than 20 μm are easy to spread while particles smaller than 5 μm occupy the interstitial positions between the larger particles, decreasing porosity as shown in Figure 3.3 [80]. Lanzetta *et al.* observed improved surface finish by introducing 2.5 μm size platelet-shaped alumina powder additives and 5 μm equiaxial alumina powder to 20 and 30 μm spherical alumina powder [80]. They observed that binder-jetted samples with bimodal powder had better surface finish compared to unimodal powder because of the movement of fines towards the exterior surface of the printed profiles [80]. From Figure 3.3, bimodal distribution of alumina powders of sizes 20 μm and 5 μm in a printed line on the powder layer in BJP process can be visualized.



Figure 3.3: SEM image of line formed by bimodal powder of 20 μm spherical and 5 μm equiaxial alumina powder (12.5 wt%) [80].

Gonzalez *et al.* studied the effect of particle size on the density of the final printed part. They used aluminum oxide powders of three different sizes: 53 μm , 45 μm , and 30

μm . Individual samples of each particle size and sample with mixed particle sizes were printed and then heat-treated for two hours at $195\text{ }^{\circ}\text{C}$ to cure the binder. The cured samples were then sintered at two different time intervals of 2 hours and 16 hours and their density and compressive strength were determined. It was observed that mixed particle size sample had a high relative density of 96.51% while samples with particle size of $53\text{ }\mu\text{m}$ had a low relative density of about 64%. From the compression test, it was observed that mixed powder samples sintered for 16 hours had highest compressive stress value of 146.6 MPa [65].

Crane *et al.* added iron nanoparticles to the printing liquid during binder jetting and printed steel parts. Parts subjected to sintering tend to have high shrinkage as a consequence of high porosity, leading to creep deformation under self-weight of the part. Crane *et al.* reported that shrinkage rate and deformation depends on the bond size between the filler particles. Addition of nanoparticles into the skeleton of the part being printed through printing liquid increases the size and number of bonds, reducing both creep and shrinkage. Variation in shrinkage reduction was decreased from 2.75% to 1% with increase in content of the nano-iron (0 - 2.7 wt.%) in printing liquid. The parts with highest wt.% of iron nanoparticles were observed to have 60% reduction in shrinkage and 95% decrease in the creep deflection compared to the parts printed without nanoparticles [81]. Nanoparticles tend to occupy inter-particulate pores in powders dispersions and improve the density of the green printed parts, resulting in reduced shrinkage and improved mechanical properties after post processing. Bai *et al.* showed that silver parts printed with the printing liquid containing 20% silver nanoparticles by weight have less shrinkage and distortion on

sintering with sharper corners compared to the parts printed using printing liquid without nanoparticles [52]. In addition, they demonstrated that including nanoparticles increased sample green density from 2.116 g/cm^3 to 2.184 g/cm^3 and an increased engineering tensile strength from 46 to 55 MPa after sintering at 850°C for 20 minutes [52]. Figure 3.4 shows the change in dimensions in their samples and substantial decrease in the shrinkage of the printed parts due to the addition of nanoparticles to the printing liquid.



Figure 3.4: Substantial difference in the shrinkage of the sintered parts printed without (top) and with nanoparticles (bottom) [52].

Zhao *et al.* used a 10 wt.% zirconia nanoparticle suspension in the printing liquid to print zirconia ceramic samples [82]. They showed that by increasing the binder content (amount of printing liquid dispensed into each layer of powder bed) from 50% to 125%, the relative density of the printed parts increased from 75.2% to 86.8% while linear shrinkage decreased from 22.3% to 10.6% after sintering [82].

3.5.Effect of Nanoparticle Suspensions on the Powder-Binder Interaction

Optimal powder-binder interaction is crucial for achieving ideal structural integrity in a binder-jetted part. The ability of the printing liquid to penetrate a layer of filler particles

in the powder bed is an important factor for determining green strength and printing accuracy of the binder-jetted part. Washburn *et. al* showed that the penetration depth of a liquid in a powder bed is directly proportional to the interparticle pore size, as well as surface tension and wettability of the fluid, and inversely proportional to fluid viscosity [83]. High penetrability leads to excessive spreading of the printing liquid and results in poor printing accuracy with respect to part dimensions. In contrast, insufficient penetration of the filler particles by the printing liquid causes improper bonding between adjoining layers, resulting in poor green strength of the printed part [35], [80], [84].

While penetration depth has not been examined extensively from a BJP standpoint for ceramic samples, each of the individual factors affecting penetration depth of a fluid in a powder bed have been explored in other contexts. Nanoporous alumina, typically used as bioceramics [85], has been demonstrated to be a hydrophilic material [86] in that it has a contact angle with water which is less than 90° . These results were confirmed by Tasaltin *et al.* [87] and Shatty *et al.* [88]. Tasaltin *et al.* showed that porous alumina is hydrophilic in nature with a water contact angle of $82.9 \pm 3^\circ$ [87]. Shatty *et al.* measured the static contact angle of films containing alumina nanoparticles (2 wt.%) with water and found it to be as low as $22 \pm 2^\circ$ [88], establishing that the wettability of alumina by water is high.

Several researchers have demonstrated that addition of alumina nanoparticles to water increases the viscosity of the suspensions. Viscosity of water at room temperature (20°C) is typically measured to be 1.002×10^{-3} Pa.s [89]. Ewais *et al.* observed that addition of alumina nanoparticles with a mean particle size $5\ \mu\text{m}$ by 65 wt.% to deionized (DI) water in the presence of surfactant Duramax C, increased the viscosity to 3500 – 4000

Pa.s. The increase in the concentration of the surfactant was observed to reduce the viscosity of the solution but the lowest viscosity of alumina slurry was still greater than that of water [90]. It was found that content of surfactant and solid loadings in the slurry has significant effect on the viscosity of the printing slurry. Keeping the surfactant content constant, Subbanna *et al.* showed that the viscosity of the alumina suspension increases with the increase in the solid loadings of alumina. The alumina suspension was found to be highly viscous at 40 vol.% solid loading even after adding optimal concentration of surfactant [91]. Palmqvist *et al.* showed that increased concentration of alumina nanoparticles in DI water in the presence of surfactants such as polyacrylic acid and liginosulphonate increases the viscosity of the resultant slurry. They observed an increase in viscosity from 1.5 Pa.s to 10 Pa.s with increase in solid loadings from 55 to 59 vol.% [92]. Similar results were shown by Michalkova *et al.* [93], Ohji *et al.* [94], Harikrishnan *et al.* [95], and Murshed *et al.* [96] where they attributed the increase in the viscosity of the slurries with increase in the solid loadings to the increase in the packing of number of solid particles per unit area [94].

While the trends of wettability and viscosity have been extensively established for the interaction between water and nanoparticles, similar results have not been documented for the surface tension of a slurry with nanoparticle inclusions. Adding nanoparticles can both decrease or increase the surface tension of a fluid, depending on the interaction between the adhesive forces in the fluid and the surface functionalities on the nanoparticles. Kim *et al.* observed an increase in surface tension of alumina/DI water slurry to 75 mN/m on addition of 0.1 vol.% alumina nanoparticles at room temperature from 72.6 mN/m [97].

Similarly, Murshed *et al.* observed increase in surface tension of water with carbon nanotubes at 0.1 vol.% compared to the base fluid (deionized water) without nanoparticle inclusions by approximately 19% [98]. On the other hand, Bello *et al.* showed that the addition of 1 wt.% magnesium oxide nanoparticles to RP2 fuel decreased the surface tension of the base fluid from 24.01 mN/m to 23.18 mN/m [99]. Similarly, Harikrishnan *et al.*, and Murshed *et al.* showed that the surface tension of water decreased with the addition of titanium oxide by 0.1 vol.% and silver nanoparticles by 2 vol.% to 64 mN/m and 35 mN/m respectively at room temperature. They hypothesized that this may be due to the formation of monolayer of nanoparticles at the fluid - gas interface which may have disrupted the adhesive forces between the fluid molecules [95], [96], [100]. Till date, there are no defining studies on the surface tension of alumina slurries with different surfactants, which is a critical need for understanding the penetration depth of the binder slurry in the powder bed.

Most of the current research focused on improving density and related mechanical properties of binder-jetted specimens by including nanoparticles in the printing liquid examined the effects of binder saturation level and post processing parameters such as sintering profiles on mechanical performance of the samples. However, the effects of nanoparticle densifier concentration in the printing liquid on porosity, density and mechanical performance are still largely unexamined. There is a critical need to bridge this knowledge gap in order to effectively design additive manufacturing process such that parts manufactured possess optimal performance parameters desired for the variegated applications.

CHAPTER 4: EXPERIMENTAL SETUP

This section describes the materials used in the sample preparation, testing techniques, and characterization methods to analyze the samples for their mechanical and structural properties.

4.1. Materials

Alumina (Al_2O_3) powder (AdValue Technology, USA, 99.9% purity) with mean particle diameter of 40 μm was used as the filler material in this study. Alumina nanoparticles (Sigma-Aldrich, USA) with a particle size less than 50 nm were used as nanoparticle densifiers. Polyvinyl alcohol (PVA) (Sigma Aldrich, USA, M_w : 9,000-10,000 g/mol, 80% hydrolyzed) was used as both binder and dispersant/surfactant. Deionized (DI) water was used as the solvent in the printing liquid. The filler powder was sieved through 150 mesh and the rest of the materials were used as received.

4.2. Sample Preparation

To prepare the printing liquid, requisite quantities of PVA and water were mixed with a stirrer for 60 minutes at room temperature until the PVA powder completely dissolved in water. Alumina nanoparticle densifiers were then dispersed in the printing liquid using a Qsonica Q500 ultrasonic processor with a titanium microtip for 12 minutes such that the nanoparticles are homogeneously distributed in the printing liquid without any agglomerations. DI water and PVA quantities were maintained at a weight ratio of 9:1 in the printing liquid. Four different printing slurries were prepared with the nanoparticle densifier concentrations of 0, 5, 10 and 15 wt.%.

In this study, alumina samples were prepared manually such that the synthesis process resembles the BJP process by layering filler particles and depositing printing slurry on them in the desired geometry. After printing slurry was deposited over each powder layer, samples were vibrated for 45 seconds on a Vortex Genie Mixer² at 2240 rpm. Layering process was repeated till the desired sample height was achieved.

Two types of cylindrical samples were made for density testing and compression test testing as per ASTM B962-15 and ASTM E9. Density test samples were made with an aspect ratio (diameter/length) of 0.5, while the compression test samples were synthesized with an aspect ratio of 2. Each type of sample was made with the four types of the printing slurries to make slurry-jetted alumina samples with varying densifier content. The dimensions and composition of filler, printing liquid and densifier of each type of sample is provided in Table 4.1. All the samples were synthesized to have a constant printing slurry volume of 2 mL per gram of filler particles per layer. The synthesized green alumina samples with varying densifier content were then cured on a Corning PC-420D hot plate as per temperature profile shown in Table 4.1.

Table 4.1: Experimental parameters considered for sample synthesis.

Sample type	Length (mm)	Diameter (mm)	Filler per layer (g)	Curing time (h)	Curing temperature (°C)
Density test samples	7.7	15.5	0.5	2	60
Compression test samples	31	15.5	1	12	60

4.3.Characterization

4.3.1. Bulk Density and Porosity Testing

To measure the bulk density of the printing slurry, a 1 mL volume pipette was filled with requisite volume of the fluid and deposited into a beaker placed in a Ohaus Discovery DV214C analytical balance with an accuracy of 0.1 mg to measure its weight. Bulk density of the printing slurry (ρ_{PS}) was then calculated from the measured volume and weight of the samples.

