YXLON

WHITE PAPER

How to Gain Better Perspective in Direct Ink Writing with X-ray Microtomography

What you will learn:

- Why direct ink writing (DIW) is a great AM solution for ceramics, and which challenges have to be mastered
- How the printing strategy, incl. the choice of material, the preparation, and the drying process, affects the product quality
- How computed tomography can enrich and accelerate your research

Abstract

Additive manufacturing (AM), also known as 3D printing, is the construction of a three-dimensional object from a CAD model or a digital 3D model. It has become increasingly popular over the past several years due to its unique benefits. AM enables the creation of specific geometries such as channels or undercuts that are not possible with conventional manufacturing methods. The fact that it requires no special tools for manufacturing is especially beneficial for small series or single part production as it reduces time and cost. It also requires less material as you use only what is required for the specific design.

Much like an artist sculpting a masterpiece, additive manufacturing requires imagination, strict attention to detail and the perspective to identify any obstacles that will interfere with the finished piece. This is especially important when the end product is a critical part to be used in a medical device, automotive or aerospace product where safety and quality are of the utmost importance. Silicon Nitride, a ceramic compound, is often used in these applications because of its physical stability, heat resistance, bio compatibility and electrical properties.

One of the most used additive manufacturing methods for ceramics is Direct Ink Writing (DIW). DIW applies a liquid-phase ink which should have a consistency similar to toothpaste. It is dispensed out of small nozzles under controlled flow rates and deposited along digitally defined paths to fabricate 3D structures layer by layer. However, printing bulk parts by DIW is quite challenging. Aspects like the printing strategy or drying parameters can have a significant influence on the quality of the resulting sample. The printing process only creates the green parts. After that is completed, the process of sintering begins. This process poses additional problems that are also very important to consider.

KYOCERA Fineceramics Precison GmbH, an expert in the art of 3D printing of fine ceramics, teamed up with the University of Padova in Italy, one of the top 250 universities in the world to investigate these challenges. Kyocera offers precise and efficient fine ceramic solutions for a wide range of applications including aerospace, semiconductor and other industries who require unique printing properties for their products.

Yxlon supported the research project by utilizing x-ray microtomography to test the residual pore structure in silicon nitride bars manufactured by DIW using different printing patterns. This white paper will outline the findings and demonstrate how nondestructive testing performed with x-ray microtomography can help you gain a better perspective in DIW.

Tools of the Trade

The Material: Silicon Nitride

To better understand the principles of the investigation, it’s important to identify some of the key elements that were relevant to the research. One of the most significant is silicon nitride. Silicon nitride parts have excellent properties for high temperature and structural applications. That’s why this material is often used in applications such as automotive engine components, aerospace, and medical devices. However, it does pose some challenges.

Typical values for silicon nitrides with glass phase are 15 GPa for Vickers hardness, which is very high. Silicon nitrides are not only very hard in the sintered state but also in the green state. This hardness makes machining expensive and leads to an immense wear of the tools. Near net shaping with additive manufacturing is a great way to reduce these machining costs and increase the range of designs that are possible. There are several AM methods used for the production of silicon nitride parts, such as stereolithography, binder jetting, laser induced slip casting, or direct ink writing.

Direct Ink Writing

Direct Ink Writing (DIW) allows for the production of medium to large size parts with high geometrical freedom and dense components, using inks with high solid loading and a low amount of binder. It is mostly used for fabricating porous structures, as the stacking of the filaments always creates a textured structure at the surface of the part. Dense silicon nitride components as well as scaffolds for medical applications have already been fabricated via DIW offset filling. While there are many benefits to DIW there are also some challenges to overcome.

One of the biggest challenges in DIW is developing an ink with the right behavior. When printing dense parts, it’s critical to choose an ink with the most appropriate rheological properties to ensure a quality outcome. Given a specific nozzle diameter, layer height and filament width are strongly dependent on the rheological properties of the ink and on its shape retention capabilities.

