Fabrication of porous silicon nitride ceramics using binder jetting technology

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Abstract. This paper presents the results of the binder jetting technology application for the processing of the Si₃N₄-based ceramics. The difference of the developed technology from analogues used for additive manufacturing of silicon nitride ceramics is a method of the separate deposition of the mineral powder and binder without direct injection of suspensions/slurries. It is assumed that such approach allows reducing the technology complexity and simplifying the process of the feedstock preparation, including the simplification of the composite materials production. The binders based on methyl ester of acrylic acid with polyurethane and modified starch were studied. At this stage of the investigations, the technology of green body’s fabrication is implemented using a standard HP cartridge mounted on the robotic arm. For the coordinated operation of the cartridge and robot the specially developed software was used. Obtained green bodies of silicon powder were used to produce the ceramic samples via reaction sintering. The results of study of ceramics samples microstructure and composition are presented. Sintered ceramics are characterized by fibrous α-Si₃N₄ structure and porosity up to 70%.

1. Introduction

Silicon nitride ceramics have excellent mechanical, thermal and dielectric properties. Silicon nitride parts are widely used in different technical fields [1, 2], particularly in jet engine structural components, in the fuel systems, in the braking system components. Porous silicon nitride ceramics are applied in cooling system, filtration components and as refractory materials.

Over the last twenty years, several additive fabrication technologies for silicon green bodies and silicon nitride parts, which possess a complex geometry and different pore volume, were suggested [3-11]. The laminated object manufacturing (LOM) process of silicon nitride products was suggested in the work [3]. The laying of thin polymer film, which contains particles of α-Si₃N₄, was carried out. Layers of tape were stacked together with a preheated roller and cut off with a laser to fabricate a defined shape product. Up to 90% β-Si₃N₄ and 6% porosity were formed during the material sintering process. The flexural strength of the material was up to 900 MPa. Fabrication of micro-sized silicon nitride nozzles using mould shape deposition manufacturing technology was applied during the work [4]. Fused deposition modelling was used in the work [5]. Fusing layers of the product were carried out by heating and extruding of thermoplastic polymer filament with 55% silicon nitride powder content. The technology requires careful control over the powder dispersion – the agglomerate size should not exceed the nozzle diameter (250 µm). Various schemes of filament laying were used to
produce isotropic material. The flexural strength was about 900 MPa, and the fracture toughness of 8.5 MPa·m$^{0.5}$. The papers by Cappi et al. [6, 7] introduced the fabrication of silicon nitride ceramics by direct inkjet printing technology using HP DeskJet 930c inkjet printer. Printing was carried out using suspensions with volume content of about 30% silicon nitride, 0.7 μm average size, and additives of yttrium aluminum garnet and boron nitride. The slurry was formed by the mixture of polyacrylic and carboxylic acids with the addition of ethanol and ethylene glycol. The printer used two cartridges that separately applied the main and supporting materials by suspending silicon nitride particles. The composition of final samples includes β-Si3N4, silicon oxynitride, pure silicon and yttrium silicate. The material fracture toughness was 4.4 MPa·m$^{0.5}$, Vickers hardness – 17 GPa.

In the recent papers [8-10] it was considered three-dimensional printing technology for highly porous silicon nitride ceramics containing more than 70% pores. The powder containing more than 90 wt.% of α-Si$_3$N$_4$ was used as a feedstock. Products were fabricated by three-dimensional printing carried out on a standard 3D-printer using water-based solvents. It was found that obtained material has the highest porosity (68% versus 45% for traditional technology), and its properties are relatively low. Due to high porosity, its strength, elastic moduli, fracture toughness and hardness were significantly reduced. The capability of good dielectric properties of the material was mentioned. The work [10] presented the development of technology to produce porous silicon nitride composites reinforced with in-situ formed twinned silicon carbide nanowires. An increase of SiC content in the fabricated composites resulted in the growth of permittivity. The reinforced SiC samples had a minimal reflection coefficient at microwave frequencies and had excellent absorption properties.

