PROSPECTS FOR USING 3D PRINTING TO FORM CERAMIC MEMBRANES: A BRIEF REVIEW

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The article presents a discussion of the potential applications of 3D printing in the formation of ceramic membranes. In recent years, additive technologies for ceramic materials have become a prominent area of research, suggesting that they can be effectively employed to design and produce hierarchical porous ceramic structures, combining flexible design and advanced approaches to their formation. The objective of this paper is to analyse the potential of additive technologies for the production of ceramic membranes, identify the most promising technologies, and provide a comprehensive evaluation of their achievements, challenges, and limitations. The present study considers seven principal additive manufacturing processes, which are based on the utilization of diverse 3D printing technologies. It is demonstrated that the most promising technologies for the manufacture of ceramic membranes are currently Vat Photopolymerisation, which enables the production of products with complex geometry and high accuracy, and those that utilize Powder Bed Fusion processes, which ensures the mechanical strength and density of ceramic products. The article presents an analysis of the printing parameters of Stereolithography, Liquid Crystal Display and Selective Laser Sintering technologies, and their potential for the production of ceramic products in general and membranes in particular. The problems and challenges of creating ceramic membranes by 3D printing, such as optimization of the composition of ceramic suspensions and post-processing of products, are noted. Possible ways to solve them are discussed, including the improvement of printing materials and technological processes. The prospects for the use of the obtained ceramic membranes in various industries are also considered. The directions of further research aimed at improving additive technologies for printing ceramic membranes and expanding their application in industry are identified.

Keywords: additive technologies, ceramic membranes, 3D printing, Liquid Crystal Display technology, microstructure, Stereolithography technology, Selective Laser Sintering technology.

dimensional printing in the production of ceramic products has the potential to overcome these limitations. It has been demonstrated that additive technologies facilitate the production of products with highly complex internal and external geometries (Chen et al., 2019), which were previously either unfeasible or economically infeasible. This presents an opportunity for the development of new products with enhanced properties and functions.

In recent years, 3D printing technique of ceramic materials has become a focus of research, with successful applications in the design and production of hierarchical porous structures through the combination of flexible design and advanced manufacturing procedures (Prabhakar et al., 2020).

It has been reported (Issac et al., 2020) that 3D printing, also known as additive technology, has the capacity to create a wide range of complex geometric shapes of varying sizes and scales through a process of layer-by-layer moulding. Consequently, 3D printing of three-dimensional ceramics, which is both lightweight and highly durable, is currently regarded as a revolutionary and attractive tool for the formation of 3D porous ceramics, offering high accuracy and manoeuvrability of any complex structure.

In recent years, 3D printing has significantly expanded its capabilities and applications. Initially focused on polymers, this technology is already being actively implemented in the production of ceramic products (Ngo et al., 2018; Wang et al., 2024).

One illustrative example of the utilization of 3D-printed ceramics is the fabrication of biomedical implants, including dental prostheses and bone substitutes. The high precision and capacity for the creation of complex porous structures afforded by 3D printing facilitate the production of implants that promote osseointegration and enhance the effectiveness of treatment (Zhang et al., 2018). In the aerospace industry, ceramic components printed on 3D printer are employed in the fabrication of parts capable of withstanding elevated temperatures and exhibiting high strength, including heat shields and engine components (Zocca et al., 2015). In the energy sector, 3D printing of ceramics is employed to fabricate components for solid oxide fuel cells and batteries, which exhibit enhanced performance due to optimised porosity and geometry (Cramer et al., 2022). Furthermore, ceramic filters and catalysts produced via 3D printing are employed in the chemical and petrochemical industries to enhance process efficiency and curtail pollutant emissions (Wang et al., 2019).

One of the most promising applications of 3D-printed ceramics is the manufacture of ceramic membranes. Ceramic membranes are employed extensively in filtration processes, gas and liquid separation, as well as in catalysis and sensor technologies. Their properties, including high thermal and chemical resistance, render them suitable for deployment in extreme conditions where polymeric membranes are unable to function (Chen et al., 2023; Sreedhar et al., 2023).

