Recent Research and Prospect of 3D Printing Technology in the Preparation of New Ceramic Materials

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Abstract: 3D printing, as a new generation of molding technology, has the advantages of simple operation, high molding efficiency and high precision, so that 3D printing molding functional ceramic components in medicine, aerospace and other fields have broad application prospects. This paper mainly introduces the forming process and materials of 3D printed ceramics, as well as the development and application status of 3D printed ceramics in functional ceramics and research status at home and abroad.

Keywords: 3D Printing, Ceramic molding, laser sintering technology, ceramic materials, Bone tissue engineering, Porous ceramics

1. Introduction

Due to various excellent properties, functional ceramics are widely used in chemical, mechanical, electronic, aerospace and biomedical engineering fields. The properties of new ceramics usually include high mechanical strength and hardness, good thermal and chemical stability, and excellent optical, thermal, electrical and magnetic properties. Functional ceramics have such great performance mainly because of their special raw materials. The raw materials of new ceramics are mostly compounds, among which the chemical bonds are mainly covalent bonds. Due to the stable chemical properties of the raw materials, it is difficult to prepare finished products of ceramic materials. In composition, ceramic materials are usually powdered powders containing adhesives and other additives, so a molding process is required to form a suitable embryo.

Compared with traditional cutting technology, such as the subtraction of materials to achieve the forming technology, 3D printing is the precise forming of materials by a computer-controlled printer, so it is also called additive manufacturing. In 3D printing, the required device data is first modeled, and then the 3D printer is controlled by the computer to construct the ceramic embryo layer by layer [1].

3D printing technology is considered a manufacturing revolution, with the flexibility to prepare highly complex and precise structures that can build many objects in a single run, resulting in a significant increase in production efficiency. Therefore, since 3D printing appeared in the 1980s, it has attracted rapid attention [2].

2. New ceramic 3D printing technology

At present, ceramic 3D printing technology mainly includes inkjet printing technology (IP), melting deposition forming technology (FDM, FDC), photocuring forming technology (SLA, DLP), layered solid manufacturing technology (LOM), laser selective melting technology/laser selective sintering technology (SLM, SLS), 3D printing forming technology (3DP), and paste direct writing DIW (DIW) [3-4]. The comparison of various technologies in terms of raw materials and scale of finished products is shown in Table 1[5].

Table 1. Comparison of common 3D printing technologies

	IP	FDM	SIA	LOM	SLS
Raw materials	Ceramic inks	Filamentous materials	Mixture of ceramic and photosensitive resin	Thin-film materials	Powders
Size	Small scale	Large scale	Small scale	Large scale	Large scale
Costs	Low cost	Low cost	Higher cost	Higher cost	Higher cost
Complexity	Complex	Complex	Complex	Simple	Complex
Support structure	Not required	Required	Requi red	Not required	Not required
Two cure rocesses	Not required	Not required	Required	Not required	Not required
Laser technology	Not required	Not required	Required	Required	Required

In addition, 3D printing processes are divided into direct 3D printing and indirect 3D printing according to whether subsequent processes are required. Indirect 3D printing decomposes the one-step forming process of direct 3D printing into forming and sintering, inheriting the advantages of 3D printing technology in forming ceramic materials and avoiding the internal stress caused by rapid cooling, thus ensuring the stability of complex ceramic components [6].

2.1. Inkjet printing technology (IP)

The raw material of IJP is "ceramic ink", which is composed of ceramic aggregate, binder and surface active material[7]. The molding method is to build a three-dimensional model by computer through CAD and other software, and then the nozzle draws the ceramic material layer by layer according to the model to complete the printing. The performance of IJP's ceramic preparation depends to a large extent on the ceramic powder and ceramic ink formulation. Because of its high positioning accuracy and small droplet size, IJP has become an important development direction of 3D printing.

2.2. Melting deposition forming technology(FDM)

Melting deposition forming technology (FDM), also called ceramic melt Deposition (FDC), is one of the most commonly used 3D printing techniques. Thermoplastic polymers [8], including ABS, PC, PA and polylactic acid (PLA), are the most commonly used materials for FDM. The raw material is heated and softened, then ejected, printed out the corresponding shape and solidified on the previous layer. Since the printing process is the accumulation of material layer by layer, FDM printing requires auxiliary support.

In the process of FDM, the material needs to be heated to realize printing, so the hot-melt filamentous raw material should be stable at room temperature, and it should have a certain mechanical strength, and at the same time, after the material is melted, it should have a certain fluidity, viscosity and appropriate shrinkage rate to ensure the molding.

2.3. Photocuring molding technology (SLA)

The raw material of photocuring molding technology (SLA) is a paste made by mixing photosensitive resin and ceramic powder. The technological principle of SLA is to use ultraviolet light to sintered uniformly coated ceramic raw materials layer by layer according to software design[9]. SLA is UV in the micron scale, so it can be used to prepare ceramic devices with higher accuracy.

According to the process principle of SLA, the ceramic paste used in the process must ensure that each layer is evenly coated. The blank body prepared by this process has the advantages of good surface performance and high precision, and has advantages in the preparation of complex and high precision ceramic devices. At the same time, the shortcomings of photocuring molding technology are very obvious, such as embryo easy to damage, raw material ratio is difficult to master. Due to the participation of ultraviolet rays, the working environment is demanding, and it is required to ensure the protection from light and ventilation [10].