Bulk density of slurry-jetted alumina samples with and without nanoparticle densifiers was measured using Archimedes' principle according to ASTM B962-15. Mass of the samples in air (m) and in vegetable oil (M) (with a bulk density equal to 8921 kg/m³ (ρ)) was measured using the analytical balance. Bulk density of the alumina samples (ρ_a) was determined as shown in Equation 4.1 below.

$$\rho_a = \left[\frac{m}{m - M} \right] \rho \quad \text{Equation (4.1)}$$

Porosity of the slurry jetted alumina samples was determined using a TriFoil Imaging eXplore CT 120 X-Ray scanner with a resolution of 25 μ m. Alumina samples were irradiated with 80 kV energy for 120 minutes to obtain their 3D images. Using BoneJ plugin of the ImageJ open source software, alumina material volume fraction (v_f) of each sample was estimated. Consequently, volume fraction of pores, also referred to as porosity (p) was determined using Equation 4.2.

$$p = 1 - v_f \quad \text{Equation (4.2)}$$

4.3.2. Compressive Strength Test

Compressive strength of the slurry jetted alumina samples was characterized per ASTM E9 using an MTS Q25 load frame as shown in Figure 4.1. Ram displacement speed was maintained at 0.5 mm/min and compressive load was gradually applied axially on both the lateral sides of the slurry-jetted alumina samples. The maximum load (F) carried by the sample before complete fracture was recorded during testing. Subsequently, compressive strength of the sample was obtained by dividing load at sample fracture by the cross-sectional area of the sample as shown in Equation 4.3.

$$\sigma_c = \frac{F}{A} \quad \text{Equation (4.3)}$$

where A is the cross-sectional area of the sintered sample, σ_c is the compressive strength of the sintered sample and F is the maximum force applied on the sample before fracture.

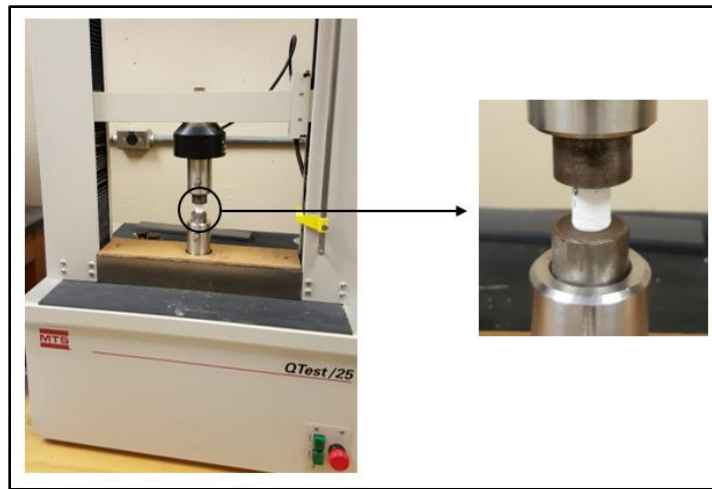


Figure 4.1: Experimental set up for compressive strength using MTS machine; enlarged view of the sample in the inset.

4.3.3. Printing Slurry Surface Tension

Surface tension of the printing slurry was measured using pendant droplet test method [101]. The apparatus shown in the schematic in Figure 4.2 consisted of a syringe pump housing a syringe with the printing slurry connected to a needle clamped to a stand. The syringe pump was adjusted to produce a static droplet hanging from the needle. A photography LED light source with 5500K output and 120 degrees beam angle was focused from behind the droplet. Image of the largest droplet is taken to minimize the measurement error.

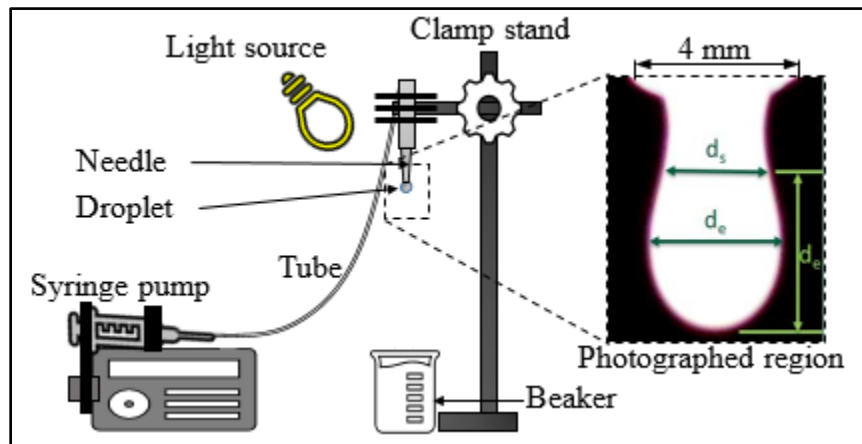


Figure 4.2: Schematic of pendant droplet test set up. Inset shows the image of a droplet captured during testing, showing the equatorial and selected-plane diameters.

At the beginning of the experiment, the image of the static printing slurry droplet suspended from the needle was captured using a Canon EOS 80D DSLR camera at an f-stop of 1.8 placed at a distance of about 0.5 m from the clamp stand. Using ImageJ software, droplet images were analyzed and equatorial diameter (d_e) and selected-plane diameter (d_s) of the droplet were measured. Selected-plane diameter is defined as the

smallest diameter of the droplet formed after the necking region between needle tip and droplet, and equatorial diameter is the largest diameter of the droplet as shown in the Figure 4.2. Surface tension (γ) of the printing liquid was calculated from the Equations 4.4 – 4.6 [101], [102].

$$\gamma = \frac{(\rho_{PS} - \rho_{air})gd_e^2}{H} \quad \text{Equation (4.4)}$$

$$S = \frac{d_s}{d_e} \quad \text{Equation (4.5)}$$

$$\frac{1}{H} = \frac{0.3161}{S^{2.6040}} \quad \text{Equation (4.6)}$$

where ρ_{air} is the density of air, g is the acceleration due to gravity, S is the shape factor of the suspended droplet, and H is the shape function obtained from shape factor through power law fitting.

4.4. Statistical Analysis

One-way analysis of variance (ANOVA) methodology was used to evaluate data collected from all the experiments in this study. One-way ANOVA is typically used to determine if the variances of a data set are equal assuming a certain confidence interval to ascertain if the selected sample size is optimal. In this study, ANOVA analysis was used to test the statistical significance of the reported experimental variables at a confidence interval of 95% (i.e. $\alpha = 0.05$). In this project, four different printing slurries were prepared with increasing alumina nanoparticle densifier concentrations implying that there were four data sets for each experiment performed. Hence the source of variation in this evaluation was considered to be the concentration of alumina nanoparticle densifiers in the printing liquid. The null hypothesis in this study was stated as “*there is a lack of significant*

differences in the averages of the data sets obtained in each experiment with varying concentration of alumina nanoparticles suspended in the deionized water". On the other hand, the alternate hypothesis was framed as *"there is a significant difference among the averages of the data sets obtained in each experiment with varying concentration of alumina nanoparticles suspended in deionized water"*.

To perform the analysis, initially, grand mean ($\bar{X}_{GM}$) of all the data values recorded from all the data sets was calculated. Grand mean is the average of each data set means which is given by the Equation 4.7,

$$\bar{X}_{GM} = \frac{\sum n\bar{x}}{\sum n} \quad \text{Equation (4.7)}$$

where $\bar{x}$ is the mean of the data values from each data set, and n is the number of samples in each data set. Subsequently, between group variation (BGV) defined as the variation between the sum of squares between different data sets, denoted as SS_B , was calculated as given by the Equation 4.8.

$$SS_B = \sum n(\bar{x} - \bar{X}_{GM})^2 \quad \text{Equation (4.8)}$$

Degrees of freedom (df_B) was then obtained as given by Equation 4.9,

$$df_B = k - 1 \quad \text{Equation (4.9)}$$

where k is the number of data sets used, which in this study is equal to 4. Following this, variance in mean squares between the different groups, denoted as MS_B , was calculated as shown in Equation 4.10.

$$MS_B = \frac{SS_B}{df_B} \quad \text{Equation (4.10)}$$

Degrees of freedom within the data set (df_W) was then calculated by subtracting number of data sets from total number of samples from all the data sets (N) as shown in Equation 4.11. Sum of the squares within the data set (SS_W) and mean of the squares (MS_W) within the data set were calculated using Equations 4.12 and 4.13 respectively.

$$df_W = N - k \quad \text{Equation (4.11)}$$

$$SS_W = \sum_{j=1}^k \sum_{i=1}^{N_j} (x_{ij} - \bar{X}_M)^2 \quad \text{Equation (4.12)}$$

$$MS_W = \frac{SS_W}{df_W} \quad \text{Equation (4.13)}$$

where i is the group number, and j is the observation number. Next, total variation (SS_T) was obtained by adding the variations in sum of the squares of both between and within groups as shown in Equation 4.14. Total degrees of freedom (df_T) was calculated as the summation of degrees of freedom within and between the groups as shown in Equation 4.15. Next, F -value was obtained as shown in Equation 4.16.

$$SS_T = SS_B + SS_W \quad \text{Equation (4.14)}$$

$$df_T = df_B + df_W \quad \text{Equation (4.15)}$$

$$F = \frac{MS_B}{MS_W} \quad \text{Equation (4.16)}$$

Finally, $F_{critical}$ and P -values were obtained based on the degrees of freedom between and within the groups from the table of $F_{critical}$ for a critical significance level of $\alpha = 0.05$ using the MS_B , MS_W , df_B and df_W values calculated during the analysis.

For a given data set in an experimental test, the effect of increasing alumina nanoparticle densifier concentration in the printing slurry on the response was considered

highly significant, if the calculated F -value was greater than or equal to $F_{critical}$ value, and subsequently, the null hypothesis was rejected. On the other hand, if the calculated F -value was less than the $F_{critical}$ value, then the null hypothesis was considered as highly significant [103].

As a follow up to One-way ANOVA, post hoc analysis was performed to identify where the differences occurred between the groups of datasets. Post hoc analysis was performed only after the null hypothesis was rejected from One-way ANOVA. Tukey's honestly significant difference (HSD) analysis is a single step method which performs multiple comparisons to find the means of data sets that are significantly different from the means of the remaining datasets for a given experimental setup. It uses the studentized range distribution (SRD) for making pairwise comparisons between the datasets. Studentized range is obtained from the difference between the highest and lowest observations among the data sets in terms of standard deviations. SRD is the probability distribution generated using the studentized range. The SRD is used to identify the Q -value which is compared against the calculated HSD value to test the significance of difference observed between individual datasets, as shown below.

The number of combinations that are possible from k datasets taken r at a time is given by the Equation 4.17.

$$C(k, r) = \frac{k!}{r! \times (k - r)!} \quad \text{Equation (4.17)}$$

Tukey's formula used to run the test was given by Equation 4.18.

$$HSD = \frac{\bar{x}_A - \bar{x}_B}{\sqrt{MS_W/n}} \quad \text{Equation (4.18)}$$

where Q is the upper critical value of the SRD obtained from the Q table at $\alpha = 0.05$ using k and df_W values. The obtained Q -value is compared with the HSD. The averages of two data sets A and B in a pair-wise comparison are said to be significantly different when the HSD is greater than the Q -value obtained from the Q table at a confidence interval of 95%.

CHAPTER 5: PROPOSED PLAN OF WORK

This chapter reviews the plan of work to fulfil each of the thesis objectives.