When producing dense parts, it’s important to reach a compromise between shape retention and certain welding of the single struts. Ideally the ink should show a time-dependent shear-thinning behavior, so that it flows easily under high shear stresses (such as those generated at the nozzle tip), but its viscosity increases over time as the filament exits the nozzle, ultimately allowing to retain the printed shape. This can be attained with gelling agents that build a reversible network which is ruptured during extrusion but recovers after deposition.

Drying of dense parts is also critical due to warping issues, to pores coalescence, and to cracks development. A high solid content in the ink usually helps avoiding or limiting such issues and contributes to the development of dense components with low shrinkage upon sintering. In order to test the influence of the printing strategy procedure on the residual porosity of Si3N4, x-ray microtomography is the inspection technology of choice.

In-Depth Material Analysis Using X-Ray

X-ray microtomography (also known as micro computed tomography or µCT) uses X-rays to penetrate an object from various angles and generate many radioscopic pictures. These pictures get reconstructed by software to a 3D volume, the virtual model of the scanned object (3D model). By means of cross sections, an in-depth analysis can be performed at any region of interest. It's the only technology that provides deep insights of the interior structures without destroying the object which makes it ideal for research, development, and production in the field of Additive Manufacturing. Mainly it is used to check for unwanted porosity for example caused by incorrect printing parameters, or to prove the dimensional accuracy of a part. Furthermore, it can quantify surface roughness and other characteristics of the printed structure.

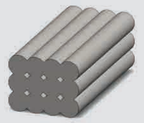
X-ray microtomography can also play an important role in the discovery phase of research and development. Utilizing CT in R&D can avoid many issues later in the production process by identifying key information about part design, raw materials and how well it matches the intended geometry, all of which are vital to the success of the product.

The Path to Discovery

The path to discovery is paved with a variety of methods and materials that need to be studied. In this case the first step was to prepare the ink which was a spray dried silicon nitride powder with sintering additives, mixed with water, dispersant, and a gelling agent. An additive was used to slow down the drying rate.

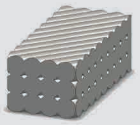
Proof of Concept

Next step was to test the methodology. The DIW device used was equipped with a screw extrusion system, which can mount conical nozzles of various sizes ranging from 0.15 to 2.00 mm. The material was deposited following a path provided by a digital file (.gcode). Rectangular bars were produced using four different printing patterns:



ALIGNED PATTERN

Within the layer, linear struts are deposited on the long side of the bar and each layer is exactly on top of the one underneath.

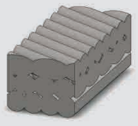


DIAGONAL PATTERN

Within the layer, the filaments are deposited at an angle of 45° with the sides of the bar; the next layer is deposited perpendicular on top of the underneath layer.

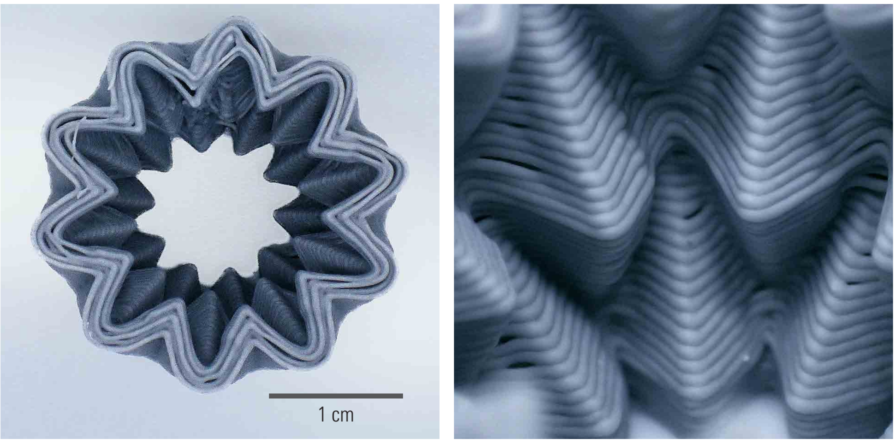
HEXAGONAL PATTERN

The deposition direction is the same as the aligned pattern, but the next layer is shifted by one strut radius.