The traditional methods of manufacturing ceramic membranes lack the precision required to control porosity and pore structure, which in turn affects the performance of the membranes and limits their use in specialised processes (Wang et al., 2024). The utilization of 3D printing technology enables the precise manipulation of the microstructure of membranes,

allowing for the control of pore size, shape and distribution. This ensures the creation of membranes with optimised characteristics for specific applications (Chen et al., 2024; Hwa et al., 2017). Moreover, the optimisation of filtration process performance and energy efficiency hinges on the design of ceramic membranes that can enhance their transportation characteristics. The utilization of 3D printer to create membranes with precisely positioned apertures and shapes facilitates the enhanced transportation and flow of liquid or gaseous media along the membrane surface, while concurrently reducing membrane fouling (Ngo et al., 2018).

The prospects for utilizing threedimensional printing in the fabrication of ceramic membranes encompass several potential benefits, including the capacity for individualised membrane design (Zeng et al., 2022), increased membrane performance (Mei et al., 2021), reduced production costs (Chen et al., 2024), and functionalization (Hwa et al., 2017). The capacity to fabricate membranes with unique geometries (design customisation) is a highly demanded attribute in specific applications, such as medical and biotechnology, where highly specialised solutions are often required. The precise control of porosity allows for the optimisation of the flow of liquids or gases through the membrane, thus increasing the efficiency of filtration and/or separation processes. This results in improved productivity. Additive technologies typically reduce production costs by reducing material waste and prototyping time, and allow for the combination of multiple functions in one product (cross-functional integration). For example, in the case of photocatalytic or gassensitive membranes, in addition to their filtering function, the membranes also have photocatalytic and analytical functions, respectively.

Despite the already significant advantages of 3D printing of ceramic materials, researchers face a number of challenges in the implementation of their 3D printing, including the need to improve materials intended for additive technologies and optimise sintering processes (He et al., 2023; Lakhdar et al., 2021), given that ceramic materials have high melting points. To guarantee the integrity and quality of the printed products, it is essential to exercise meticulous control over the sintering process, encompassing the precise calibration of the temperature profile, holding time, heating and cooling rates, and sintering atmosphere. Inconsistencies in these parameters can result in the formation of defects, including cracks, deformation, porosity, and internal stresses. These defects have a detrimental impact on the mechanical properties and durability of the final products (Chen et al., 2024). It is therefore evident that optimisation of the sintering process represents a crucial and pivotal stage in the production of highquality ceramic products via 3D printing.

The steady progress being made in this area provides a promising indication that these and other obstacles will be overcome in the near future.

Furthermore, it is important to note that in the context of global challenges, such as environmental pollution and the need for efficient use of resources, ceramic membranes produced through 3D printing can play a pivotal role. The utilisation of these membranes will facilitate the development of more efficient and sustainable solutions for water purification, emission control and waste treatment (Wang et al., 2022; Kim et al., 2023). The application of 3D printing to ceramic products will also contribute to the development of new materials and their compositions. The incorporation of diverse components into ceramic compositions, including metal nanoparticles and carbon nanotubes, enhances the mechanical, electrical, and thermal properties of the resulting material (Han et al., 2023). Consequently, 3D printing of ceramic products represents an innovative direction that will facilitate the production of ceramic membranes with improved characteristics, opening up new opportunities for industry and science to meet the needs of modern society.

The objective of this paper is to

examine the potential of additive technologies for the production of ceramic membranes, identify the most promising technologies, and conduct a comprehensive analysis of their achievements and challenges.

2. Analysis of additive technologies for the production of ceramic membranes

The ISO/ASTM 52900:2021 (International standart, 2021) standard identifies seven principal additive manufacturing processes, each of which is accompanied by a distinct printing technology (Fig. 1).

Fig. 1. The main technologies of additive manufacturing

The fundamental principles of the processes may vary depending on the specific type of 3D printing technology employed, with each technology exhibiting distinctive advantages and disadvantages.

Binder Jetting (BJ) process offers several advantages, including rapid production times and cost-effectiveness of the equipment. Additionally, the model does not require supporting structures during printing, which is a notable benefit (Sarila et al., 2024). However, the resulting parts are characterised by low mechanical strength and high porosity, necessitating additional sintering steps that can potentially result in shrinkage.