5.1.Objective 1

The first objective of this research project is to determine the effect of nanoparticle densifiers on the density of slurry-jetted alumina parts. Samples made with alumina fillers containing nanoparticle densifiers with concentration of 0 – 15 wt.% will be evaluated.

5.1.1. Objective 1 Plan of Work

Density testing of slurry-jetted alumina samples with nanoparticle densifiers will be performed as per ASTM B962-15. Results of each test will be used to determine the relative density of each sample as a function of alumina nanoparticle content. A minimum of three test samples of each nanoparticle concentration will be tested to evaluate standard error and ensure repeatability of results.

5.2.Objective 2

The second objective is to determine the effect of nanoparticle densifiers on the strength of a green slurry-jetted alumina part. Samples made with alumina fillers containing nanoparticle densifiers of with concentration of 0 – 15 wt.% will be evaluated. Compressive strength will be determined for each sample concentration.

5.2.1. Objective 2 Plan of Work

Compressive testing of the slurry-jetted alumina samples with varying nanoparticle densifier content will be determined as per ASTM E9. Stress-strain curves from each test will be used to determine the compressive strength of the alumina samples. A minimum of three test samples of each nanoparticle concentration will be tested to evaluate standard

error and ensure repeatability of results.

5.3.Objective 3

The third objective of this work is to determine the effect of nanoparticle densifiers in the printing slurry on its surface tension. Printing slurry with alumina nanoparticle densifiers of average particle size less than 50 nm with concentration varying from 0 – 15 wt.% suspended in a solution of polyvinyl alcohol dissolved in deionized water will be evaluated.

5.3.1. Objective 3 Plan of Work

Images of static printing slurry droplets will be obtained using a droplet pendant test procedure. ImageJ software will be used to measure droplet dimensions. Results from the images will be used to determine the surface tension of the printing slurry. A minimum of ten test droplets of each printing slurry with varying nanoparticle concentration will be tested to evaluate standard error and ensure repeatability of results.

CHAPTER 6: RESULTS AND DISCUSSION

This chapter describes the results obtained after the performance of experiments as per the plan of work towards the completion of each research objective described in Chapter 3.

6.1.Objective 1: Density and Porosity of Slurry-Jetted Alumina Samples

Figure 6.1 shows the bulk density of cured, slurry-jetted alumina samples as a function of varying nanoparticle densifier content. The error bars in Figure 6.1 indicate the standard deviation in the density values depicting the standard error in measurement calculated as recommended by ASTM E2655. Theoretical density of alumina is 3987 kg/m^3 [104]. As the concentration of densifier in the printing slurry was increased from 0 to 15 wt.%, results show a linear increase in the bulk density from 2008.8 kg/m^3 to 2605 kg/m^3 which is an overall increase of 29.6%.

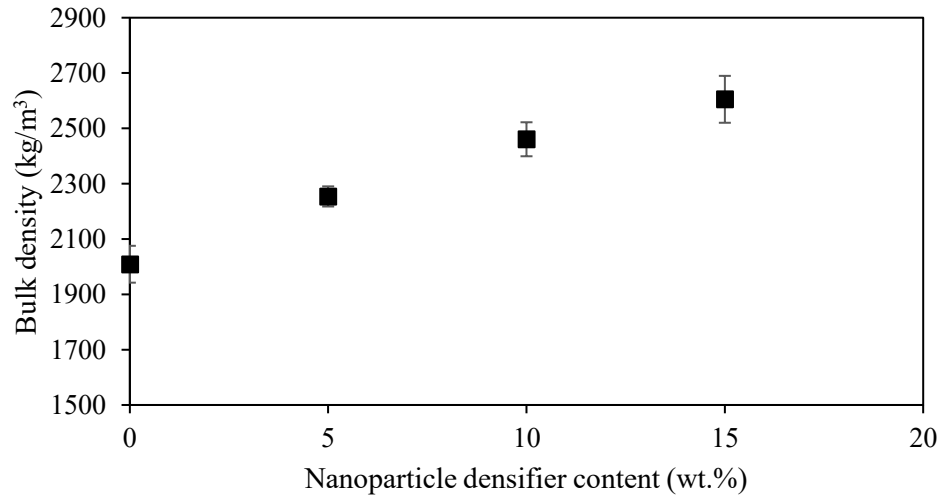


Figure 6.1: Bulk density of alumina samples as a function of nanoparticle densifier content varying from 0 to 15 wt.% in the printing slurry.

Three test specimens per concentration of the nanoparticle densifier were tested to ensure repeatability. The results of One-way ANOVA analysis are shown in Table 6.1. P -value was calculated to be less than 0.05 indicating that the null hypothesis can be rejected and the sample size selected was sufficient to support the hypothesis. From Tukey's HSD method, the calculated Q -value was 4.5. The results of post hoc analysis are provided in Table 6.2. From the pair wise comparisons, it was revealed that the average densities of the pairs Sample 5% - Sample 10% and Sample 10% - Sample 15% are not significantly different and the remaining pairs have significant difference in densities.

Table 6.1: One-way ANOVA analysis of data sets in density test.

Source of variation	Sum of squares	Degrees of freedom	Mean of squares	F	Probability value (P)	F_{critical}
Between groups	385.7	3	128.6	28.1	13.5×10^{-5}	4.1
Within groups	36.7	8	4.6			
Total	422.3	11				

Table 6.2: Post hoc analysis of data sets in density test.

Comparison (A-B)	HSD
Sample 0% - Sample 5%	5.0
Sample 0% - Sample 10%	9.2
Sample 0% - Sample 15%	12.1
Sample 5% - Sample 10%	4.2
Sample 5% - Sample 15%	7.1
Sample 10% - Sample 15%	2.9

Linear regression was performed to evaluate the statistical relation between the nanoparticle densifier content (x) and density of slurry jetted sample (y). The linearity between the nanoparticle densifier content and bulk density is shown in Equation 6.1. The

coefficient of determination (R^2) indicates the effectiveness of the linear fit i.e. the ‘goodness’ of linear fit increases as the R^2 value approaches unity. An R^2 of 987×10^{-3} indicates that the linear regression closely fits the data points.

$$y = 1.0x + 51.3 \quad \text{Equation (6.1)}$$

Adding nanoparticle densifiers to ceramic substrates for improving their overall density has been a prevalent practice. Assaedi *et al.* showed that as clay nanoparticle content increased from 0 to 2 wt.%, density of the fly ash samples was increased from 1.84 g/cm³ to 2.05 g/cm³ [105]. Wu *et al.* demonstrated that addition of fine alumina particles with 50 nm size to a micron-sized ceramic slurry of alumina with particle size of 9 µm improved the relative density of the parts produced by stereolithography by almost 39% [106]. Similar results were observed in a study conducted by Zhao *et al.* when they 3D printed zirconia parts using a suspension of zirconia nanoparticles as the printing liquid. As the printing liquid content (binder saturation level) was increased from 50% to 125%, while maintaining the densifier content at 10 wt.%, the relative sintered density of the zirconia samples increased from about 75% to nearly 87% [82].

With the addition of nanoparticles in the printing liquid, higher volume fraction of material in the samples and lower porosities were observed when compared to the samples without nanoparticle densifiers in the present study. Samples without nanoparticle densifiers showed a high amount of porosity of 58.2%. These were in the form of lack-of-fusion pores, distributed around the sample volume. Additionally, there were large isolated pores, possibly occurring due to gases released from the samples during curing. As the concentration of nanoparticle densifiers in the samples was increased to 15 wt.%, porosity

of the slurry-jetted alumina samples was found to be 37.4%, which is a decrease of about 35.7%. Alumina samples with 15 wt.% nanoparticle densifiers showed a more uniform pore distribution with much fewer lack-of-fusion pores.

Figure 6.2 shows the microCT images with only the pores highlighted in 3D using Avizo Lite FEI 9.1.1 software. Close examination of Figure 6.2 shows that the nanoparticle densifiers occupy the interparticle voids between the fillers. This, in turn, decreases the porosity of the green samples while enhancing their density prior to post-processing.

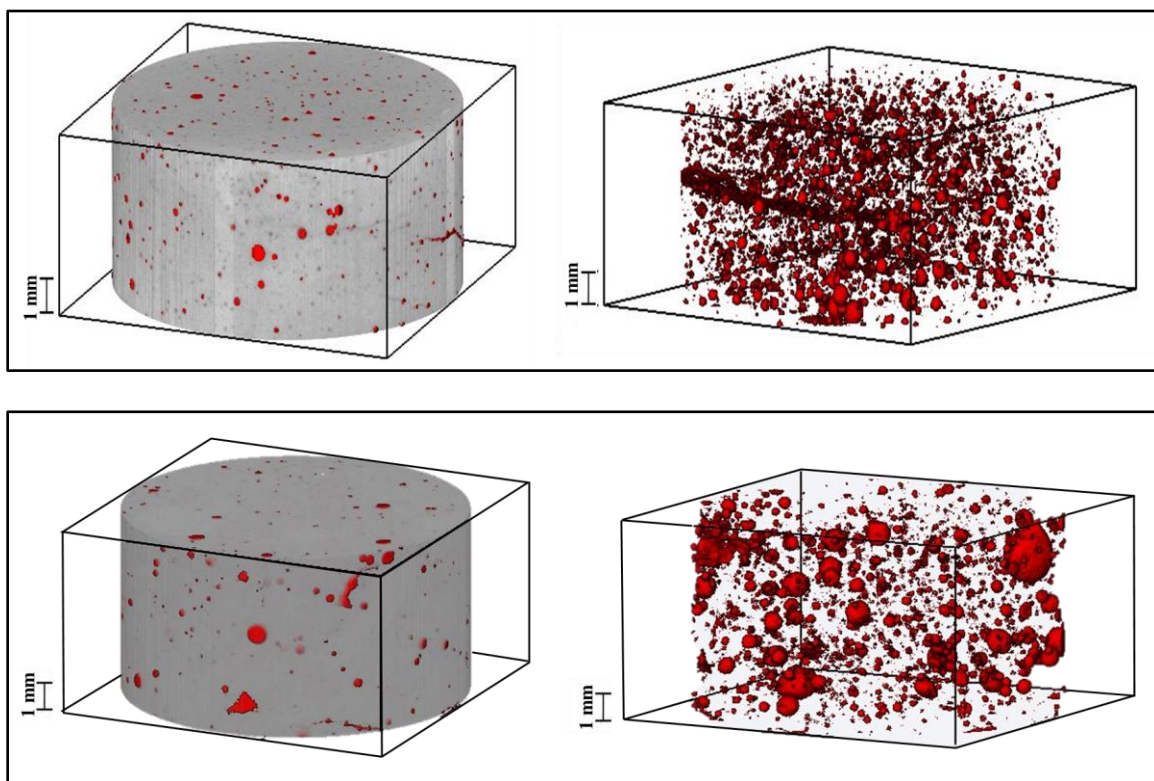


Figure 6.2: Separation of pore phase (shown in red) from the solid phase (shown in grey) in the binder-jetted alumina samples. A. Alumina with 0 wt.% nanoparticle densifiers and 58.2% porosity (top); and B. Alumina with 15 wt.% nanoparticle densifiers and 37.4% porosity (bottom).

Similar trends were seen by Maleksaeedi *et al.* whose alumina samples showed a gradual decrease in porosity on vacuum infiltration with alumina slurries. As the concentration of alumina powder acting as densifier in the infiltrate was increased from 0 to 50 vol.% , the porosity of the parts gradually decreased from ~75% to ~43% [46]. Another study by Li *et al.* proved that nanocomposites prepared by adding 0.5 wt.% surface treated carbon nanotubes (20 nm - 40 nm) to a Portland cement paste (water/cement/sand) reduced the pore volume of their samples from 17.76% to 10.8% [107].