BOULIGAND PATTERN

Hierarchical architecture in which uniaxial filament layers are assembled into a helicoidal pattern.



AM allows the the production of complex geometries which are impossible or expensive to manufacture with traditional shaping methods.

All patterns were printed with a nozzle with diameter d = 410 μm. The selected layer height was h = 360 μm (~0.9 d) to ensure better adhesion between the layers and provide appropriate stacking. In the hexagonal pattern, the distance between the filaments on the same layer was also set at w = 360 μm to provide a slight overlap between adjacent filaments; the excess material being extruded would flow and fill the cavities below the previously deposited filament, and therefore promote densification. The theoretical porosity of the four different patterns was evaluated comparing the volume of the struts in the CAD files, assuming that the ink would not flow and fill the pores, with that of a rectangular bar with nominal dimensions of 60.5 x 7.2 x 4.32 mm (equal for all designs). The bars were printed on different substrates in order to compare results.

The printed samples were dried under ambient conditions in closed containers with a water reservoir (100% relative humidity), in order to minimize the evaporation rate.

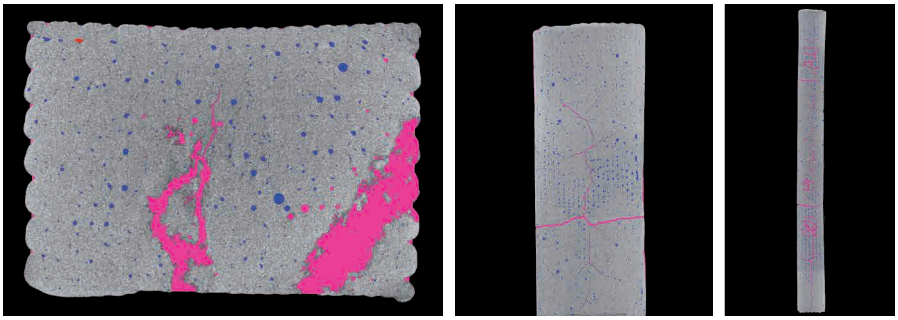
Sintering and Characterization

All samples were debindered and sintered under nitrogen pressure. The bulk density of the sintered bodies was calculated based on their measured mass and dimensions. The bulk density of the sintered parts was measured by the Archimedes' method, while the sintering shrinkage was estimated based on their measured dimensions before and after the heat treatment. At least 6 samples for each combination of printing pattern and substrate were printed; one representative sample for each printing pattern was characterized by CT Analysis.

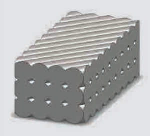
CT Analysis

Green and sintered parts were inspected by X-ray microtomography at YXLON International in Hamburg by an YXLON FF35 CT system with a Micro-focus X-ray tube running with 122 kV and 200 μA. Microfocus mode was chosen with a voxel size of 6.4 μm for the printed parts and a voxel size of the smaller isostatically pressed sample of 2.2 μm. Analysis and measurements were performed with VGSTUDIO MAX from Volume Graphics.

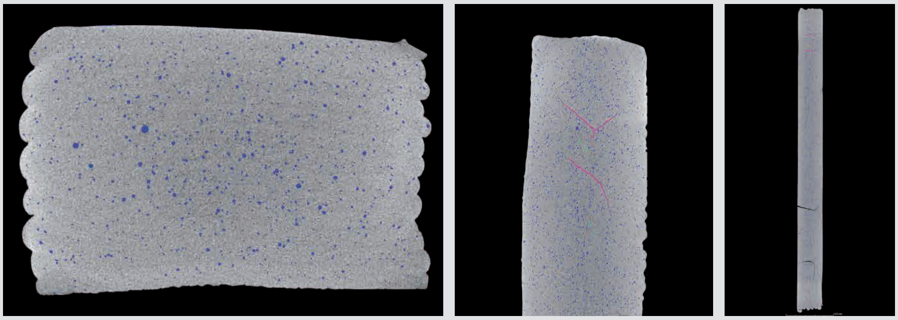
CT cross-sections, **Bars Aligned,** green status[1]:



