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A LITERATURE REVIEW ON ADDITIVE MANUFACTURING OF CERAMIC PARTS PRODUCED BY PASTE EXTRUSION

Luigi Roehrig Segala
Gustavo Peres
Sergio Lucas Santos Rocha
Luciano Zart Olanyk
Lucas Freitas Berti
Neri Volpato
Universidade Tecnológica Federal do Paraná (UTFPR) - R. Dep. Heitor Alencar Furtado, 5000 - Cidade Industrial de Curitiba, Curitiba - PR, 81280-340
segalla@alunos.utfpr.edu.br
gustavoperes@alunos.utfpr.edu.br
srocha@alunos.utfpr.edu.br
olanyk@utfpr.edu.br
lenberti@gmail.com
nvolpato@utfpr.edu.br

Abstract. *Additive manufacturing (AM), also known as 3D printing, is a technology that allows the creation of three-dimensional objects by adding material layer by layer based on a digital 3D model. Among the different technologies of 3D printing available material extrusion technology (MEX) is the most popular because of its simplicity and low cost. This equipment can use different position systems such as the cartesian printing system, which uses a 3D printer with three axes to control the extruder's position. Also, there are different types of raw materials that can be used in MEX technology, such as polymers, ceramics, composites, etc. These materials can be used in different feedstock forms such as filaments, pellets, or paste. By using paste extrusion technology, it is possible to create complex and precise ceramic parts using a 3D printer. This research aims to review this subject in order to find out printed ceramic results with high variability and quality for different purposes. To do so, this review will focus on pastes using ceramics, such as alumina, hydroxyapatite (HAp), and zeolite, and the properties of these ceramics for use in AM, gathering information about the methods of paste production, reagents, additives used, and their benefits to the process. Concerning the desirable printability, this research would clarify if these materials and the process can maintain the filament form, not tear apart during the printing process, and retain its structure during the subsequent steps of ceramic parts production. To conduct this review, it was used R programming language to run the bibliometrix algorithm for selecting articles from the Web of Science and Scopus databases. Following, the articles were filtered using relevant keywords to identify the most appropriate studies. After finishing the review, it was concluded that the materials obtained with alumina, hydroxyapatite, and zeolite are printable using proper reagents and additives to produce the ceramic paste using a piece of specific equipment. This research provides valuable insights into the production of ceramic paste and the factors that influence its printability. Through this knowledge, it will be possible to advance in laboratory practices to produce AM ceramic parts in research activities.*

Keywords: *additive manufacturing, paste extrusion, ceramic paste, hydroxyapatite, alumina*

1. INTRODUCTION

Additive manufacturing (AM), also known as 3D printing and previously referred to as rapid prototyping, is a modern manufacturing method that emerged in the late 1980s. In this process, parts are created by depositing material in successive layers, following a computational geometric model of the desired product. This enables the production of prototypes or functional parts in small batches. Since the creation of 3D printers, additive manufacturing has been increasingly adopted in various sectors of society. One sector that has greatly benefited from this new technology is the medical field, with contemporary examples such as 3D printing of tissues and organs. (Ippolito et al., 1995; Lopes et al., 2018; Volpato, 2017)

Traditional methods of creating porous ceramics encounter numerous challenges when attempting to establish a fully interconnected pore network. These issues include the use of highly toxic organic solvents, inadequate removal of residual particles in the polymer matrix, irregularly shaped pores, limited interconnectivity, and delicate structures. As a result, repeatability suffers, the process becomes time-consuming, and a significant labor force is required. Common approaches such as fiber bonding, solvent casting, particulate leaching, membrane lamination, melt molding, and gas foaming have their limitations. Even with casting or molding techniques, controlling the porosity and pore size of the porous ceramic independently proves to be challenging, further compounded by restrictions on shape control.(Hwa et al., 2017)

In the healthcare and petrochemical industry, porous ceramics play a crucial role due to their unique properties. These materials are widely used for their ability to enhance catalytic efficiency, replicate the porosity of natural systems, and provide suitable surface area, among other benefits. To meet these specific demands, it is necessary to produce complex structures with the appropriate porosity. The conventional shaping of both traditional and advanced ceramics involves a series of steps, from powder processing to shaping using expensive molds or matrices, followed by sintering. These components are often machined to achieve the final dimensions. Currently, three 3D printing processes are being explored for ceramic shaping: stereolithography (SLA), binder jetting, and ceramic paste extrusion.(Biswas et al., 2019; Faccio et al., 2021)

This paper seeks to offer a comprehensive demonstration of the essential steps and precautions needed to facilitate the production of ceramic pieces through additive manufacturing. Additionally, it will explore some of the limitations inherent in the process.