Material jetting (MJ) represents a further additive manufacturing process that offers high levels of application accuracy and the capacity to print with multiple materials. This enables the creation of prototypes and parts with complex geometries. Nevertheless, the high cost of the equipment and the difficulties encountered in ensuring the uniform distribution of ceramic particles in the ink restrict the applicability of this technology for mass production (Ly et al., 2022).

The main advantage of Vat Photopolymerisation (VP) process is its capacity to produce models of high print accuracy and resolution, which renders this method particularly well-suited to the production of microstructured parts, such as medical implants and membranes. Concurrently, the process requires expensive photopolymers, meticulous research into the rheological behaviour of the ceramic slurry particles and control of its viscosity, and careful post-treatment of the wash waste to remove resin (Dommati et al., 2019).

Directed Energy Deposition (DED) process allows the rapid and accurate manufacture of dense and durable ceramic parts of large dimensions and complex geometries, which is an advantage for metalceramic composites. However, when working with ceramics, the process has the disadvantage of high temperature gradients which can cause cracking and deformation (Fan et al., 2024).

Powder Bed Fusion (PBF) process offers high resolution, which enables high quality printed design, resulting in dense and strong parts with complex geometries, which is an advantage for functional components. However, the production of ceramic products is challenging due to the high temperature

conditions, which can cause the powder itself to stick together, making it difficult to reuse and contributing to the formation of defects in printed parts. In addition, the process requires sophisticated and expensive equipment and is associated with high power consumption (Singh et al., 2019; Abdelkader et al., 2024).

An affordable and simple 3D printing process is Material Extrusion (ME), which has the advantage of being able to use pastes with high ceramic powder content. However, despite its cost-effectiveness, this method has limited accuracy and resolution and requires a thorough study of paste particle rheology and viscosity control, making it suitable for the production of simpler structural elements (Rouf et al., 2022).

Sheet Lamination (SL) is also characterised as a simple and relatively inexpensive method suitable for the manufacture of large components with a structure where layers are bonded, i.e. laminated. However, it is limited in its ability to produce parts with complex geometry and high precision, resulting in potential delamination problems and poor part surface quality (Bose et al., 2024).

Therefore, taking into account the advantages, disadvantages and conditions of the processes, the most promising technologies for the production of high-quality ceramic products, namely ceramic membranes, are currently Vat Photopolymerisation, which allows the production of products with complex geometry and high precision, and those using Powder Bed Fusion processes, which ensure the mechanical strength and density of ceramic products.

3. SLA technology

Stereolithography (SLA) is one of the most widely used technologies for printing ceramic products, particularly membranes, and belongs to the photopolymerisation (VP) process, which takes place under the influence of ultraviolet radiation emitted by a laser. To do this, the working suspension is placed in a tank with a platform for building the future shape, where the laser beam is directed and reflected by a scanning mirror (Abdelkaber et al., 2024). When exposed to ultraviolet rays, the process of light-activated polymerisation takes place, selectively curing the material from point to point, layer by layer. The printer utilizing additive SLA technology was the first to produce porous ceramics with intricate shapes in the form of a series of porous cells with complex shapes, including micro-lattices, honeycombs, micro-scale trusses and convex structures, among others.

One of the most significant advantages of SLA method is the production of components with a high resolution of up to micrometres (Schmid, 2024), resulting in a smooth surface. Furthermore, the superior quality of printing enables the intricate structural features of the membranes to be crafted with greater precision, which is crucial for attaining the desired porosity. SLA also has an advantage over other technologies in terms of economic feasibility and speed (Deshmane et al., 2021). For example, in (Pechlivani et al., 2023) the printing of ceramic membranes based on SLA technology was considered for further use in the process of gas purification and separation. According to the study, a suspension containing a photopolymer resin with silicon oxide nanoparticles $(SiO₂)$ was used for the 3D printing of ceramic structures. The printing process was performed by stereolithography on a Formlabs Form 2 printer at a temperature of 35°C, with a layer thickness of 50 µm, which allowed to obtain high quality parts. After printing, the samples were heat treated at different temperatures: 450°C, 600°C and 1250°C. The study showed that an increase in temperature treatment contributes to a more homogeneous sample structure with high crystallinity and developed porosity. In another study (Chevarin et al., 2023), tubular ceramic membranes were fabricated using aluminium alpha-oxide (average particle size: 1.75 µm) mixed with a photopolymer resin. Membranes printed from this suspension with a thickness of 1.5 mm were sintered at temperatures above 1200°C, which ensured the stability of the membrane microstructure. The analysis showed that the average pore size of the membranes was about 0.2μ m, the porosity was 33% and the specific surface area was $2.5 \text{ m}^2/\text{g}$, making them suitable for use in microfiltration.