View: top front right side

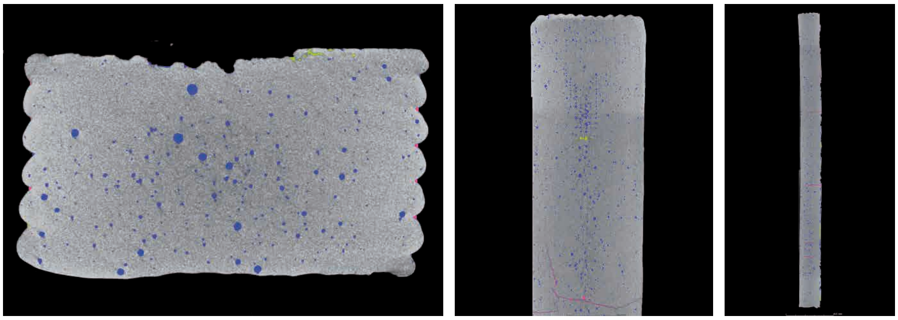


CT cross-section, **Diagonal Bars,** green status:

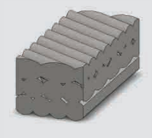


View: top front right side

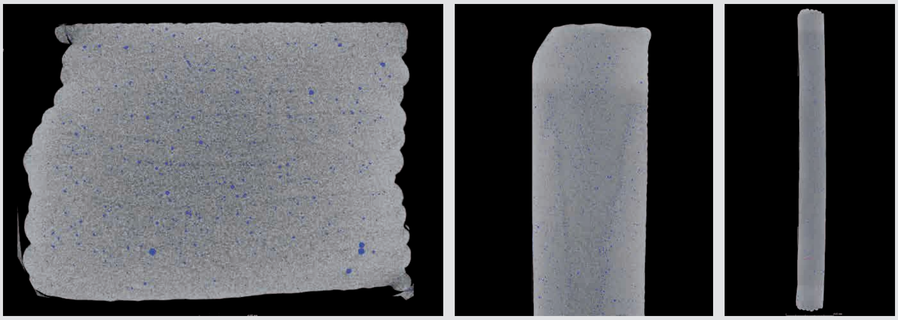
CT cross-section, **Hexagonal Bars,** green status:



View: top front right side



CT cross-section, **Boulingand Bars,** green status:



View: top front right side

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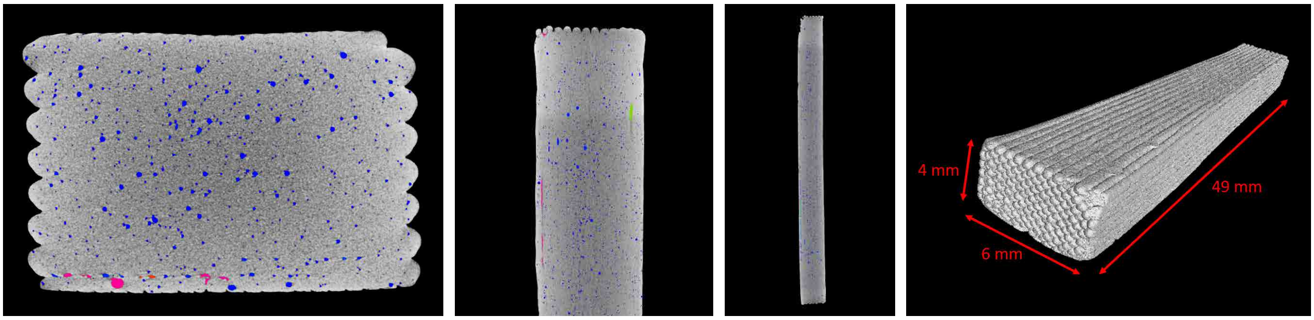
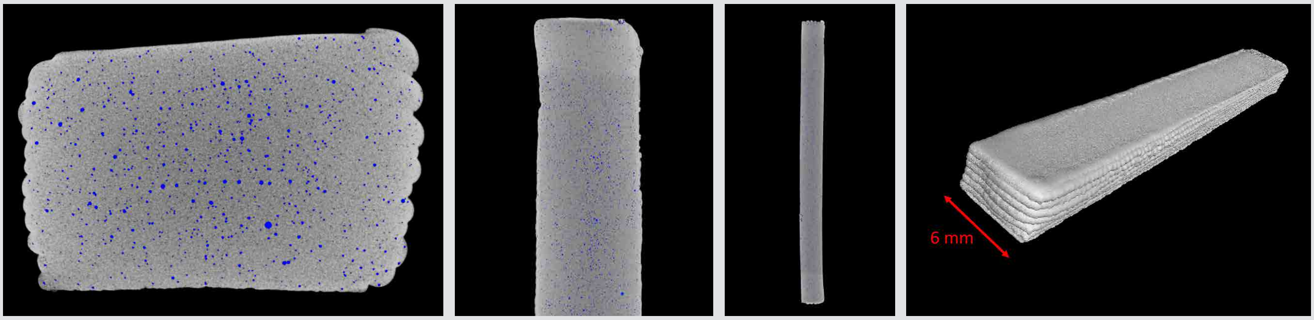
[1] Many defects; pores and cracks. Are there improvements after sintering?