In the recent paper [11] small-size complex shape samples were fabricated using LOM technology. The films were prefabricated using suspensions of silicon nitride powder with averaged particles size of 130 nm. These pieces were stacked, pressing and then sintered at temperature of 1800 °C. The porosity of the obtained material was 50% and the flexural strength was 475 MPa.

It could be mentioned that one of disadvantages of existing silicon nitride additive manufacturing technologies is a difficulty of feedstock preparation: powder dispersion in the direct inkjet printing or preparation of films with Si$_3$N$_4$ particles in the LOM technology. FDM technology requires solving the additional problem of thermoplastic binder removal from the fabricated products. This is a time-consuming and non-environmentally friendly process, which often results in defects of the parts with complex geometry. One of the technologies with no such manufacturing operations is a binder jetting. This technology is widely used for the synthesis of gypsum, mortar sand etc.

In the present work, we offer the method of silicon green bodies fabrication using binder jetting technology. The silicon nitride ceramics are obtained using the pressureless reaction sintering process. This technology does not use the mentioned complex preliminary processes. In this case, the binder is injected into each applied layer of dry ceramic powder with controlled thickness. Layer-by-layer bonding of the powder particles leads to the shaping of the future products or green bodies. Part of the powder in each layer that not exposed to a binder, acts as a support for the synthesized parts with complex shapes. General description and principles of the binder jetting technology are presented, for example, in the work [12]. In order to implement the three-dimensional printing process we used a modified system based on an industrial robotic arm and printing block of original design. Software for printing process control was developed. The study and comparison of two variants of binders and silicon powder preparation methods were undertaken. The composition and microstructure of the first obtained ceramic samples, which have high porosity, were studied.

2. Experimental Procedure

2.1. Powders

In the experiments the commercially available technical silicon powder KR00 (TU-1711-5072130-01-2012) with fraction of 10-100 μm was subjected to vibrating grinding in ball mills SVM-2. The duration of grinding was varied in the range of 9-36 hours, grinding bodies were the high-strength
steel balls with diameter of 16 mm. Grinding was carried out in the presence of surfactants: oleophilic (oleic acid 0.6 wt.%) or hydrophilic (sulfanol 0.6 wt.%). The average diameter of powder particles was 0.4-1.5 µm. This value of particles ensures the successful and complete process of reaction sintering in the temperature range of 1170-1500 °C. The special criterion for the selection of the required fineness of the powder was the minimal weight content of the selected binder required to obtain the reliable formation of silicon green bodies. The particle size was controlled by a combined electro-acoustic analyzer Dispersion Technology DT 1201.

It should be noted that coarse powder requires less binder but does not provide the complete reaction sintering process. Using a large amount of the binder for the ultrafine powder tends to reduce the accuracy and speed of modeling, elongation of the drying process time and increase the number of defective articles. Therefore, two compromise variants of the silicon powder preparation were developed to solve mentioned mutually exclusive issues. In the first case, silicon powder was coated by the aluminum isopropoxide to decrease the wettability of a binders’ solution on solid particles surfaces. After hydrolysis and drying, the nanoscale layer of aluminum oxide was formed on the silicon particles. Size of silicon particles was insignificantly increased but the amount of binder used in the synthesis was reduced. In the second case, the ultrafine silicon powder pre-aggregated (using binder that employed during synthesis) to the state of granules of 50-100 µm, which also reduced the amount of binder used in the synthesis.

2.2. Binders

Two types of binders were used to prepare the green-body preforms:

- A first binder based on a copolymer of methyl ester of acrylic acid with polyurethane with additives of photoinitiator and a diluent – the monomer acrylic acid (the binder 1). Solidification of this binder was initiated by the ultraviolet radiation in the process of three-dimensional printing and proceeded within 20-100 sec depending on thickness of the curable layer. In this technique, the silicon powder coated with alumina is used.