2.4. Layered physical manufacturing technology (LOM)

Layered solid manufacturing technology (LOM) adopts ceramic sheet material as the printing material. Its working principle is to cut ceramic sheet layer by layer according to the design through a laser cutter to form a section of the workpiece and use a binder and other ways to achieve the bonding of each layer. LOM utilizes the cutting and additive molding of a raw sheet to realize directsurface-to-body, which optimizes the processing process from point to line and from line to the surface of other 3D printing molding processes, thus improving the molding efficiency and stability.

LOM technology has high molding speed but low material utilization rate. Its forming principle is simple, the working space is large, suitable for processing large size parts, but the mechanical properties of the parts processed by LOM technology are poor, low precision, not suitable for processing precision parts.

2.5. Laser selective melting technology(SLM)/laser selective sintering technology(SLS)

Laser selective melting (SLM) and Laser selective sintering (SLS) both use laser beam to print the printed material. The powdery material is laid on the platform to form a powdery thin layer. The laser beam is sintered according to the design. The forming process and principle of SLM technology is similar to that of SLS technology. The difference is that SLM technology uses ceramic powder material, which is sintered and formed by direct irradiation of laser beam.

The current raw materials of SLS include carbide, oxide, nitride, and et al., SLS technology has the advantages of high molding efficiency and low cost. SLS technology uses laser beam to sinter ceramic materials, so it has high requirements for working environment and printing equipment. At the same time, it is difficult to solve the problems of high shrinkage rate and high porosity of ceramic products sintered by SLS technology, which can easily lead to the accumulation of thermal stress in ceramic embryos and reduce the strength, thus limiting the application of SLS technology.

3. Progress in the application of ceramic 3D printing

Considering the characteristics of various 3D printing processes and the characteristics of raw materials, 3D printing forming technology is mainly applied to the forming of complex or high-precision functional ceramic components at the present stage. Common application directions are biomedical and aerospace[13]. At present, the commonly used raw materials are calcium phosphate, silicon carbide, silicon nitride, alumina and so on.

3.1. Calcium phosphate ceramics

The chemical composition of tricalcium phosphate is similar to the mineral of human bone, so it is a good material for bone repair because it combines well with bone tissue and does not produce rejection reaction. Yang et al. successfully produced produced ceramics with spatial resolution less than 100μm and periodic porous structure using calcium phosphate as raw material by using FDM technology[11]. These pore structures have precise size and multi-scale internal hierarchy, which is more conducive to the repair and growth of bone cells.

3.2. Silicon carbide ceramics

Silicon carbide (SiC) ceramics have good mechanical properties at high temperature, and its oxidation resistance is the best among all non-oxide ceramics. Polzin et al. used SiC fine powder with particle size less than 50 μm to prepare ceramic powder, which was formed by direct inkjet printing[12]. Under the protection of Ar atmosphere, 2200C insulation for 3 h can prepare porous silicon carbide ceramics with porosity of 55%, bending strength, 9.74MPa, compressive strength, 19.65MPa. The 3D printing technology makes the raw materials in the ceramic embryo more evenly mixed and the pore-forming more controllable. Compared with the traditional high temperature sintering or reaction sintering of silicon carbide ceramics, the purity and compressive strength have been improved.

3.3. Silicon nitride ceramics

Silicon nitride (Si_3N_4) ceramics are mainly covalent bonding compounds, so they have high strength, low density, high temperature resistance and other characteristics. Its strength can not change at 1200°C, while the heat does not appear melt, until 1900°C decomposition. Cappi et al. prepared SiN ink, and used 30.2% (volume fraction) Si_3N_4, 2.3% sintering agent and dispersant to mix with 2h high-speed ball milling to obtain Si_3N_4 with guaranteed printing effect[13]. 3D printing porous silicon nitride ceramics combines the advantages of porous ceramics and silicon nitride ceramics. At the same time, the non-uniformity of the traditional porous silicon nitride ceramic template deposition method is avoided.

3.4. Alumina ceramics

Alumina ceramics are the most widely used and most productive ceramic materials among oxide ceramics. There are α, β and γ phases, among which corundum phase has high strength and stable chemical properties, making it the most widely used alumina ceramics. Stable chemical properties mean that it is difficult to sinter, so the traditional process of producing alumina ceramics is inefficient. Seerden et al. used alumina to make ceramic inks with a content of up to 40vol% to produce ceramic parts with characteristic sizes of less than 100μm through 3D printing[14]. The use of 3D printing technology molding to obtain strength, bypassing the sintering process, plays a role in promoting the production efficiency of load catalysis and filtration components, which have low strength requirements but require precision structure.

4. Summary and Outlook

As a representative of the third industrial revolution, the application of 3D printing technology in ceramic molding enables ceramic components with highly complex structures that cannot be prepared by traditional manufacturing methods to now be prepared by 3D printing technology, thus showing great potential and value. What's more, the 3D printing process mainly involves the molding during the preparation of ceramic parts, but the final performance of ceramic materials also depends on the composition and microstructure, which are partly determined by the raw material itself and the subsequent sintering process.

At the present stage, the application of 3D printing technology is still quite limited. In addition to the problems of accuracy improvement and raw material optimization, 3D printing technology is difficult to apply to the processing of large quantities and large sizes of parts due to the limitation of equipment. At the same time, the combination of this technology and the existing process widely used in ceramic production is not perfect. Therefore, the following research objectives are: improve the accuracy and improve the raw material; Expand scale and improve efficiency; Combined with the existing technology, the system can be optimized by exploiting strengths and avoiding weaknesses[15].

The aerospace and medical industries remain two of the most promising markets for ceramic 3D printing in the near future, due to the large number of low-size parts customized and relatively low-cost considerations. Thus, 3D printing technology is likely to develop and mature in related industries before being introduced to a wider market.

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