4. LCD technology

Liquid crystal display (LCD) technology has become a prevalent form of display technology in the field of additive manufacturing. Similarly, LCD 3D printing is founded upon photopolymerisation (PV) processes, as is SLA technology. The principal distinction between LCD and SLA technology lies in the utilization of an alternative light source within the printer structure. The radiation source is constituted by an array of light-emitting diodes (LEDs) that collectively comprise the LED matrix. The printer structure comprises a reservoir, a liquid crystal display with an LED matrix, a support that moves the build platform in the direction of the OZ axis, and the build platform itself, on which the printed part is fixed. The reservoir, which is placed on the surface of the transparent film,

serves as a transmissive layer for the passage of UV radiation and thus constitutes an intermediate layer between the LCD screen itself and the photopolymer suspension solution (Dommati et al., 2019).

The cost of LCD 3D printing technology is significantly lower than that of other technologies, due to the possibility of using cheaper light source systems. However, this technology provides high precision and has a larger moulding format, which facilitates its use in industrial production. The economic advantage and the absence of the need for optical systems make it possible to achieve large-format production of ceramic products (Wu et al.,2024).

The primary stage of the printing process for ceramic products is the preparation of the raw materials, which consist of photopolymer resin, ceramic powder, and other auxiliary reagents. The selection of these materials has a significant impact on the properties of the final product. The selection of an appropriate composition, taking into account the physical and chemical properties of the components, is a crucial factor influencing the quality of the printed part. The ratio of components in ceramic suspensions must be selected in a manner that avoids overloading during printing. It is essential to ensure the homogeneous and effective dispersion of the ceramic powder in the resin to guarantee the long-term stability and viscosity of the suspension (Chen et al., 2019).

For example, researchers in (Wu et al., 2024) employed LCD technology to print ceramic products based on zirconium (IV) oxide. The study revealed that the photopolymer resin was manufactured using 2,4,6-trimethylbenzoyl-diphenylphosphine oxide, polyethylene glycol diacrylate, 1,6 hexanediol diacrylate, and trimethylolpropane triacrylate. Additionally, zirconium (IV) oxide, stabilised with 3% (mol) yttrium oxide (3Y-TZP) and with an average particle size of 0.3 µm, was employed as the ceramic powder. Subsequently, the printed ceramics were subjected to a heat treatment. Initially, they were heated to 1000°C, then to 1480°C for a period of three hours, in order to attain the requisite density. The resulting zirconia ceramic exhibited high quality characteristics, with solid content of 72.5%, a bending strength of 255 MPa, and a relative density of 98.1%.

Paper (Chen et al., 2024) explored the potential of printing ceramic membranes using LCD technology, with the introduction of titanium (IV) oxide nanoparticles into the ceramic component. The objective of incorporating titanium (IV) oxide nanoparticles was to facilitate the sintering of aluminium oxide nanoparticles. This resulted in enhanced interparticle bonding, which led to an improvement in the permeability and strength of the ceramic membrane matrices (support). The resulting membrane matrix exhibited a pore size of approximately 1.36 µm, a porosity of 42%, and a permeability to pure water of $3700 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$.

5. SLS technology

Selective laser sintering (SLS technology) represents a specific type of three-dimensional printing that enables the creation of robust and durable products. This technology is based on the sintering of powdered materials with a laser beam, thereby creating three-dimensional objects (PBF process). The process begins with the application of a thin layer of powder to the work platform. The laser selectively sinterises the powder particles in accordance with the digital model, depositing them in the areas that correspond to the cross-section of the object in question. Once a layer has been sintered, the platform is lowered and a subsequent layer of powder is applied. This process is repeated until the object has been fully formed (Xing et al., 2013).