- The binder based on polysaccharide – modified starch (binder 2). The pre-aggregation of silicon powder using this binder was conducted. Consolidation of the powder granules was performed by applying the aqueous solution through the cartridge nozzle during the printing process.

2.3. Binder jetting procedure

Binder jetting procedure is based on the layer-by-layer binder impregnation on the silicon powder in the area of cross-section of the produced sample. To implement this process, the robot arm KUKA KR 6 (KUKA AG) was modified. On the flange of the robot it was installed the printing unit, which consists of Arduino controller, InkShield controller and HP 6022B cartridge with integrated nozzle array. Resolution 96 ppi of the cartridge ensures the efficient printing on media with complex structure. The cartridge is controlled by Arduino system through the combinations of control signals for the nozzle array. For this, the special program was developed using C programming language. Data transmission from the PC to the printing unit was done through a serial COM-port. The developed software provides synchronization of the controller of the printing block with a robotic arm. The swivel rotary table is used as the base for the samples in three-dimensional printing process. The powder supply system on the work platform is carried out using roller mechanism, which provide full and uniform laying of each layer of the powder in the chamber. Once a layer of the powder is supplied, the inkjet printheads print the lower section of the part on the smooth surface of the powder, gluing particles together. Thereafter, the plunger lowered the working platform onto the layer thickness down and a new layer of the powder is applied. The printing unit prints the next section on the new layer surface, gluing it to the previous layer. This process is repeated for all sections of the sample. The technology does not require solid or attached supports during the printing process, so all amount of unused powder can be used again.
2.4. Reaction sintering

Reaction sintering of ceramic samples was carried out in the vacuum furnace, and consisted of the following main operations:

- Vacuumization and heating up to 360 °C at the rate not exceeding 65 °C per hour for degassing;
- Heating up to 1170 °C at a rate not exceeding 65 °C per hour to warm the samples up to the initiation temperature of the reaction of nitrogen supplied to the furnace with silicon particles in the printed green bodies;
- Further heating up to the 1400 °C at a rate not exceeding 20 °C per hour, which allows the complete nitridation of the samples during for 8-10 hours;
- Cooling of the samples with the furnace for at least 1 hour.

2.5. Binder jetting procedure

Density of materials were determined by direct measurement. X-ray diffraction analyses have been performed using ALRX™TRA (Thermo-FisherScientific) diffractometer with copper anode using the Crystallographica Search-Match Version 3.1.0.0 software and PDF-2 crystallographic database. The study of microstructure of the samples fracture surfaces and X-ray microanalyses were conducted using two-beam scanning electron microscope Versa 3D LoVac. The surface of the samples was coated with gold.

3. Results and Discussion

The weight content of the binder which is necessary for reliable forming of the green bodies during three-dimensional printing via binder jetting using different powders is presented in Table 1. Analysis of the results shows that used surfactants during the grinding, are not effective for the binder 1 and it requires additional studies. Therefore, further experiments with this binder 1 were carried out with the silicon powder obtained by grinding in a vibrating mill without surfactant for 18 hours. The second binder showed an affinity for sulfanol. Therefore, experiments with binder 2 were carried out with silicon powder obtained by milling for 9 hours in the presence of sulfanol.

Table 1. The weight contents of the binders, which are necessary for reliable forming of the green bodies during three-dimensional printing via binder jet using different fractions of silicon powders.

| Milling time, h | Surfactant | Particles size, μm | Binder 1 | Binder 2 |
|----------------|------------|--------------------|----------|----------|
| 9              | oleic acid | 0.45               | do not mix | 50       |
| 18             | oleic acid | 0.3                | do not mix | 70       |
| 36             | oleic acid | 0.1                | do not mix | 100      |
| 9              | sulfanol   | 0.6                | 55       | 12       |
| 18             | sulfanol   | 0.4                | 77       | 18       |
| 36             | sulfanol   | 0.15               | 105      | 24       |
| 9              | -          | 3                  | 32       | 20       |
| 18             | -          | 1.5                | 45       | 32       |
| 36             | -          | 0.5                | 60       | 40       |