Ceramic samples made from consolidated powders have been shown to improve density and mechanical performance when the particle precursors were chosen to have a bimodal distribution with an order of magnitude difference in their average particle sizes. While it is easy to assume that similar results may be seen when 3D printing ceramics by BJP using nanoparticles and micron particle precursors as the fillers placed together in the printing bed, literature shows that there is a non-uniform distribution of the particles. This is because incorporating the densifier with the fillers in the fabrication bed of the BJP will lead to the nanoparticles settling at the bottom of the fabrication platform by effectively getting sieved from through the pores between the micron particles causing density inhomogeneities along the vertical axis in the 3D printed parts. The approach of using nanoparticles to densify the ceramic parts during 3D printing is effective when they are delivered to the samples *in situ* when the pores are formed in each layer.

6.2.Objective 2: Compressive Strength of Slurry-Jetted Alumina Parts

Axial compressive strength of the slurry-jetted alumina samples with and without nanoparticle-densifiers measured as per ASTM E9 is shown in Figure 6.3. In this

experimental setup three samples of each composition were tested to ensure repeatability. The error bars in Figure 6.3 indicate the standard deviation of the testing results obtained. The results show that compressive strength of the alumina samples improved linearly with increasing nanoparticle densifiers content, from 76 kPa at 0 wt.% to 641.5 kPa at 15 wt.%, which is an increase of over 740%.

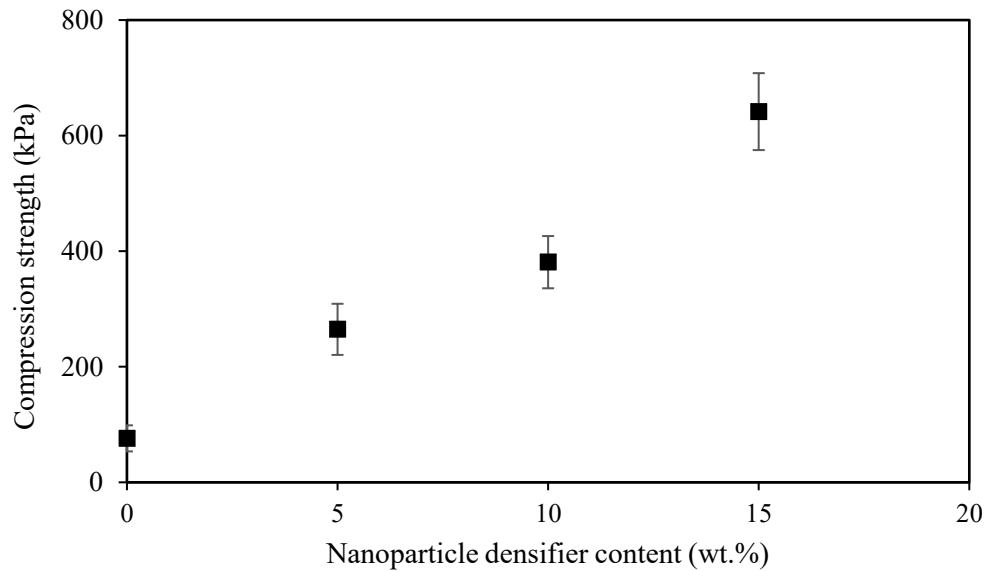


Figure 6.3: Compressive strength of alumina samples as a function of varying nanoparticle densifier content in the printing slurry.

The results of One-way ANOVA analysis are shown in Table 6.3. P -value from statistical analysis was found to be less than $\alpha = 0.05$ determining that the difference in means at each concentration was significant [108]. Using Tukey's HSD method, the Q -value was calculated to be 4.5. As noted in Table 6.4, the pairwise comparisons of the datasets yielded the HSD values to be greater than 4.5, which implied that the differences in compressive strengths were significant.

Table 6.3: One-way ANOVA analysis of data sets in compressive test.

Source of variation	Sum of squares	Degrees of freedom	Mean of squares	F	Probability value (P)	F_{critical}
Between groups	5.2×10^{11}	3	1.7×10^{11}	62.4	6.8×10^{-6}	4.0
Within groups	2.2×10^{10}	8	2.7×10^9			
Total	5.4×10^{11}	11				

Table 6.4: Post hoc analysis of data sets in compressive test.

Comparison (A-B)	HSD
Sample 0% - Sample 5%	5.5
Sample 0% - Sample 10%	10.5
Sample 0% - Sample 15%	18.6
Sample 5% - Sample 10%	5.0
Sample 5% - Sample 15%	13.1
Sample 10% - Sample 15%	8.0

The linearity between the nanoparticle densifier content and compressive strength is shown in Equation 6.2. An R^2 of 978×10^{-3} indicates that the linear regression closely fits the data points.

$$y = 36.2x + 68.9 \quad \text{Equation (6.2)}$$

Compressive strength of a part is dependent on its porosity [109]. Material around pores in sample microstructure has higher stress than the material in the microstructure without pores due to granular arrangement. On the application of compressive forces, due to the granular movement as well as load distribution mechanisms, areas around pores become regions for crack formation [110].

During the application of the uniaxial compressive loads, stresses are formed around the void spaces which are determined from the stress components of compressive

stress. These stress components control the forces that deform voids and cause failure. Jaeger *et al.* showed that at the walls of pores, [111] stresses developed in material microstructure are maximized; away from pore walls, intensity of the stress decays. Therefore, at the pore walls, tensile stresses are concentrated in a direction perpendicular to external compressive loads applied which lead to the development to cracks due shear failure. As porosity increases in the ceramic microstructure, distance between the pores decrease resulting in higher stress concentrations in the material and therefore, the part failure occurs at lower confining stress [110]. The results observed in this work adhere to the theory constructed by Jaegar *et al.* in that samples with low nanoparticle densifier content and high porosity demonstrated lower compressive strength compared to samples with higher densifier content, and correspondingly low porosity. The nanoparticles embedded between the fillers act as load bearing elements in addition to densifying the samples as well as decreasing porosity. The PVA effectively transfers the load from the filler microstructure to the nanoparticles whose large surface area to volume ratio as well as inherent high strength enables them to bear the applied compressive stresses. This is also another contributing reason for increased compressive strength of the slurry-jetted alumina samples at increased nanoparticle densifier concentrations.

Similar improvement in compressive strength with addition of nanoparticles was observed by Fathy *et al.* They made copper composites infused with alumina nanoparticles of an average particle size of 30 nm using a thermo-chemical processing route and showed that as the concentration of alumina nanoparticles was increased from 0 to 12.5 wt.%, compressive strength of their samples was increased from 300 MPa to 650 MPa by about

117% [112]. A study conducted by Assaedi *et al.* to test the mechanical performance of clay nanoparticles infused in geopolymer paste made primarily of fly-ash particles showed that compressive strength was directly proportional to density and inversely proportional to porosity. They demonstrated that the compressive strength of the fly-ash samples increased from 37.2 MPa to 47.9 MPa as the clay nanoparticle concentration increased from 0 to 2 wt.% with a corresponding increase in density from 1.84 g/cm³ to 2.05 g/cm³ while porosity decreased from about 22% to 20% [105].

Relation between bulk density and compressive strength of the slurry jetted samples was studied by plotting a graph between them. Figure 6.4 shows the correlation between bulk density and compressive strength of the slurry-jetted samples. A positive correlation was observed which shows an increase in the compressive strength with increase in the density of the samples. The bulk density is assumed to be homogenous throughout the volume of the synthesized samples. With the addition of the nanoparticle densifiers, for samples of identical heights and cross-sectional areas, the increase in density can be attributed to the improved particle packing per unit cross-sectional area. This results in lower porosities (as discussed earlier in section 6.1), and higher cohesive strength between the powder particles. Consequently, the reduced stress concentrations and improved load transfer capabilities in the substrate aids in improving the compressive strength of the sample.

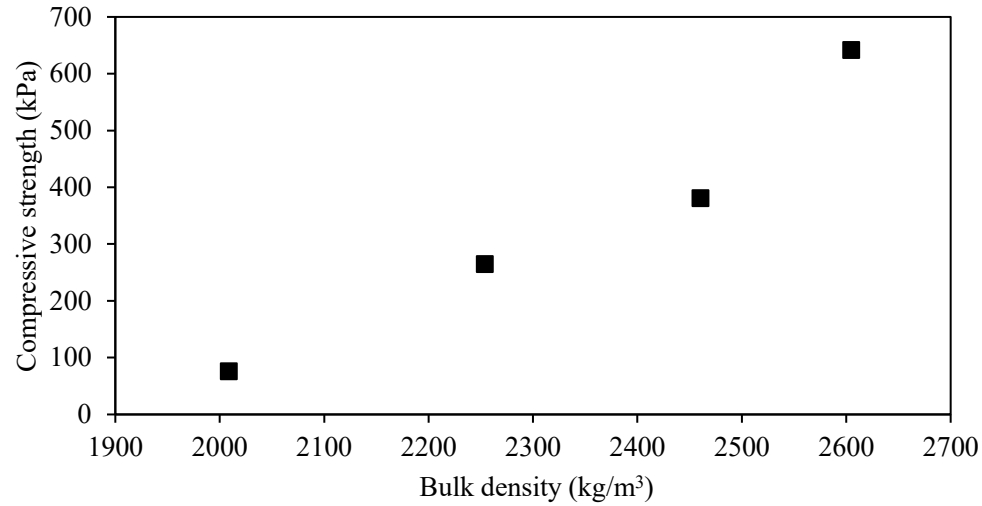


Figure 6.4: Compressive strength of slurry-jetted alumina samples as a function of varying bulk density of the slurry-jetted alumina samples.

6.3.Objective 3: Surface Tension of Printing Slurry with Nano-Densifiers

Table 6.5 presents the printing slurry density as a function of nanoparticle densifier concentration. As anticipated, addition of nanoparticles to the printing slurry increased its density. These values were used in the determination of printing slurry surface tension.

Table 6.5: Density of printing slurry shown with respect to the nanoparticle densifier content.

Printing slurry	Nanoparticle densifier content (wt.%)	Density ρ_{PS} (mg/mL)
PS1	0	1004.7 ± 0.7
PS2	5	1007.0 ± 1.0
PS3	10	1012.7 ± 1.7
PS4	15	1019.7 ± 1.8

Since the printing slurry is to be deposited via an extruder onto the powder layers during SJP, the ease of printing slurry delivery was estimated as a function of nanoparticle

densifier content in terms of surface tension, and correlated to penetration depth of printing slurry in the powder layer. Figure 6.5 shows the variation in surface tension of the printing slurry as a function of nanoparticle densifier concentrations. Surface tension of the printing liquid without nanoparticles was found to be 43.7 mN/m. As the concentration of nanoparticle-densifier was increased from 0 to 15 wt.%, surface tension of the printing slurry (PVA + DI water + alumina nanoparticles) decreased from 43.7mN/m to 22.6 mN/m as shown in Figure 6.5. The error bars in the Figure 6.5 indicate the standard deviation in the test results.