2. CERAMIC PASTE

Ceramic pastes are made of homogeneous and heterogeneous systems containing solids, water and/or additives. They have a plastic behavior that allows for shaping through extrusion or other plastic deformation-based methods. The solids usually consist of a ratio between clays and non-clay materials. The additives might be polymeric plasticizers, which may or may not be added, and/ or inorganic electrolytes. The rheology of pastes can be adjusted by optimizing milling operations or selecting clay components with different levels of plasticity.(Ruscitti et al., 2020)

By utilizing ceramic slurries with specific viscoelastic properties, it becomes possible to manufacture parts that can maintain their original shape regardless of the forces exerted by freshly deposited layers. These slurries typically have a high concentration of ceramic particles, along with carefully selected additives and binders. With this technique, it is now feasible to produce structures of varying configurations, ranging from intricate parts with interconnected cavities to composite materials, solid monolithic components, and filaments with diverse cross-sectional shapes.(Shahzad & Lazoglu, 2021)

It is known that to achieve good results in the extrusion process, attention must be given to the parameters that affect the plasticity of the ceramic paste itself. These parameters include the type of material being extruded, the temperature of the paste during extrusion, the use of additives, the particle size distribution of the ceramic paste, and the moisture content at the beginning of extrusion. These factors influence the final plasticity of the paste and, as commonly said, its greater or lesser extrudability.(Ribeiro, 2021)

2.1 Ceramics

Ceramic materials are known for their hardness, brittleness, and resistance to heat and corrosion.(Bhatia & Sehgal, 2021) Advanced ceramics are a significant technological advancement that has a profound impact on a wide range of industries, sectors, and markets. It is recognized as a transformative technology with the potential to provide valuable solutions for the challenges we face in the future. Broadly speaking, the advanced ceramics sector encompasses some categories:

- Functional ceramics: Electrical and magnetic ceramics
- Structural ceramics: Monoliths and composites.
- Bioceramics: e.g., hydroxyapatite and alumina.
- Ceramic coatings: Oxides, nitrides, carbides, borides, cermets and diamond-like coatings, deposited by technologies such as spraying, vapour deposition, and sol–gel coating.
- Special glasses: Processed flat glass, fire-resistant glazing, and glasses for optoelectronics.

(Rödel et al., 2009)

Most part of the ceramic powders used in fabrication process can be found at commercial sources. Another way to obtain these materials is through a powder synthesis, which can be either mechanical or chemical. The mechanical synthesis consists mainly of the reduction in size of granular material, using grinding or milling steps. The chemical is generally more expensive than the mechanical synthesis, but it gives an unprecedented level of control over the powder characteristics, such as the size distribution as seen at Figure 1. Other characteristics of great relevance for the process are the particle size, shape, degree of agglomeration and purity.(Rahaman, 1995)