As result of X-ray analysis of samples subjected to reaction sintering, it was found that the resulting ceramics consists of α-Si₃N₄ with possible content of silicon oxynitride up to 10%. The resulting X-ray diffraction pattern and its comparison with the standard data for the alpha-Si₃N₄ is shown on Figure 1. As result of X-ray microanalysis, the elemental composition of the samples fracture surfaces was determined which is listed in the Table 2. It was found that usage of the binder 1 tend to increase the carbon (presumably SiC) content in the ceramics composition. The presence of aluminum in the
ceramic composition is explained by the preliminary treatment of silicon powder with aluminum isopropoxide.

Figure 1. Results of X-ray analysis of ceramic samples composition (top pattern) and the standard data for the alpha-Si₃N₄ from the PDF-2 database (bottom pattern).

Table 2. The weight content (%) of the chemical elements identified by X-ray microanalysis on the fracture surfaces of ceramic samples prepared using different binders.

| Elements | Binder 1 | Binder 2 |
|----------|----------|----------|
| Si       | 68.3     | 58.6     |
| N        | 14.5     | 26.4     |
| C        | 11.1     | 7.4      |
| O        | 3.5      | 6.6      |
| Al       | 2.6      | 1        |

Investigation of the microstructure of the obtained ceramic samples is shown in Figures 2 and 3. Samples have a fibrous structure with dispersed inclusions (ceramic grains) with size of 1-20 µm. The first variant of the binder allows to obtain a denser structure consisting of shorter and thicker fibers, compared with the second variant of the binder. Porosity of the samples obtained using the binder of the first and second type was up to 60% and 70%, respectively.
Figure 2. Microstructure of ceramic samples obtained using binder jetting and reaction sintering technologies using binder 1 (a), binder 2 (b).

Figure 3. Microstructure of ceramics obtained using binder 2: large inclusions (a) and high-resolution images of α-Si₃N₄ fibers (b).

4. Conclusions
The development of silicon nitride ceramic additive fabrication using binder jetting and reaction sintering technology was carried out. The control system of binder jetting three-dimensional printing process was developed. The method of silicon powder preparation was offered. Two types of binders based on acrylic acid with polyurethane and based on modified starch were used. Optimal parameters of silicon powder preparation were determined. Porous silicon nitride samples, for which the composition and microstructure parameters were examined, were fabricated resulting from the reaction sintering of the obtained preforms. It was found that the material consists mostly of α-Si₃N₄ fibers with particle inclusions of 1-20 µm. Silicon oxynitride and silicon carbide with total volume content of not more than 20% are also present in the material composition.

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References
[1] Krstic Z and Krstic V 2012 J. Mater. Sci. 47 535
[2] Somiya S 2013 Handbook of Advanced Ceramics: Materials, Applications, Processing, and Properties (NY: Academic Press)
[3] Rodrigues S et al 2001 Proc. of the SFF Symp. 1
[4] Liu H et al 2004 Rapid Prototyping J. 10 239
[5] Iyer S et al 2008 Int. J. Appl. Ceram. Techn. 5 127
[6] Cappi B et al 2008 J. Europ. Ceram. Soc. 28 2625
[7] Cappi B et al 2011 J. Amer. Ceram. Soc. 94 111
[8] Li X et al 2012 Scr. Mater. 67 380
[9] Li X et al 2012 Mater. Sci. Eng. A 549 43
[10] Duan W et al 2015 Mater. Lett. 159 257
[11] Liu S et al 2015 Mat. & Des. 66 331
[12] Gibson D et al 2013 Additive Manufacturing Technologies. 3D Printing, Rapid Prototyping, and Direct Digital Manufacturing (NY: Springer)