CT cross-sections, **Bars Aligned,** sintered status[2]:



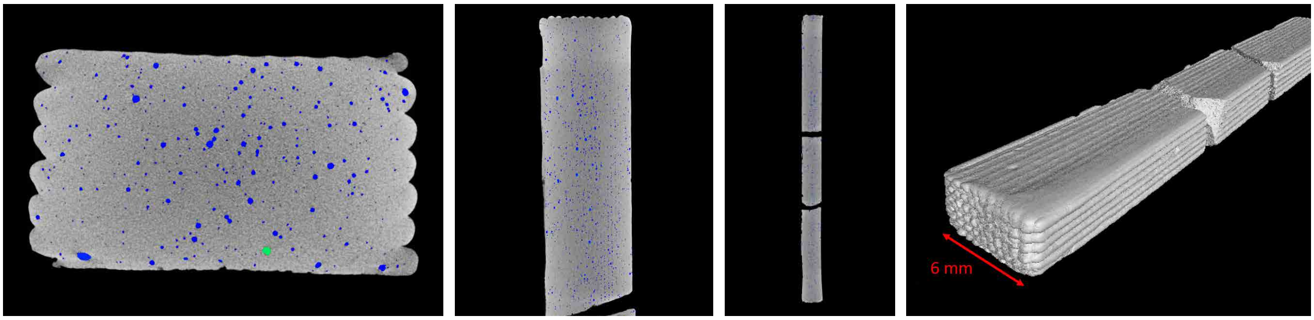
View: top front right side

CT cross-section, **Diagonal Bars,** sintered status:



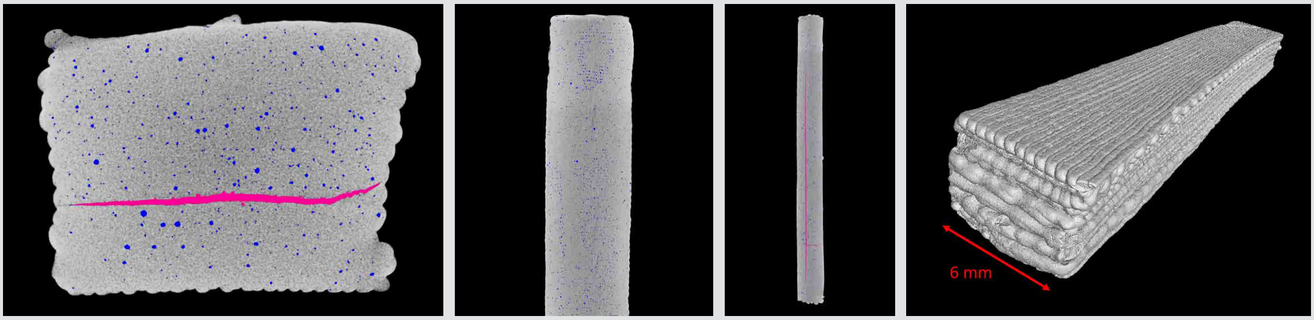
View: top front right side

CT cross-section, **Hexagonal Bars**, sintered status:



View: top front right side

CT cross-section, **Boulingand Bars,** sintered status:



View: top front right side

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[2] Due to overall shrinkage, there is also a shrinkage of the pore volumes, but the amount stays the same

Printing Pattern	Apparent Density [g/cm³]	Measured Volume Shrinkage [%]	Porosity measured by µCT [%]
Alligned	3.11	54.8	2.68
Diagonal	3.15	51.9	2.00
Hexagonal	3.13	broken	2.17
Bouligand	2.51	49,2	2.65

The Results are In

Careful examination of the information lead to clear results. Here are the main findings:

Printing Substrate

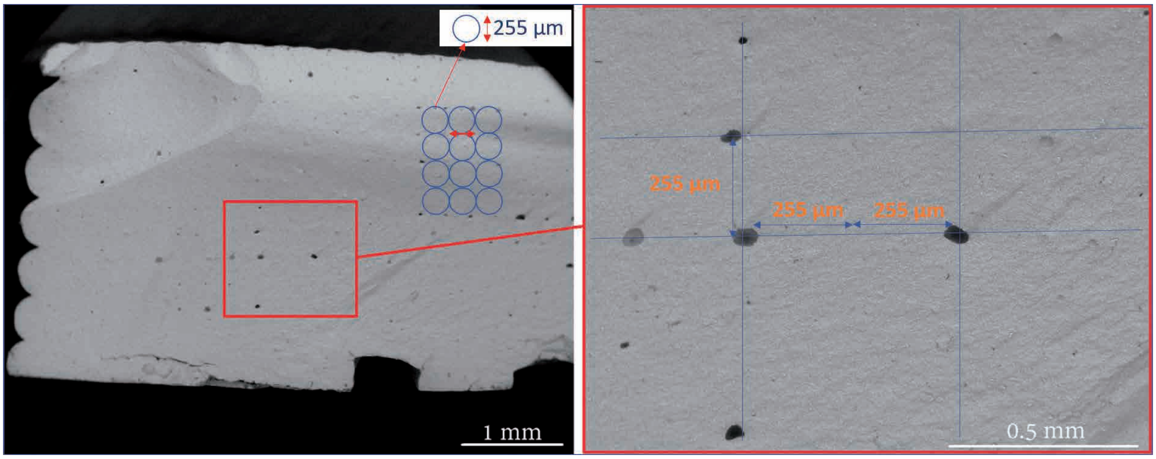
Both printing and drying are influenced by the substrate. The extruded ink should show enough adhesion to the substrate to secure appropriate printing, however, should also be easy to remove after deposition and drying.

Drying of the just printed samples is a critical process. Too fast evaporation of the solvent can lead to cracks. Moreover, warping, delamination and voids at the bottom can result from inhomogeneous drying. The substrate itself should promote homogeneous drying: porous substrates allow for solvent evaporation not only from the top and lateral surfaces, but also from the bottom of the bars.

Dense Teflon and alumina plates and porous silicon carbide plates were tested. The adhesion of the silicon nitride filament to the Teflon plates was not satisfying. Warping of the parts could already be seen during the printing stage, which resulted in the tip of the nozzle running into already printed areas. In addition to that, obvious voids appeared at the bottom surface of the bar. These problems were almost entirely overcome by switching to a porous silicon carbide plate as the printing substrate, thanks to a more homogeneous water removal also from the bottom and possibly a subsequent slip casting effect similar to what observed in the Layerwise Slurry Deposition (LSD) process.