Due to its high precision and the capacity to create complex geometric shapes without the necessity for supporting structures, SLS technology has a wide range of capabilities and is employed in a variety of industries. The absence of the necessity to create additional support structures during the printing process simplifies the production process and reduces material consumption (Wang et al., 2024). This feature renders this technology especially efficacious in areas where the intricacy and complexity of structures are paramount, such as medicine, engineering, and the fabrication of ceramic membranes. In the field of prototyping and design, SLS technology enables the rapid production of functional models and prototypes, thereby notably reducing the time required to develop new products. This technology has gained particular attention in the fields of medicine and dentistry, where it is used for the production of bespoke implants, orthopaedic devices and dental models. This has the effect of improving the quality and accuracy of medical devices (Awad et al., 2020). Furthermore, SLS technology enables the fabrication of intricate components for robotics and the automotive industry, where the precision and structural integrity of products are of paramount importance (Gao et al., 2008).

It is of particular interest to consider the potential of using SLS technology to create ceramic membranes. Although this technology was originally developed for the production of products from polymer powders, its subsequent evolution has opened

up prospects for printing ceramic materials. The utilization of 3D SLS technology for the fabrication of ceramic membranes enables the generation of a sophisticated porous structure, thereby enhancing their functional attributes and performance (Dommati et al., 2019). However, there are also disadvantages, such as a limited choice of materials, which can present a challenge for certain applications. Furthermore, the use of ceramic printing requires the availability of specialised materials and set-ups, which can be complex and require additional investment (Xing et al., 2013).

6. Problems and challenges of creating ceramic membranes by 3D printing and their solutions

The development of three-dimensional printing technology for ceramic materials, in particular membranes, is resulting in ongoing enhancements to the printing process, including improvements in accuracy, speed, the size of printed materials, and other characteristics. Furthermore, the types and structures of the ceramic materials produced are also undergoing constant improvement. Nevertheless, the application of 3D printing technology in the field of ceramic membranes is still in its infancy, and as a result, there are numerous challenges to be overcome in the printing process itself, as well as in the selection of materials, the justification of the economic component and the assessment of the environmental impact (Chen et al., 2023).

The principal challenge in the production of ceramic items is the incorporation of a ceramic component in 3D printing, due to the specific properties inherent to the material. These include a high melting point, low viscosity and ductility, and high hardness, among others (Han et al., 2023).

The precision with which ceramic membrane materials can be formed using additive technology is also a significant challenge. Indeed, for the majority of ceramic 3D printing technologies, the print resolution and accuracy of layer thickness control on the XY plane typically exceeds tens of microns, with the resulting pore diameter usually exceeding $100 \mu m$. This makes it challenging to utilise additive technologies to fabricate ceramic membranes that necessitate the formation of pores with a diameter of less than 1 micron. Additionally, the current limitations in printing accuracy can result in the formation of a surface and appearance that is not as smooth as desired, necessitating post-processing techniques such as grinding and polishing (Chen et al.,2023).

The speed of 3D printing of ceramic materials is relatively slow, especially when printing large-scale elements with high resolution. Despite the advancement of 3D printing technology for polymeric and metal materials from prototyping to industrial production, the development of 3D printing technology for ceramic materials in this field has been notably slower (Chen et al., 2024).

In comparison to conventional moulding processes, such as injection moulding and extrusion, the size of ceramic products that can be printed using additive technologies is limited. For instance, commercially available tubular ceramic membranes are typically over 1 m long, necessitating the ability of additive technologies to print accurately within a range of at least 1 m. This is currently difficult to achieve for 3D printing of ceramic materials (Dommati et al., 2019).

In order for the starting materials for additive technologies to be suitable, they must not only have satisfactory printing properties, but also be able to meet the need for precise construction of the porous structure of membrane materials in terms of pore diameter and porosity. In view of this, the selection of ceramic materials for 3D printing is constrained, which impedes the advancement of 3D printing of ceramic membranes (Chen et al., 2019).

In comparison to traditional ceramic membrane formation techniques, 3D printing technology has the advantage of reducing the loss of raw materials. However, the overall production cost remains relatively high (Chen et al., 2023).

