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3D Printing of Silicon Nitride Ceramics and Exploration of Their Properties

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Abstract: Silicon nitride (Si_3N_4) offers significant advantages such as high strength, high hardness, thermal shock resistance, good stability, wear resistance, and chemical corrosion resistance. It is lighter than many other materials, has a low thermal expansion coefficient, excellent thermal shock resistance, and high fracture toughness. Leveraging these advantages, it has found promising applications in aerospace, the military industry, mechanical engineering, metallurgy, and other fields. In the future, it is expected to unleash greater value through the innovative development of big data and artificial intelligence technologies. The author believes that traditional silicon nitride forming processes face insurmountable challenges, making it necessary to use 3D printing technology—with its own unique advantages—to mitigate risks and enhance performance and utility. This paper discusses the 3D printing of silicon nitride ceramics and their properties, providing a detailed analysis to offer references for relevant practitioners.

Keywords: 3D printing; Silicon nitride ceramics; Properties

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1. Overview of 3D printing and silicon nitride

3D printing, also known as additive manufacturing, constructs components by layer-by-layer material deposition based on a 3D model. It boasts significant advantages such as short manufacturing cycles, high design freedom, and personalized customization [1–3]. Applying 3D printing to the preparation of silicon nitride ceramics has become a research hotspot in materials science and engineering, offering a new approach to breaking through the bottlenecks of traditional manufacturing processes and achieving efficient production of complex-structured silicon nitride ceramic components. With the advancement of information technology, big data, and artificial intelligence, the in-depth application of 3D printing in this field is expected to expand, warranting further exploration and practice.

Silicon nitride ceramics exhibit enormous application potential in aerospace, mechanical manufacturing, electronic information, biomedical, and other fields due to their excellent mechanical properties (high hardness, strength, and wear resistance), outstanding thermal properties (low expansion coefficient, high thermal conductivity), and superior chemical stability (strong corrosion resistance) [4]. However, traditional preparation processes for silicon nitride ceramics suffer from limitations such as difficulties in forming complex shapes, long production cycles, and high costs, failing to meet the demands of modern industry for complex-structured silicon nitride ceramic components. Therefore, auxiliary 3D printing technology is crucial to address the challenges in silicon nitride ceramic fabrication, improve manufacturing efficiency and quality, and requires further research and promotion.

2. 3D printing technologies suitable for silicon nitride ceramics

2.1. Digital Light Processing (DLP) technology

Digital Light Processing was first proposed and experimentally validated by Nakamoto and Yamaguchi, who used projection equipment to directly project cross-sectional images of objects onto photosensitive resins. Bertsch et al. later contributed significantly by replacing dynamic mask generators with LCDs [5]. Texas Instruments commercialized the technology by using digital micromirror devices (DMDs) to replace LCD displays. The success of DMDs lies in their higher resolution and contrast: mirror rotation controls the light path, projecting directly onto photosensitive resins to form a mirror matrix with pixel pitches ranging from a few to ten micrometers [6–8]. This high resolution at the micrometer level is a key advantage for applying DLP technology to silicon nitride preparation.

2.2. Two-Photon Polymerization (TPP) technology

Two-Photon Polymerization (TPP) is a polymerization reaction activated by the simultaneous absorption of two photons from infrared or green laser light, occurring locally only at high laser intensity focal points. Compared to traditional single-photon processes that polymerize only at the liquid surface, TPP offers significant advantages by enabling polymerization of submicron-scale focal volumes in polymer liquids via Two-Photon Absorption (TPA) [9]. To prepare silicon nitride ceramics using this process, a nanoscale 3D polymer structure is first created via TPP. Subsequent steps include coating with ceramic nanoparticles through chemical vapor deposition or atomic layer deposition, followed by surface milling using FIB or RIE. This results in silicon nitride ceramics with excellent optical and mechanical properties.

2.3. Inkjet Printing (IJP) technology

Inkjet Printing (IJP) has become ubiquitous in daily life, from small household devices to expensive large industrial printers. The technology sprays liquid materials as small droplets onto paper, plastic, or other substrates. Commercially adopted in the 1970s, IJP was truly realized with computer assistance. Classified by working modes, it includes continuous and drop-on-demand types. With technological advancements, IJP now uses diverse inks, including polymers, metal components for electronic patterning, solder pastes, and even cells for tissue engineering. However, its key limitation—the inability to eject large volumes of ink at once—restricts IJP to printing miniature components.