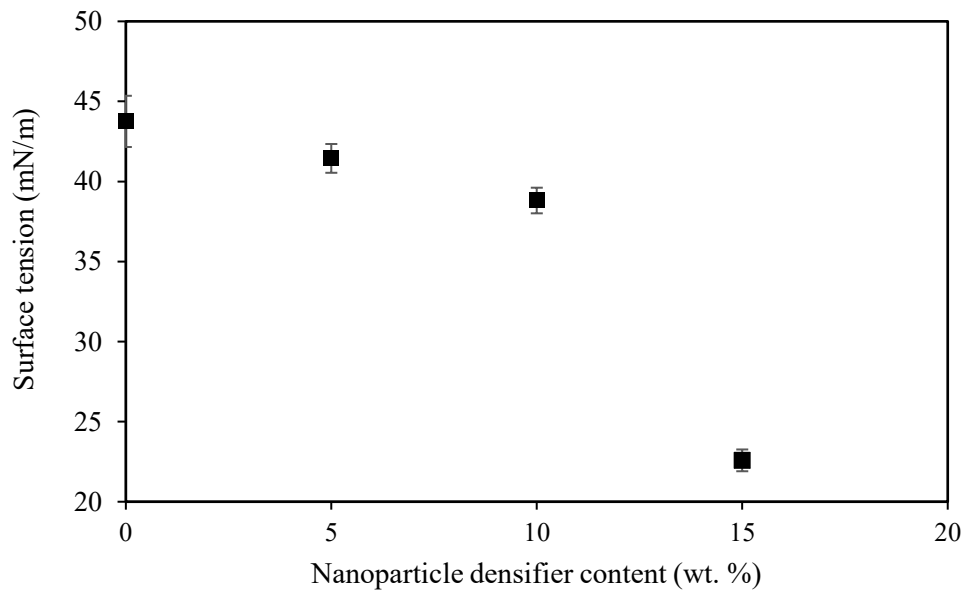


Figure 6.5: Surface tension of printing slurry as a function of varying nanoparticle densifier content.

Surface tension of 10 droplets for each concentration of the densifier was measured which gave a *P*-value less than 0.05 ensuring the difference between the data sets to be significant. One-way ANOVA results are shown in Table 6.6. From Tukey's HSD method,

the calculated Q -value was 3.9. The results from the Tukey's HSD method are shown in Table 6.7. The pairwise comparisons indicated that the difference in surface tension between all the pairs was significant, as their HSD values are all greater than 3.9.

Table 6.6: One-way ANOVA analysis of data sets in surface tension measurement.

Source of variation	Sum of squares	Degrees of freedom	Mean of squares	F	Probability value (P)	F _{critical}
Between groups	2759.5	3	919.8	711.7	4.3×10^{-32}	2.9
Within groups	46.5	36	1.3			
Total	2806.0	39				

Table 6.7: Post hoc analysis of data sets in surface tension measurement.

Comparison (A-B)	HSD
Sample 0% - Sample 5%	6.4
Sample 0% - Sample 10%	13.7
Sample 0% - Sample 15%	58.9
Sample 5% - Sample 10%	7.3
Sample 5% - Sample 15%	52.5
Sample 10% - Sample 15%	45.1

In a droplet, liquid molecules are pulled towards each other equally from all the directions resulting in zero net force. These attractive intermolecular forces are called as cohesive forces [113]. However, liquid molecules present on outer surfaces of droplets are subjected to a predominantly inward pull by the internal molecules. This builds an internal pressure causing a contraction of the molecules to maintain low surface area to minimize surface free energy resulting in surface tension of the droplet [114].

Surface tension is mainly dependent on gravitational force and surface energy forces [115]. The addition of nanoparticles to the printing liquid affects the weight of the droplet as well as its surface energy. The nanoparticle densifiers disrupt the cohesive forces holding the water molecules together, resulting in a decreased surface tension. As the concentration of the nanoparticles in the printing slurry increases, the number of nanoparticles driven towards the liquid-gas interface of the printing slurry droplet increases and consequently, surface tension of the printing slurry decreases.

Zhu *et al.* also observed similar trends in surface tension of slurries containing alumina nanoparticles with an average particle size of 40 nm. As concentration of alumina nanoparticles increased from 0.1 to 0.5 vol.%, surface tension was found to decrease from 63 mN/m to 52 mN/m, which is a total reduction of 19.8% [116]. This was interpreted as a result of the disturbances in the interaction forces in the base fluid layer (water) due to the addition of nanoparticles [116]. Similarly, a decreasing trend in surface tension of alumina nanofluids (10 - 20 nm) was observed by Wang *et al.* as the alumina content in the nanofluid was increased from 2 to 2.5 vol% [117]. Vafaei *et al.* found a decreasing trend in surface tension of slurries with nanoparticles of average size of 2.4 nm with the increasing concentration of bismuth telluride (Bi_2Te_3) nanoparticles from 3.09×10^{-6} to 3.18×10^{-3} g in 1 g of water [118]. A maximum reduction of 50% in surface tension was observed in this work. However, contrary to the present results, the surface tension gradually decreased until it reached a minima at the negative logarithm (concentration) equal to 8.5 and then increased with increasing concentration of the nanoparticles [118]. They hypothesized that a saturation in surface tension was achieved in nanofluids at the minima; the subsequent increase in the nanoparticles concentration develops

dominating van der Waals forces between the nanoparticles, resulting in an increase in the surface energy at gas-liquid interface [118].

In case of powders, Washburn *et al.* [83] theorized the penetration depth achieved by the liquid medium in the powder bodies and is given by Equation 6.3

$$l^2 = \frac{rt\gamma_{lv}\cos\theta}{2\eta} \quad \text{Equation (6.3)}$$

where l is the liquid penetration depth, r is the pore radius of the powder bed, t is the time required for penetration, γ_{lv} is the surface tension of the liquid, θ is the contact angle and, η is the viscosity of the liquid. This implies that the penetration depth of the printing slurry in the SJP process is directly proportional to the interparticle pore radius in the powder bed, surface tension of the printing slurry, time allowed for slurry penetration, cosine of the contact angle, and inversely proportional to the printing slurry viscosity. As discussed in the Literature Review section, alumina is hydrophilic by nature. The pore radius of the filler powder remains constant for a chosen filler particle size distribution in the powder bed. This implies that time to penetration, surface tension of the printing slurry, and its viscosity are the dominant variable factors that control penetration depth. However, during SJP, time to penetration is desired to be as low as possible and is controlled independently. Subsequently, printing slurry viscosity and surface tension remain material properties that majorly influence slurry penetration depth and therefore can be tailored to achieve desired binding between the filler particles and printing efficiency. It was discussed previously in the Literature Review that with the increase in nanoparticle concentration in a base liquid, its viscosity typically increases. Therefore, the combined effect of decreasing surface tension and increasing viscosity of the printing slurry owing to an increase

nanoparticle densifier concentration will lead to a decrease in its penetration depth in a layer of filler particles in the powder bed. Lower penetration depth has been shown to cause improper binding of the filler powder particles; hence concentration of alumina nanoparticle densifiers in the printing slurry, while causing improved mechanical performance of the printed parts, may be seen as a limiting factor for the SJP process. Therefore, it is important to find an optimum nanoparticle concentration in the printing slurry in the design phase such that the surface tension and viscosity of the slurry are ideal for the process to achieve high permeability of the printing slurry through the filler powder layers for improved printing efficiency.

CHAPTER 7: CONCLUSION AND FUTURE WORK

In this research project, a new additive manufacturing process was suggested to synthesize high density green ceramic parts called slurry jetting printing, which resembles binder jetting printing (BJP). Slurry-jetted alumina samples were fabricated using alumina nanoparticle densifiers as inclusions in DI water in the presence of polyvinyl alcohol surfactant, used as the printing slurry. The effect of varying concentration of alumina nanoparticle densifiers in the printing slurry on density, porosity, compressive strength of the slurry-jetted alumina samples was evaluated. As hypothesized, adding alumina nanoparticle densifiers into the printing liquid showed improvement in both density and compressive strength as the concentration of the densifier was increased from 0 to 15 wt.%. At highest densifier concentration of 15 wt.%, the bulk density of the slurry-jetted cylindrical alumina samples was 2605 kg/m^3 with an overall increase of 29.6% compared to samples without nanoparticle densifiers with a density of 2008.8 kg/m^3 . Compressive strength of these samples was measured to be 641.5 kPa which is an overall increase of 740% compared to samples without nanoparticle densifiers whose compressive strength was measured to be 76 kPa. Decrease in porosity in samples without and with nanoparticles from 58.2% to 37.4%, respectively, demonstrated that alumina nanoparticles deposited via the printing slurry may have filled the interparticle void spaces between the filler particles in the powder bed.

Additionally, the effect of the nanoparticle densifier inclusions in printing slurry on the viability of the manufacturing process was examined by measuring the surface tension of the printing slurry with alumina nanoparticles and examining its effect on the penetration

depth of the printing slurry in the filler particle layers in the powder bed during slurry jetting. Results showed that increasing the concentration of alumina nanoparticles in the printing slurry from 0 to 15 wt.% decreased the surface tension from 43.7 mN/m to 22.6 mN/m, which is a decrease by 48.4%. This was attributed to the disruption of the adhesive forces between the DI water molecules by the alumina nanoparticle densifiers added to the printing slurry. Further analysis also showed that owing to this decreasing trend in surface tension, the penetration depth of the printing slurry in a layer of alumina filler particles in the powder bed will be decreasing with increasing alumina nanoparticle densifier content in the printing slurry. These results suggest that the densifier content may be a limiting factor during the design of the slurry jetting process protocol.

The next step in this research is to apply the proposed slurry jetting process using a specially designed inkjet head capable of depositing printing slurries with the observed surface tension values. The parts printed need to be tested for physical (density, porosity and mechanical properties) and microscopic (uniform distribution of the nanoparticle densifiers) properties. Additionally, it may be beneficial to evaluate the effect of using different surfactants on the wettability and surface tension of the printing slurry. Finally, in the future work, it would be interesting to examine if the proposed slurry jetting process may be applied to other material systems such as metals and polymers as well as composites and cermets, in addition to ceramics for making high density green parts.

REFERENCES

- [1] M. M. Subedi, “Ceramics and its Importance,” *Himal. Phys.*, vol. 4, no. 4, pp. 80–82, 2013.
- [2] M. D. Vlajic and V. D. Krstic, “Strength and Machining of Gelcast SIC Ceramics,” *J. Mater. Sci.*, vol. 37, no. 14, pp. 2943–2947, 2002.
- [3] R. Hochsmann and I. Ederer, “Methods and Systems For the Manufacture of Layered Three-Dimensional Forms,” 2010.
- [4] H. Miyanaji, S. Zhang, A. Lassell, A. Zandinejad and L. Yang, “Process Development of Porcelain Ceramic Material with Binder Jetting Process for Dental Applications,” *J. Miner. Met. Mater. Soc.*, vol. 68, no. 3, pp. 831–841, 2016.
- [5] I. Denry and J. R. Kelly, “Emerging Ceramic-based Materials for Dentistry,” *J. Dent. Res.*, vol. 93, no. 12, pp. 1235–42, 2014.
- [6] J. E. Grau, S. A. Uhland, J. Moon, M. J. Cima and E. M. Sachs, “Controlled Cracking of Multilayer Ceramic Bodies,” *J. Am. Ceram. Soc.*, vol. 82, no. 8, pp. 2080–2086, 2004.
- [7] K. Sasaki, “Ohmic Electrode Materials For Semiconductor Ceramics And Semiconductor Ceramics Elements Made Thereof,” 1994.
- [8] J. P. Tyson, “Piezometric Ground Water Pressure Sensing Apparatus,” 2002.
- [9] M. A. Jenny and O. O. Omalete, “Method For Molding Ceramic Powders Using a Water-Based Gel Casting Process,” 1992.
- [10] L. C. Hieu, E. Bohez, J. Vander Sloten, P. Oris, H. N. Phien, E. Vatcharaporn and P. H. Binh, “Design and Manufacturing of Cranioplasty Implants by 3-axis CNC Milling,” *Technol. Heal. Care*, vol. 10, no. 5, pp. 413–423, 2002.
- [11] V. M. Sglavo, S. Maurina, A. Conci, A. Salviati, G. Carturana and G. Cocco, “Bauxite ‘Red Mud’ in the Ceramic Industry. Part 2: Production of Clay-based Ceramics,” *J. Eur. Ceram. Soc.*, vol. 20, no. 3, pp. 245–252, 2000.
- [12] C. R. Deckard, “Method and Apparatus for Producing Parts by Selective Sintering,” 1989.
- [13] K. Weinert, V. Petzoldt and D. Kötter, “Turning and Drilling of NiTi Shape Memory