Effect of printing pattern on density (green, sintered) and shrinkage shown by SEM images:
- Pores are located at the interface between the filaments, as one can observe that the interconnections of the pores would form a rectangular grid with an edge length of about 255 µm, which fits the aligned printing pattern.
- The distance between the pores in the printing state is the same as the diameter of the filament. Considering a dry linear shrinkage of about 10–20% and a sintering shrinkage of about 18–20%, for the struts with a diameter of 360 µm we obtain a value between 230.4 and 265.7 µm after sintering, which fits well the measured value of about 255 µm.
- The rheological characterization confirms that the ink behaves as a Herschel-Bulkley fluid with an initial yield stress of about 165 Pa, a consistency of 505 Pa s and a flow index of 0.71 proving its shear-thinning behavior.

Characterization of printed parts (SEM)



Printing clearly obvious from pore structure

360 µm printed

Shrinkage during drying

Shrinkage during sintering

255 µm sintered

Evaluation of CT data

The bars manufactured in this work were inspected in the green and sintered state to see if any conclusions can be drawn by observing defects in the green state and defects in the sintered state, and if predictions on the resulting flaw size are possible. The reconstruction of the CT scan and its analysis was able to show the influence of different printing patterns on the pore size distribution and pore locations.

Conclusions

- CT enables the detection of main characteristics of residual pores including size, distribution, and shape.
- Non-detection of large flaws in the green state can't rule out large voids developing in the sintered parts.
- Final inspection of sintered parts is essential.
- CT offers a nondestructive quantitative test to detect critical defects.
- CT helps gain a perspective of complex shaped parts and aids process control.
- No clear effect on the final pore characteristics of silicon nitride bars fabricated using different printing patterns was observed.
- Printing by DIW of silicon nitride bulk parts with a density of at least 97.3% of the theoretical density was possible. Improvement of the microstructure and porosity, as well as mechanical and thermal characterization of samples, will be the object of further work.
- The number of pores can likely be greatly reduced by degassing of the ink and filling the syringe under vacuum. Additional modification of the geometrical features of the printing patterns, such as the distance between the center of adjacent filaments, as well as changes in the rheological characteristics of the ink (e.g., reducing the yield stress) would also help in further reducing the final porosity of sintered parts.
- To provide more widely valid predictions and statements on residual porosity according to printing patterns, more complex structures as well as other filament sizes should be tested.

Summary

Imagination meets Reality with X-ray Microtomography
The fast-evolving technology of additive manufacturing technology won't be slowing down anytime soon. The demand for more intricate designs as well as new processes is predicted to increase substantially over the next few years. As additive manufacturing becomes a popular choice for more applications in the future, it's critical to ensure that the masterpiece you create performs the same after it's produced. That's why the art of additive manufacturing requires the imagination of a designer, the mind of an engineer, and the insight of X-ray Microtomography.

Meet the Discovery Team

Dr. Giorgia Franchin

Giorgia is a Research Fellow at the University of Padova in Italy where she is focusing on additive manufacturing of ceramic materials (mainly direct ink writing, digital light processing and binder jetting). She works on innovative additive manufacturing technologies and inks for fabricating ceramic and glass components with high porosity and complex shapes. Materials of interest include: preceramic polymers to produce bioceramic scaffolds, electrical components and ceramic matrix composites; geopolymers to develop advanced filters and catalysts; sol-gel materials to increase resolution and expand the materials window.

Sarah Diener

Sarah is the Head of Additive Manufacturing at KYOCERA Fineceramics Precision GmbH in Germany, where she is responsible for all activities in the field from research projects to transfer of new processes and materials to production. Kyocera is involved in many activities regarding 3D printing like the AMITIE project funded by the European Union to strengthen the network of universities and companies working on additive manufacturing of ceramics. The focus on material development is on non-oxide ceramics for high precision parts.

Nils Achilles

Nils is Sales Manager at Yxlon International, responsible for the Labs & R&D markets. In this role, he focuses on the quality assurance and analysis of additively manufactured parts using x-ray computed tomography. CT enables users to analyze the inner structures of objects such as porosity, cracks, and delamination. And additionally, CT is the perfect tool to perform 3-dimensional measurements of internal features of AM parts.

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