Although additive technologies are not yet fully developed for use in the synthesis of ceramic membranes, the flexibility they offer in designing and preparing complex structures is attracting a lot of attention from scientists and practitioners. Indeed, 3D printing technologies present significant opportunities for enhancing the performance of ceramic membranes. It is further anticipated that the resolution of ceramic 3D printing will reach 100 nm with the continued advancement of additive technologies, thereby enabling the direct 3D printing of micro- and ultrafiltration porous ceramic membranes. Direct ceramic powder 3D printing technologies, such as DED, can eliminate the necessity for subsequent sintering processes and reduce the preparation time for ceramic membrane materials.

While the production of conventionalsized ceramic membranes remains a challenge, this technology has demonstrated potential in the fabrication of other ceramic materials. It is anticipated that the advancement of continuous

3D printing technologies will markedly enhance the efficiency of 3D printing processes. The implementation of innovative 3D printing strategies can also result in a reduction of overall energy consumption. Additionally, this process does not necessitate the use of organic binders and additives. This not only serves to reduce the cost of the raw materials used but also circumvents the environmental issues that arise from the decomposition of organic materials.

7. Conclusions

This study considers seven principal processes of additive manufacturing, based on the utilization of diverse technologies for the 3D printing of ceramic membranes. It is demonstrated that the utilization of 3D printing as a novel approach to the fabrication of ceramic materials has markedly simplified their design and formation due to the capacity for discrete stacking of three-dimensional structures.

It has been established that, in comparison to existing methods of forming ceramic membranes, such as extrusion, casting and dry pressing, 3D printing technologies in industrial applications are currently not competitive. Nevertheless, with the ongoing advancement of 3D printing technologies for ceramic membranes, along with the associated equipment and materials, there is considerable potential for their use in the design and production of hierarchical porous ceramic structures. It was determined that the most promising technologies for the manufacture of ceramic membranes are additive technologies using the Vat Photopolymerisation and Powder Bed Fusion processes. This study analyses the parameters of SLA, LCD and SLS printing using these processes and their prospects for the production of ceramic

membranes. Additionally, it identifies the problems and challenges of creating ceramic membranes by 3D printing, discusses potential solutions, and indicates ways to further improve additive technologies for printing ceramic membranes.

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ПЕРСПЕКТИВИ ВИКОРИСТАННЯ 3D-ДРУКУ ДЛЯ ФОРМУВАННЯ КЕРАМІЧНИХ МЕМБРАН: КОРОТКИЙ ОГЛЯД

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В статті обговорені перспективи використання 3D-друку для формування керамічних мембран. В останні роки адитивні технології керамічних матеріалів стали центром досліджень, які свідчать про те, що вони можуть з успіхом використовуватись для проектування і отримання ієрархічних пористих керамічних структур, поєднуючи гнучкий дизайн і передові підходи до їх формування. Метою даної роботи є аналіз адитивних технологій для виробництва керамічних мембран, вибір найбільш перспективних технологій, ретельний аналіз їх досягнень та проблем і викликів. Розглянуті сім основних процесів адитивного виробництва, які засновані на використанні різних технологій 3D-друку. Показано, що для виготовлення керамічних мембран наразі найбільш перспективними є технології Vat Photopolymerization, які дозволяють отримати вироби зі складною геометрією і високою точністю та ті, які використовують процеси Powder Bed Fusion, що забезпечує механічну міцність і щільність керамічних виробів. Проаналізовані параметри друку технологій стереолітографії, рідкокристалічного дисплея, селективного лазерного спікання та їх перспективи для одержання керамічних виробів в цілому та мембран зокрема. Зазначені проблеми та виклики створення керамічних мембран 3D-друком, такі як оптимізація складу керамічних суспензій та пост-обробка виробів. Обговорено можливі шляхи їх вирішення, включаючи вдосконалення матеріалів для друку та технологічних процесів. Також розглянуто перспективи застосування отриманих керамічних мембран у різних галузях. Визначено напрямки подальших досліджень, спрямованих на покращення адитивних технологій для друку керамічних мембран та розширення їх застосування в промисловості.

Ключові слова: адитивні технології, 3D-друк, керамічні мембрани, мікроструктура, технологія стереолітографії, технологія селективного лазерного спікання, технологія рідкокристалічного дисплея.