- Alloys,” *CIRP Ann. - Manuf. Technol.*, vol. 53, no. 1, pp. 65–68, 2004.
- [14] D. Guo, K. Cai, Y. Huang and L.-T. Li, “A Novel Anti-Spatter and Anti-Crack Laser Drilling Technique: Application to Ceramics,” *Appl. Phys. A*, vol. 76, no. 7, pp. 1121–1124, 2003.
 - [15] S. Malkin and T. W. Hwang, “Grinding Mechanisms for Ceramics,” *CIRP Ann. - Manuf. Technol.*, vol. 45, no. 2, pp. 569–580, 1996.
 - [16] N. Umehara and S. Kalpakjian, “Magnetic Fluid Grinding – a New Technique for Finishing Advanced Ceramics,” *CIRP Ann. Manuf. Technol.*, vol. 43, no. 1, pp. 185–188, 1994.
 - [17] S. Indris, D. Bork and P. Heitjans, “Nanocrystalline Oxide Ceramics Prepared by High-Energy Ball Milling,” *J. Mater. Synth. Process.*, vol. 8, no. 3, pp. 245–250, 2000.
 - [18] B. Lauwers, J.-P. Kruth and K. Brans, “Development of Technology and Strategies for the Machining of Ceramic Components by Sinking and Milling EDM,” *CIRP Ann. - Manuf. Technol.*, vol. 56, no. 1, pp. 225–228, 2007.
 - [19] W. Grzesik, “Influence of Tool Wear on Surface Roughness in Hard Turning using Differently Shaped Ceramic Tools,” *Wear*, vol. 265, no. 3–4, pp. 327–335, 2008.
 - [20] K. Uehara and H. Takeshita, “Cutting Ceramics with a Technique of Hot Machining,” *CIRP Ann. - Manuf. Technol.*, vol. 35, no. 1, pp. 55–58, 1986.
 - [21] J. A. Browning, “Hybrid Non-Transferred-Arc Plasma Torch System and Method of Operating Same,” 1985.
 - [22] A. B. Spierings and G. Levy, “Comparison of Density of Stainless Steel 316L Parts Produced with Selective Laser Melting using Different Powder Grades,” *Solid Free. Fabr. Proc.*, pp. 342–353, 2009.
 - [23] M. Castilho, C. Moseke, A. Ewald, U. Gbureck, J. Groll, I. Pires, J. Teßmar and E. Vorndran, “Direct 3D Powder Printing of Biphasic Calcium Phosphate Scaffolds for Substitution of Complex Bone Defects,” *Biofabrication*, vol. 6, no. 1, p. 15006, Mar. 2014.
 - [24] C. L. Ventola, “Medical Applications for 3D Printing: Current and Projected Uses,” *P T*, vol. 39, no. 10, pp. 704–11, 2014.

- [25] S. O. Onuh and Y. Y. Yusuf, "Rapid Prototyping Technology: Applications and Benefits for Rapid Product Development," *J. Intell. Manuf.*, vol. 10, pp. 301–311, 1999.
- [26] R. Noorani, "Rapid Prototyping-Principles and Applications," 2005, p. 400.
- [27] J. Flowers and J. Moniz, "Rapid Prototyping in Technology Education," *Technol. Teach.*, vol. 62, no. 3, p. 7, 2002.
- [28] C. K. Chua, S. M. Chou, S. C. Lin, K. H. Eu and K. F. Lew, "Rapid Prototyping Assisted Surgery Planning," *Int. J. Adv. Manuf. Technol.*, vol. 14, no. 9, pp. 624–630, 1998.
- [29] H. N. Chia and B. M. Wu, "Recent Advances in 3D Printing of Biomaterials," *J. Biol. Eng.*, vol. 9:4, 2015.
- [30] K. V. Wong and A. Hernandez, "A Review of Additive Manufacturing," *ISRN Mech. Eng.*, vol. 2012, pp. 1–10, 2012.
- [31] Y. Dong, S. Q. Fan, Y. Shen, J. X. Yang, P. Yan, Y. P. Chen, J. Li, J. S Guo, X. M. Duan, F. Fang and S. Y. Liu "A Novel Bio-carrier Fabricated Using 3D Printing Technique for Wastewater Treatment," *Sci. Rep.*, vol. 5, pp. 12400, 2015.
- [32] D. Dimitrov, K. Schreve and N. D. Beer, "Advances in Three Dimensional Printing - State of the Art and Future Perspectives," *Rapid Prototyp. J.*, vol. 12, no. 3, pp. 136–147, 2006.
- [33] B. Utela, D. Storti, R. Anderson and M. Ganter, "A Review of Process Development Steps for New Material Systems in Three Dimensional Printing (3DP)," *J. Manuf. Process.*, vol. 10, no. 2, pp. 96–104, 2008.
- [34] Y. Bai and C. B. Williams, "An Exploration of Binder Jetting of Copper," *Rapid Prototyp. J.*, vol. 21, no. 2, pp. 177–185, 2015.
- [35] S. F. S. Shirazi, S. Gharekhani, M. Mehrali, H. Yarmand, H. S. C. Metselaar, N. Adib Kadri and N. A. A. Osman, "A Review on Powder-Based Additive Manufacturing for Tissue Engineering: Selective Laser Sintering and Inkjet 3D Printing," *Sci. Technol. Adv. Mater.*, vol. 16, no. 3, p. 33502, 2015.
- [36] L. T. Bang, S. Ramesh, J. Purbolaksono, B. D. Long, H. Chandran and R. Othman, "Development of a Bone Substitute Material Based on Alpha-Tricalcium Phosphate

- Scaffold Coated with Carbonate,” *Biomed. Mater.*, vol. 10, p. 45011, 2015.
- [37] C. Barnatt, “3D Printing,” <http://explainingthefuture.com/3dprinting.html>, Date of access: 01/19/2017.
- [38] Y. Tang, Y. Zhou, T. Hoff, M. Garon and Y. F. Zhao, “Elastic Modulus of 316 Stainless Steel Lattice Structure Fabricated via Binder Jetting Process,” *Mater. Sci. Technol.*, vol. 32, no. 7, pp. 648–656, 2016.
- [39] N. Guo and M. C. Leu, “Additive Manufacturing: Technology, Applications and Research Needs,” *Frontiers of Mechanical Engineering*, vol. 8, no. 3, pp. 215–243, 2013.
- [40] L. C. D. Jonghe and M. N. Rahaman, “Sintering of Ceramics,” *Handbook of Advanced Ceramics: Materials, Applications, Processing and Properties*, vol. 1–2, pp. 187–264, 2003.
- [41] N. B. Crane, J. W. E. Sachs, S. M. Allen, N. B. Crane and S. M. Allen, “Improving Accuracy of Powder-Based SFF Processes by Metal Deposition from a Nanoparticle Dispersion,” *Rapid Prototyp. J.*, vol. 12, no. 5, pp. 266–274, 2006.
- [42] R. Melcher, S. Martins, N. Travitzky and P. Greil, “Fabrication of Al₂O₃-Based Composites by Indirect 3D-Printing,” *Mater. Lett.*, vol. 60, no. 4, pp. 572–575, 2006.
- [43] Z. C. Cordero, D. H. Siddel, W. H. Peter and A. M. Elliott, “Strengthening of Ferrous Binder Jet 3D Printed Components through Bronze Infiltration,” *Addit. Manuf.*, vol. 15, pp. 87–92, 2017.
- [44] A. Farzadi, M. Solati-Hashjin, M. Asadi-Eydivand and N. A. A. Osman, “Effect of Layer Thickness and Printing Orientation on Mechanical Properties and Dimensional Accuracy of 3D Printed Porous Samples for Bone Tissue Engineering,” *PLoS One*, vol. 9, no. 9, pp. 1–14, 2014.
- [45] C. X. F. Lam, X. M. Mo, S. H. Teoh and D. W. Hutmacher, “Scaffold Development Using 3D Printing with a Starch-Based Polymer,” *Mater. Sci. Eng. C.*, vol. 20, no. 1–2, pp. 49–56, 2002.
- [46] S. Maleksaeedi, H. Eng, F. E. Wiria, T. M. H. Ha and Z. He, “Property Enhancement of 3D-Printed Alumina Ceramics Using Vacuum Infiltration,” *J. Mater. Process. Technol.*, vol. 214, no. 7, pp. 1301–1306, 2014.

- [47] A. Elliott, S. AlSalihi, A. L. Merriman and M. M. Basti, "Infiltration of Nanoparticles into Porous Binder Jet Printed Parts," *Am. J. Eng. Appl. Sci.*, vol. 9, no. 1, pp. 128–133, 2016.
- [48] A. Bailey, A. Merriman, A. Elliott and M. Basti, "Preliminary Testing of Nanoparticle Effectiveness in Binder Jetting Applications," *27th Annual International Solid Freeform Fabrication Symposium*, pp. 1069–1077, 2016.
- [49] J. Suwanprateeb, S. Kerdsook, T. Boonsiri and P. Pratumpong, "Evaluation of Heat Treatment Regimes and their Influences on the Properties of Powder-Printed High-Density Polyethylene Bone Implant," *Polym. Int.*, vol. 60, no. 5, pp. 758–764, 2011.
- [50] R. L. Coble and W. D. Kingery, "Effect of Porosity on Physical Properties of Sintered Alumina," *J. Am. Ceram. Soc.*, vol. 39, no. 11, pp. 377–385, 1956.
- [51] T. Do, C. S. Shin, D. Stetsko, G. Vanconant, A. Vartanian, S. Pei and P. Kwon, "Improving Structural Integrity with Boron-Based Additives for 3D printed 420 Stainless Steel," *Procedia Manuf.*, vol. 1, pp. 263–272, 2015.
- [52] J. G. Bai, K. D. Creehan and H. A. Kuhn, "Inkjet Printable Nanosilver Suspensions for Enhanced Sintering Quality in Rapid Manufacturing," *Nanotechnology*, vol 18, no. 18, 2007.
- [53] V. N. Koparde and P. T. Cummings, "Sintering of Titanium Dioxide Nanoparticles: A Comparison Between Molecular Dynamics and Phenomenological Modeling," *J. Nanoparticle Research*, vol. 10, no. 7, pp. 1169–1182, 2008.
- [54] Jianxin Liu and M. Rynerson, "Method For Article Fabrication Using Carbohydrate Binder," US 6,585,930 B2, 2003.
- [55] J. F. Bredt, T. C. Anderson and D. B. Russel, "Three Dimensional Printing Materials System," US 6,416,850 B1, 2002.
- [56] J. F. Bredt, D. X. Williams, S. L. Clark, M. J. DiCologero, W. B. Shambley and L. Tennenhouse, "Absorbent Fillers For Three-Dimensional Printing," US 2005/0059757 A1, 2005.
- [57] J. F. Bredt and T. Anderson, "Method of Three Dimensional Printing," US 5,902,441, 1999.
- [58] S. Palzer, "Agglomeration of Pharmaceutical, Detergent, Chemical and Food