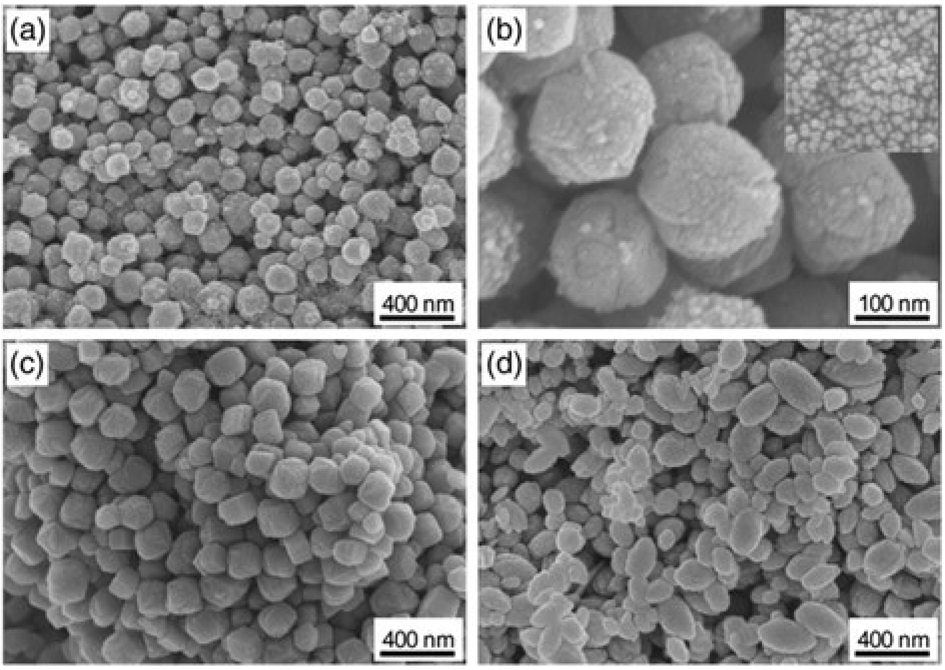

Figure 1. An example of hematite nanoparticles with different morphologies synthesized by chemical precipitation(Supattarasakda et al., 2013)

2.2 Binders

The binders are usually multi-component systems and consist of two main components. The first one being called backbone, a thermoplastic polymer that will keep the part's shape until the debinding phase. As examples it may be mentioned polyethylene (PE), polypropylene (PP) and polymethyl methacrylate (PMMA). The later component is normally a wax such as paraffin or carnauba wax, used in a similar proportion to the backbone it can improve the material flowability. Other than this improvement, the wax also may be removed early on in the debinding phase, leaving pores that will allow the diffusion of the gaseous products of the remaining polymer.(González-Gutiérrez et al., 2012)

2.3 Additives

Additives are optional components that may or may not be added to the paste depending on the paste rheology, process requirements, and properties needed in the final part. The additives may be used as plasticizers, dispersants, gelation agents, lubricants and add necessary properties on specific extrusion methods, such as the prevention of elongated ice crystals that may occur during the freeze-form extrusion method. A few of the additives used in paste production are the poly (ethylene glycol) (PEG), used as a plasticizer(Lu et al., 2009), carboxymethyl cellulose (CMC), as a multifunctional processing additive (dispersant, binder and gelation agent)(Ben-Arfa et al., 2019) and Darvan C, a high molecular weight ammonium polymethacrylate solution, used as dispersant(Huang et al., 2009). There are also additives that help other steps of the process than the extrusion, one of them being MgO, which can be used as an Al_2O_3 sintering aid.(Huang et al., 2009; Ruscitti et al., 2020)

2.4 Solvents

The solvents are liquids that mainly provide fluidity for the powder during the process and allow for additives to be homogeneously incorporated into the ceramic powder. The solubility of the solid part into the liquid in most of the cases is enhanced when both parts have similar function group or molecular polarity. There are two basic choices for the solvent, water and an organic liquid, and seven characteristics relevant upon choosing them:

- Ability to dissolve the used additives
- Evaporation rate
- Ability to wet the powder
- Viscosity
- Reactivity to the powder
- Safety
- Cost

(Rahaman, 1995)

3. PASTE PREPARATION

The preparation of the paste consists basically of combining the ceramic powder of adequate particle size, at least one order magnitude smaller than the final part resolution, with the binder and the necessary additives in deionized water. The pastes must be blended and mixed until it is homogenous, usually done in tumbler mixers or manually, in order to achieve homogeneity, the ceramic powder can be gradually added to the solution or add an acid to the solution to facilitate mixing. After that, is done the removal of agglomerates and air bubbles in order to keep the printing controlled.(Ben-Arfa et al., 2019; Shahzad & Lazoglu, 2021; Tang et al., 2019)

One of the most important characteristics to check is the paste rheology, as it impacts greatly at the printing quality. There are a few ways of adjusting it, from changing or refining the materials used to the change of the pH, one commonly used method is changing the water proportion.(Huang et al., 2009; Ruscitti et al., 2020)

4. PASTE EXTRUSION

The paste extrusion is a method of material extrusion (MEX), which is defined by ISO/ATSM 52900(2021) as a process where the material is selectively extruded through a nozzle. There are several paste extrusion techniques such as Direct Ink Writing (DIW), solid freeform fabrication (SFF), paste deposition modeling (PDM), and robocasting (RC). This method extrudes the material through a nozzle, depositing the material that will form the part at the printer bed, as shown in Figure 2, layer by layer until the part is complete.(Mata, 2022; Ruscitti et al., 2020; Zein et al., 2002)