3. Preparation process of 3D-printed silicon nitride ceramics

3.1. Raw material preparation

Generally, silicon nitride powders with small particle size, narrow particle size distribution, and high purity are conducive to the density and performance of ceramics. Common silicon nitride powders exist in two crystal forms: α-Si_3N_4 and β-Si_3N_4. The former transforms into β-Si_3N_4 during high-temperature sintering, and powders with high α-Si_3N_4 content help form fine-grained ceramic structures, enhancing mechanical properties [10]. Additives are often included to improve sintering and printing performance: Fluxes (e.g., Y_2O_3, Al_2O_3) form low-melting-point liquids during sintering to promote densification. Binders (e.g., polyvinyl alcohol, paraffin) maintain green body shape and strength during 3D printing. Dispersants enhance powder dispersion in slurries or filaments to prevent agglomeration [11].

3.2. Slurry or filament preparation

Slurry preparation is critical: silicon nitride powder, additives, solvents, and dispersants are mixed in specific ratios and dispersed thoroughly via ball milling or ultrasonication to obtain ceramic slurries with good fluidity, stability, and appropriate viscosity. The solid content of the slurry significantly affects printing and final properties: high solid content improves density but increases viscosity, while low solid content aids printing but may cause large shrinkage and low strength. For FDM (Fused Deposition Modeling), silicon nitride powder is mixed with binders and extruded into filaments of controlled diameter and flexibility, requiring precise control of mixing ratios, temperature, and extrusion speed.

3.3. 3D printing process

The printing process involves selecting one of the aforementioned technologies, preparing materials, and optimizing process parameters.

3.4. Post-processing

3D-printed silicon nitride green bodies contain substantial binders or organic additives, which are removed via debinding (thermal or solvent-based). Thermal debinding decomposes binders at controlled heating rates to avoid cracks or deformation, while solvent debinding is faster but may leave residues. Sintering is used to improve density and performance, with main methods including: Normal pressure sintering: Simple but requiring high temperatures. Hot-press sintering: Applying pressure lowers sintering temperature and enhances properties. Reaction sintering: Silicon reacts with nitrogen, but the density is relatively low. Other methods exist but are not detailed here [12–13].

4. Performance analysis of 3D-printed silicon nitride ceramics

4.1. Mechanical properties

Hardness: Fine-grained ceramic structures from small, pure silicon nitride powders and suitable sintering processes enhance hardness. Additives (e.g., fluxes) promote grain refinement, while excessive binders may leave pores, reducing hardness.

Strength: Closely related to density—higher density yields greater strength. Optimized printing and post-processing reduce pores and defects, improving density and strength. Grain size and grain boundary properties also matter; fine, uniform grains enhance strength [14].

Toughness: As a brittle material, silicon nitride ceramics have limited toughness, restricting applications in certain fields.

4.2. Thermal properties

Thermal conductivity: High-purity, high-density, and uniformly grained ceramics exhibit high thermal conductivity. Optimized raw materials and sintering reduce pores and impurities, while some additives may form low-conductivity phases at grain boundaries.

Thermal expansion coefficient: Similar to traditional ceramics, but improper process control during printing may induce residual stresses, affecting thermal expansion. Rational process design and post-processing eliminate stresses for stable performance.

4.3. Chemical stability

Silicon nitride ceramics show good chemical stability, resisting most acids, bases, and salt solutions at room temperature. However, extreme conditions (high temperature, strong oxidation) may compromise stability [15]. Stability depends on density, microstructure, and surface condition: dense structures prevent corrosive media penetration, while rough surfaces with pores or defects are more susceptible to corrosion.

5. Conclusion

In the future, research on applying 3D printing to silicon nitride ceramic preparation will focus on optimizing processes and material systems to improve printing efficiency and precision, thereby enhancing production benefits. It is also essential to observe the relationship between microstructure and properties, explore new toughening and strengthening mechanisms, further improve comprehensive properties, and expand the application scope and practical benefits. With increasing theoretical research and technological advancements, 3D-printed silicon nitride ceramics are expected to drive modernization in aerospace, biomedical, and electronic information fields, warranting in-depth exploration and practice.

Disclosure statement

The author declares no conflict of interest.

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