- Powders- Similarities and Differences of Materials and Processes,” *Powder Technol.*, vol. 206, no. 1–2, pp. 2–17, 2011.
- [59] J. F. Bredt, S. L. Clark, D. X. Williams and M. J. DiCologero, “Thermoplastic Powder Material System For Appearance Models From 3D Printed Systems,” US 7,569,273 B2, 2009.
 - [60] J. Moon, J. E. Grau, V. Knezevic, M. J. Cima and E. M. Sachs, “Ink-jet Printing of Binders for Ceramic Components,” *J. Am. Ceram. Soc.*, vol. 85, no. 4, pp. 755–762, 2002.
 - [61] A. Zocca, P. Colombo, C. M. Gomes and J. Günster, “Additive Manufacturing of Ceramics: Issues, Potentialities, and Opportunities,” *J. Am. Ceram. Soc.*, vol. 98, no. 7, pp. 1983–2001, 2015.
 - [62] J. Yoo, S. Khanuja and M. Rynerson, “Structural Ceramic Components by 3D Printing,” in *Solid Freeform Fabrication Symposium*, pp. 479–488, 1995.
 - [63] C. Wu, W. Fan, Y. Zhou, Y. Luo, M. Gelinsky, J. Chang and Y. Xiao, “3D-Printing of Highly Uniform CaSiO_3 Ceramic Scaffolds: Preparation, Characterization and in vivo Osteogenesis,” *J. Mater. Chem.*, vol. 22, no. 24, pp. 12288, 2012.
 - [64] J. Suwanprateeb, R. Sanngam and T. Panyathanmaporn, “Influence of Raw Powder Preparation Routes on Properties of Hydroxyapatite Fabricated by 3D Printing Technique,” *Mater. Sci. Eng. C.*, vol. 30, no. 4, pp. 610–617, 2010.
 - [65] J. A. Gonzalez, J. Mireles, Y. Lin and R. B. Wicker, “Characterization of Ceramic Components Fabricated Using Binder Jetting Additive Manufacturing Technology,” *Ceram. Int.*, vol. 42, no. 9, pp. 10559–10564, 2016.
 - [66] A. Boczkowska, P. Chabera, A. J. Dolata and M. Dyzia, “Porous Ceramic- Metal Composites Obtained by Infiltration Methods,” *Metallurgija*, vol. 52, no. 3, pp. 345–348, 2013.
 - [67] C. Kawai and A. Yamakawa, “Effect of Porosity and Microstructure on the Strength of Si_3N_4 : Designed Microstructure for High Strength, High Thermal Shock Resistance, and Facile Machining,” *J. Am. Ceram. Soc.*, vol. 80, no. 10, pp. 2705–2708, 2005.
 - [68] K. Groot, “Effect of Porosity and Physicochemical Properties on the Stability,

- Resorption, and Strength of Calcium Phosphate Ceramics,” *Ann. N. Y. Acad. Sci.*, vol. 523, no. 1, pp. 227–233, 1988.
- [69] X. Chen, S. Wu and J. Zhou, “Influence of Porosity on Compressive and Tensile Strength of Cement Mortar,” *Constr. Build. Mater.*, vol. 40, pp. 869–874, 2013.
 - [70] R. L. Coble and W. D. Kingery, “Effect of Porosity on Physical Properties of Sintered Alumina,” *J. Am. Ceram. Soc.*, vol. 39, no. 11, pp. 377–85, 1956.
 - [71] R. Chumnanklang, T. Panyathanmaporn, K. Sitthiseripratip and J. Suwanprateeb, “3D Printing of Hydroxyapatite: Effect of Binder Concentration in Pre-coated Particle on Part Strength,” *Mater. Sci. Eng. C*, vol. 27, no. 4, pp. 914–921, 2007.
 - [72] U. Klammert, T. Reuther, C. Jahn, B. Kraski, A. C. Kübler and U. Gbureck, “Cytocompatibility of Brushite and Monetite Cell Culture Scaffolds Made by Three-Dimensional Powder Printing,” *Acta Biomater.*, vol. 5, no. 2, pp. 727–734, 2009.
 - [73] M. Castilho, B. Gouveia, I. Pires, J. Rodrigues and M. Pereira, “The Role of Shell/Core Saturation Level on the Accuracy and Mechanical Characteristics of Porous Calcium Phosphate Models Produced by 3D Printing,” *Rapid Prototyp. J.*, vol. 21, no. 1, pp. 43–55, 2015.
 - [74] S. Tarafder, W. S. Dernell, A. Bandyopadhyay and S. Bose, “SrO- and MgO-doped Microwave Sintered 3D Printed Tricalcium Phosphate Scaffolds: Mechanical Properties and in vivo Osteogenesis in a Rabbit Model,” *J. Biomed. Mater. Res. - Part B Appl. Biomater.*, vol. 103, no. 3, pp. 679–690, 2015.
 - [75] D. M. Liu, “Influence of Porosity and Pore Size on the Compressive Strength of Porous Hydroxyapatite Ceramic,” *Ceram. Int.*, vol. 23, no. 2, pp. 135–139, 1997.
 - [76] S. M. Gaytan, M. A. Cadena, H. Karim, D. Delfin, Y. Lin, D. Espalin, E. MacDonald and R. B. Wicker, “Fabrication of Barium Titanate by Binder Jetting Additive Manufacturing Technology,” *Ceram. Int.*, vol. 41, no. 5, pp. 6610–6619, 2015.
 - [77] R. Melcher, S. Martins, N. Travitzky and P. Greil, “Fabrication of Al₂O₃-based Composites by Indirect 3D-Printing,” vol. 60, pp. 572–575, 2006.
 - [78] B. D. Kernan, E. M. Sachs, M. A. Oliveira and M. J. Cima, “Three-Dimensional Printing of Tungsten Carbide-10 wt% Cobalt Using a Cobalt Oxide Precursor,” *Int. J. Refract. Met. Hard Mater.*, vol. 25, no. 1, pp. 82–94, 2007.

- [79] A. Kumar, Y. Bai, A. Eklund and C. B. Williams, “Effects of Hot Isostatic Pressing on Copper Parts Fabricated via Binder Jetting,” *Procedia Manuf.*, vol. 10, pp. 935–944, 2017.
- [80] M. Lanzetta and E. Sachs, “Improved Surface Finish in 3D Printing Using Bimodal Powder Distribution,” *Rapid Prototyp. J.*, vol. 9, no. 3, pp. 157–166, 2003.
- [81] N. B. Crane and E. Sachs, “Strengthening Porous Metal Skeletons by Metal Deposition from a Nanoparticle Dispersion,” *Institute of Technology. Dept. of Mechanical Engineering, Massachusetts*, 2006.
- [82] H. P. Zhao, C. S. Ye, Z. T. Fan and Y. N. Shi, “3D Printing of ZrO₂ Ceramic using Nano-zirconia Suspension as a Binder,” *Proc. 2015 4th Int. Conf. Sensors, Meas. Intell. Mater.*, vol. 43, pp. 654–657, 2015.
- [83] E. W. Washburn, “The Dynamics of Capillary Flow,” *Phys. Rev.*, vol. 17, no. 3, pp. 273–283, 1921.
- [84] H. S and P. M, “Methods for Characterizing Wetting and Dispersing of Powder,” *Chemie Ing. Tech.*, vol. 76, no. 4, pp. 385–390, 2004.
- [85] T. J. Webster, C. Ergun, R. H. Doremus, R. W. Siegel and R. Bizios, “Enhanced Functions of Osteoblasts on Nanophase Ceramics,” *Biomaterials*, vol. 21, no. 17, pp. 1803–1810, 2000.
- [86] M. Karlsson, E. Pålsgård, P. R. Wilshaw and L. Di Silvio, “Initial in vitro Interaction of Osteoblasts with Nano-Porous Alumina,” *Biomaterials*, vol. 24, no. 18, pp. 3039–3046, 2003.
- [87] N. Tasaltin, D. Sanli, A. Jonas, A. Kiraz and C. Erkey, “Preparation and Characterization of Superhydrophobic Surfaces based on Hexamethyldisilazane-Modified Nanoporous Alumina,” *Nanoscale Res. Lett.*, vol. 6, pp. 487, 2011.
- [88] W. Al-Shatty, A. M. Lord, S. Alexander and A. R. Barron, “Tunable Surface Properties of Aluminum Oxide Nanoparticles from Highly Hydrophobic to Highly Hydrophilic,” *ACS Omega*, vol. 2, no. 6, pp. 2507–2514, 2017.
- [89] B. Shapiro and E. Wertheimer, “Physical Properties of water,” *MWH’s Water Treat. Princ. Des.*, vol. 231, no. pH 3, pp. 555–556, 1946.
- [90] E. M. M. Ewais, “Rheological Properties of Concentrated Alumina Slurries:

- Influence of pH and Dispersent Agent,” *J. Australas. Ceram. Soc.*, vol. 41, no. 1, pp. 36–43, 2005.
- [91] M. Subbanna, P. C. Kapur and Pradip, “Role of Powder size, Packing, Solid Loading and Dispersion in Colloidal Processing of Ceramics,” *Ceram. Int.*, vol. 28, no. 4, pp. 401–405, 2002.
- [92] L. Palmqvist, O. Lyckfeldt, E. Carlström, P. Davoust, A. Kauppi and K. Holmberg, “Dispersion Mechanisms in Aqueous Alumina Suspensions at High Solids Loadings,” *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 274, no. 1–3, pp. 100–109, 2006.
- [93] M. M, G. K and G. D, “The Influence of Solid Loading in Suspensions of a Submicrometric Alumina Powder on Green and Sintered Pressure Filtrated Samples,” *Ceram. Int.*, vol. 36, no. 1, pp. 385–390, 2010.
- [94] T. Ohji and M. Singh, “Effect of Interparticle Interactions on the Rheology Properties of Paraffin-Wax Suspension,” in *Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials III*, pp. 231, 2009.
- [95] A. R. Harikrishnan, P. Dhar, P. K. Agnihotri and S. Gedupudi, “Effects of Interplay of Nanoparticles, Surfactants and Base Fluid on the Interfacial Tension of Nanocolloids,” pp. 1–31, 2016.
- [96] S. M. Sohel Murshed, S. H. Tan and N. T. Nguyen, “Temperature Dependence of Interfacial Properties and Viscosity of Nanofluids for Droplet-Based Microfluidics,” *J. Phys. D: Appl. Phys.*, vol. 41, no. 8, pp. 85502, 2008.
- [97] S. J. Kim, I. C. Bang, J. Buongiorno and L. W. Hu, “Surface Wettability Change during Pool Boiling of Nanofluids and its Effect on Critical Heat Flux,” *Int. J. Heat Mass Transf.*, vol. 50, no. 19–20, pp. 4105–4116, 2007.
- [98] S. M. S. Murshed, D. Milanova, and R. Kumar, “An Experimental Study of Surface Tension-Dependent Pool Boiling Characteristics of Carbon Nanotubes-Nanofluids,” *ASME 2009 7th International Conference on Nanochannels*, pp. 75–80, 2009.
- [99] M. N. Bello, M. L. Pantoya, K. Kappagantula, W. S. Wang, S. A. Vanapalli, D. J. Irvin and L. M. Wood, “Reaction Dynamics of Rocket Propellant with Magnesium