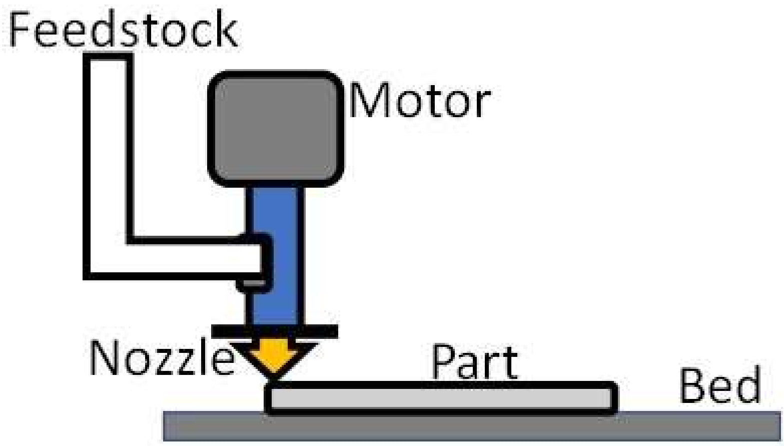

Figure 2. Schematic Representation of DIW printing technique adapted from (Mata, 2022)

The movements made by the printer head and the extruder are predetermined by a G code made based on a digital three-dimensional model. In order to fully prepare the code, it is also necessary to define all the printing parameters, such as feed rate, extrusion head speed, layer height, and others. (Volpato, 2017)

There are several types of extrusion heads for 3D printers, but most of them don't work with pastes, for this feedstock state are used only two types of single-step heads, the pneumatic piston and the mechanic piston, alongside these are the hybrid extrusion heads, as seen on Figure 3, that combines more than one type of extrusion method to fabricate the parts.

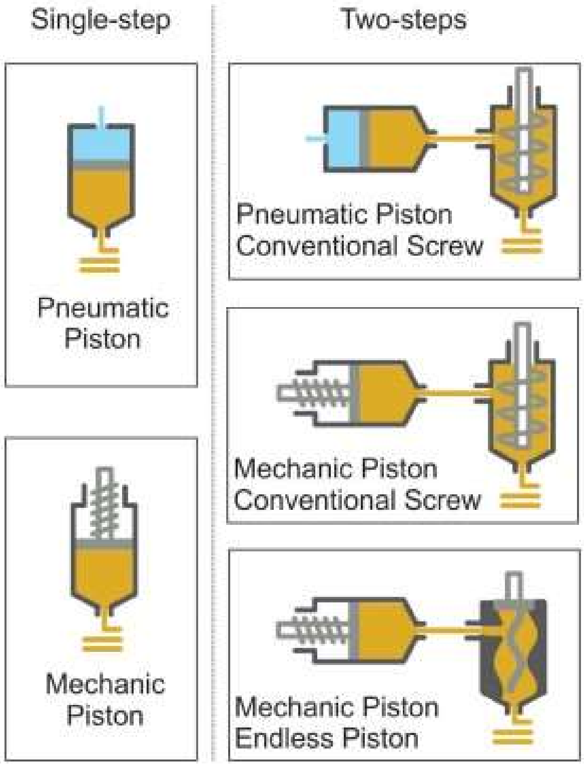

Figure 3. Classification of extrusion heads (Ruscitti et al., 2020)

5. POST PROCESS

The two main steps of the post-processing of the ceramic parts made by additive manufacturing are the debinding and the sintering, the first one aims at the removal of the binders used in the process so that it doesn't interfere during the sintering of the part. There are three main ways to proceed with the debinding process, the thermal, where the printed part is slowly heated until it reaches the binder melting or degradation temperature, in the solvent or chemical debinding, the binder is dissolute and the catalytic debinding depolymerizes the binder through the heating of the green part in a controlled atmosphere including a catalyst.(González-Gutiérrez et al., 2012)

Most of the ceramic parts need to be sintered before they can be used, this step consists of heating the green part until it reaches 70 to 90% of the melting point of the ceramic. At this temperature it starts the recrystallization process, which will transform the ceramic powder into a bulk material, giving the part its required properties to be used as a final part. During this process, the material can become porous, shrink, and suffer chemical changes on the surface particles.(González-Gutiérrez et al., 2012; Rahaman, 1995)

6. RESULTS

Xu et al. (2022) produced ceramic parts using an air-driven fluid dispenser and various powder/liquid ratios, showing the importance of finding the adequate proportion for your materials. The powder was an alumina-based (mean particle size of 80-200 nm) mixture in a mass ratio of Al_2O_3:TiO_3:CuO=95:5:1, while the liquid used was a binder solution produced via a reaction of 103.674 g of 85 % H_3PO_4 (diluted to 60 %), and 23.88 g $Al(OH)_3$. The pastes had four different solid contents, 45, 50, 55, and 58 wt%, from which only the last resulted in a functional paste for 3D printing, as the others did not support the superior layers and failed to make 3D structures.

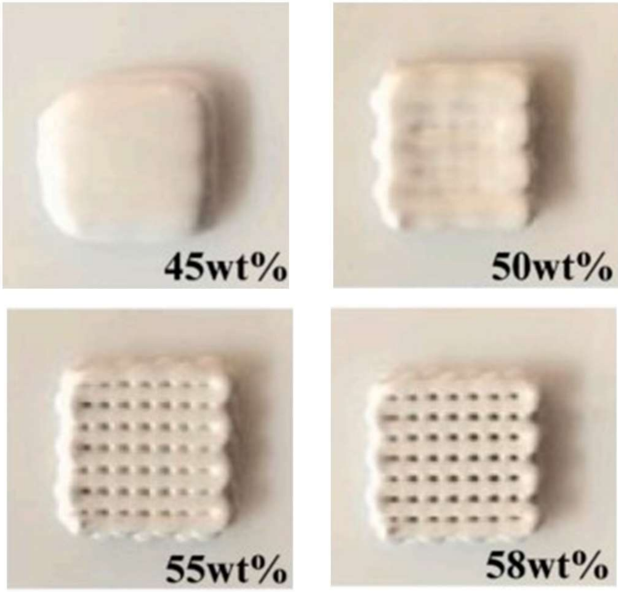

Figure 4. Ceramic parts printed using different solid contents (Xu et al., 2022)

With a two-step printer head, Figure 5, Finke et al. (2020) printed ceramic parts using a paste in which the solids contents reached 81 wt% of alumina powder (mean particle size of 2.5 µm), with the aid of a stabilizing agent, nitric acid at 1 wt%.

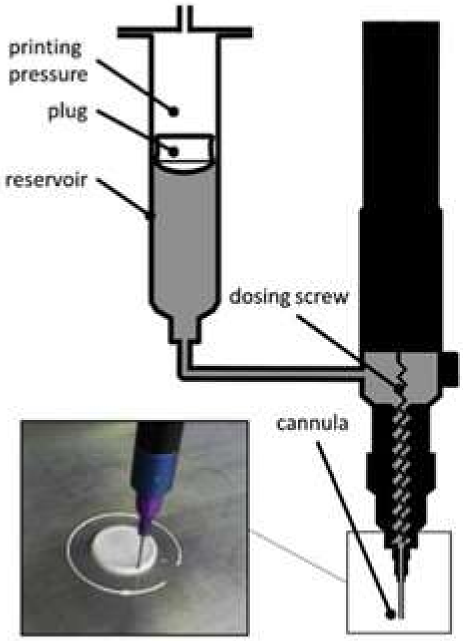

Figure 5. Two-step printer head (Finke et al., 2020)

Figure 6. Cube-shaped test specimen (Finke et al., 2020)

These results indicate the high variability of the process of 3D printing ceramic parts and the impacts of the materials used in the paste production.

7. CONCLUSION

In conclusion, this paper demonstrates that additive manufacturing holds a promising potential in producing ceramic parts. While this technique offers the possibility of manufacturing high-quality components and brings advantages such as high variability in the produced parts and low material waste, one must also consider that it involves several steps, the time-consuming nature of the process, and necessitates careful consideration of various variables and the high variability they bring to the paste characteristics, such as the difference caused in the paste rheology by minor changes in the materials used, being it changing the material, the ratio or even the particle size.

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9. RESPONSIBILITY NOTICE

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