- Oxide Nanoparticles,” *Energy and Fuels*, vol. 29, no. 9, pp. 6111–6117, 2015.
- [100] S. M. S. Murshed, S. Tan and N. Nguyen, “Temperature Dependence of Interfacial Properties and Viscosity of Nanofluids for Droplet-Based Microfluidics,” *J. Phys. D. Appl. Phys.*, vol. 41, no. 8, pp. 85502, 2008.
- [101] C. E. Stauffer, “The Measurement of Surface Tension by the Pendant Drop Technique,” *J. Phys. Chem.*, vol. 69, no. 6, pp. 1933–1938, 1965.
- [102] W. B. Tucker, “Surface Tension By Pendant Drops,” 1938.
- [103] H. Seltman, “Experimental Design and Analysis,” *Pittsburgh: Carnegie Mellon University* 2015, pp. 428, 2015.
- [104] K. Bodišová, L. Pach, V. Kovár and A. Čerňanský, “Alumina Ceramics Prepared by Pressure Filtration of Alumina Powder Dispersed in Boehmite Sol,” *Ceram. Silikaty*, vol. 50, no. 4, pp. 239–244, 2006.
- [105] H. Assaedi, F. U. A. Shaikh and I. M. Low, “Effect of Nano-clay on Mechanical and Thermal Properties of Geopolymer,” *J. Asian Ceram. Soc.*, vol. 4, no. 1, pp. 19–28, 2016.
- [106] H. Wu, Y. Cheng, W. Liu, R. He, M. Zhou, S. Wu, X. Song and Y. Chen, “Effect of the Particle Size and the Debinding Process on the Density of Alumina Ceramics Fabricated by 3D Printing based on Stereolithography,” *Ceram. Int.*, vol. 42, no. 15, pp. 17290–17294, 2016.
- [107] G. Y. Li, P. M. Wang and X. Zhao, “Mechanical Behavior and Microstructure of Cement Composites Incorporating Surface-Treated Multi-Walled Carbon Nanotubes,” *Carbon N. Y.*, vol. 43, no. 6, pp. 1239–1245, 2005.
- [108] Z. Zhou, F. Buchanan, C. Mitchell, and N. Dunne, “Printability of Calcium Phosphate: Calcium Sulfate Powders for the Application of Tissue Engineered Bone Scaffolds using the 3D Printing Technique,” *Mater. Sci. Eng. C.*, vol. 38, no. 1, pp. 1–10, 2014.
- [109] D. E. Dunn, L. J. LaFountain and R. E. Jackson, “Porosity Dependence and Mechanism of brittle fracture in sandstones,” *J. Geophys. Res.*, vol. 78, no. 14, 1973.
- [110] T. Davis, D. Healy, A. Bubeck and R. Walker, “Stress Concentrations Around Voids in Three Dimensions: The roots of Failure,” *J. Struct. Geol.*, vol. 102, pp. 193–207,

2017.

- [111] J. J. C. N and Z. R, “Fundamentals of Rock Mechanics,” *John Wiley & Sons*, 2007.
- [112] A. Fathy, F. Shehata, M. Abdelhameed and M. Elmahdy, “Compressive and Wear Resistance of Nanometric Alumina Reinforced Copper Matrix Composites,” *Mater. Des.*, vol. 36, pp. 100–107, 2012.
- [113] W. B. Tucker, “Surface Tension By Pendant Drops,” 1938.
- [114] Y. Yuan and T. R. Lee, “Surface Science Techniques,” *Springer Series in Surface Sciences*, vol. 51, 2013.
- [115] C. E. Stauffer, “The Measurement of Surface Tension by the Pendant Drop Technique,” *J. Phys. Chem.*, vol. 69, no. 6, pp. 1933–1938, 1965.
- [116] B. Zhu, W. Zhao, J. Lic, Y. Guan and D. Li, “Thermophysical Properties of Al₂O₃-water Nanofluids,” *Mater. Sci. Forum*, vol. 688, pp. 266–271, 2011.
- [117] Z. Y. Zhou, Q. Q. Di, B. Liu, X. Y. Ma and B. H. Cai, “Experimental Study on the Surface Tension of Al₂O₃-H₂O Nanofluid,” *Mater. Sci. Forum*, vol. 852, pp. 394–400, 2016.
- [118] S. Vafaei, A. Purkayastha, A. Jain, G. Ramanath and T. Borca-Tasciuc, “The Effect of Nanoparticles on the Liquid–Gas Surface Tension of Bi₂Te₃ Nanofluids,” *Nanotechnology*, vol. 20, no. 18, pp. 185702, 2009.

APPENDIX

9.1. Copy Right Clearance for the Figures/Tables of Others Work Used in the Thesis

JOHN WILEY AND SONS LICENSE TERMS AND CONDITIONS	
Jan 09, 2018	
This Agreement between Ohio University -- Pragnya Kunchala ("You") and John Wiley and Sons ("John Wiley and Sons") consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center.	
License Number	4262650057912
License date	Jan 05, 2018
Licensed Content Publisher	John Wiley and Sons
Licensed Content Publication	Journal of the American Ceramic Society
Licensed Content Title	Additive Manufacturing of Ceramics: Issues, Potentialities, and Opportunities
Licensed Content Author	Andrea Zocca, Paolo Colombo, Cynthia M. Gomes, Jens Günster
Licensed Content Date	Jul 14, 2015
Licensed Content Pages	19
Type of use	Dissertation/Thesis
Requestor type	University/Academic
Format	Print and electronic
Portion	Figure/table
Number of figures/tables	1
Original Wiley figure/table number(s)	Figure 5
Will you be translating?	No
Title of your thesis / dissertation	Slurry Jetting Printing of Ceramics with Nanoparticle Densifiers
Expected completion date	Apr 2018
Expected size (number of pages)	65

This Agreement between Ohio University -- Pragnya Kunchala ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4262270045432
License date	Jan 04, 2018
Licensed Content Publisher	Elsevier
Licensed Content Publication	Materials Letters
Licensed Content Title	Fabrication of Al ₂ O ₃ -based composites by indirect 3D-printing
Licensed Content Author	R. Melcher,S. Martins,N. Travitzky,P. Greil
Licensed Content Date	Feb 1, 2006
Licensed Content Volume	60
Licensed Content Issue	4
Licensed Content Pages	4
Start Page	572
End Page	575
Type of Use	reuse in a thesis/dissertation
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Original figure numbers	Figure. 2
Title of your thesis/dissertation	Slurry Jetting Printing of Ceramics with Nanoparticle Densifiers
Expected completion date	Apr 2018
Estimated size (number of pages)	65

This Agreement between Ohio University -- Pragnya Kunchala ("You") and Emerald Publishing Limited ("Emerald Publishing Limited") consists of your license details and the terms and conditions provided by Emerald Publishing Limited and Copyright Clearance Center.

License Number	4264290870009
License date	Jan 08, 2018
Licensed Content Publisher	Emerald Publishing Limited
Licensed Content Publication	Rapid Prototyping Journal
Licensed Content Title	Improved surface finish in 3D printing using bimodal powder distribution
Licensed Content Author	Michele Lanzetta, Emanuel Sachs
Licensed Content Date	Aug 1, 2003
Licensed Content Volume	9
Licensed Content Issue	3
Type of Use	Dissertation/Thesis
Requestor type	Academic
Author of requested content	No
Portion	Figures/table/illustration
Number of figures/tables	1
Will you be translating?	No
Format	Print and electronic
Geographic Rights	World rights
Order Reference Number	
Requestor Location	Ohio University Stocker Center 155 ATHENS, OH 45701 United States Attn: Pragnya Kunchala

Order detail ID:	70896496	Permission Status:	 Granted
ISSN:	0957-4484	Permission type:	Republish or display content
Publication Type:	Journal	Type of use:	Thesis/Dissertation
Volume:		Order License Id:	4262300092333
Issue:		☐ Hide details	
Start page:		Requestor type	Academic institution
Publisher:	IOP Publishing	Format	Print, Electronic
		Portion	chart/graph/table/figure
		Number of charts/graphs/tables/figures	7
		The requesting person/organization	Pragnya Kunchala/Ohio University
		Title or numeric reference of the portion(s)	Figure 7
		Title of the article or chapter the portion is from	Inkjet printable nanosilver suspensions for enhanced sintering quality in rapid manufacturing
		Editor of portion(s)	N/A
		Author of portion(s)	N/A
		Volume of serial or monograph	18
		Issue, if republishing an article from a serial	18
		Page range of portion	Page 4
		Publication date of portion	5 April 2007
		Rights for	Main product
		Duration of use	Life of current edition
		Creation of copies for the disabled	no
		With minor editing privileges	no
		For distribution to	Worldwide
		In the following language(s)	Original language of publication

9.2.Example Calculation for Statistical Analysis of Density Measurement Using One-Way ANOVA Test

Data measured during the density measurements,

k = Number of groups = 4

n = Number of observations in each group = 3

N = Total number of observations from all the groups = 12

Table 9.1: Summary of the data from density measurements.

Groups	Observation 1	Observation 2	Observation 3	Sum	Average	variance
Sample -0 wt. %	52.1	48.4	51.7	152.2	50.7	4.2
Sample -5 wt. %	55.6	57.8	57.3	170.7	56.9	1.3
Sample -10 wt. %	60.6	64.2	61.6	186.4	62.1	3.6
Sample -15 wt. %	69.0	65.3	63.0	197.3	65.8	9.2

$$\bar{X}_{GM} = \frac{50.7 + 56.9 + 62.1 + 65.8}{4} = 58.9$$

$$SS_B = 3 \times ((50.7 - 58.9)^2 + (56.9 - 58.9)^2 + (62.1 - 58.9)^2 + (65.8 - 58.9)^2) \\ = 385.7$$

$$df_B = 4 - 1 = 3$$

$$MS_B = \frac{385.7}{3} = 128.6$$

$$\begin{aligned}
SS_W &= ((52.1 - 50.7)^2 + (48.4 - 50.7)^2 + (51.7 - 50.7)^2 + (55.6 - 56.9)^2 \\
&\quad + (57.8 - 56.9)^2 + (57.3 - 57.0)^2 + (60.6 - 62.1)^2 + (64.2 - 62.1)^2 \\
&\quad + (61.6 - 62.1)^2 + (69.0 - 65.8)^2 + (65.3 - 65.8)^2 + (63.0 - 65.8)^2 \\
&= 36.7
\end{aligned}$$

$$df_w = 12 - 4 = 8$$

$$MS_W = \frac{36.7}{8} = 4.6$$

$$SS_T = 385.7 + 36.7 = 422.3$$

$$F = \frac{128.5}{4.5} = 28.1$$

$F_{critical}$ and P -value were determined from the table of $F_{critical}$ for a critical significance level of $\alpha = 0.05$.

$$F_{critical} = 4.0$$

$$P - value = 135 \times 10^{-6}$$

9.3. Example Calculation for Post Hoc Analysis of Density Measurement Using Tukey's HSD Method

The number of combinations that are possible from 4 groups taken 2 at a time is given by the Equation 4.17.

$$C(4,2) = \frac{4!}{4! \times (4-2)!} = 6$$

Tukey's formula to find the HSD for the used to run the test was given by Equation 4.18.

$$HSD = \frac{\bar{x}_A - \bar{x}_B}{\sqrt{MS_W/n}} \quad \text{Equation (4.18)}$$

where A and B are the 0 % and 5 % wt. datasets that are being compared in this case.

$$HSD = \frac{50.7 - 56.9}{\sqrt{4.6/3}} = 5$$

Q -value obtained from Q table at $\alpha = 0.05$ with k as numerator and df_W as denominator is equal to 4.5. Since the calculated HSD value is greater than the Q -value, it can be concluded that there is significant difference in the averages of the density between the compared pair at a confidence interval of 95%.



OHIO
UNIVERSITY

Thesis and Dissertation Services