Scalability Study of Additive Manufacturing of Silicon Nitride

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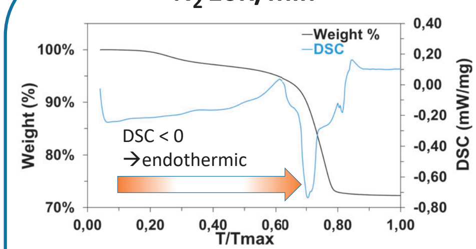
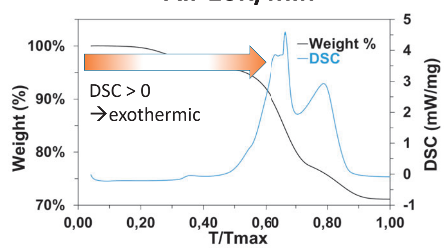
CONTEXT : Stereolithography of UV-curable ceramic suspensions is an additive manufacturing technique with high precision and great resolution to fabricate complex-shaped ceramic parts. While it widens the possibilities of applications, one of the drawback of this method is the low wall-thickness of the parts. The polymers forming the network structure upon cross-linking undergo pyrolysis in a step called debinding, to obtain a pure ceramic part. During debinding, the gaseous compounds going through evacuation channels create internal pressures, often resulting in crack formation. So far, the critical wall-thickness where crackfree parts are obtained is situated around 5 millimeters for silicon nitride. As this ceramic is used for structural applications, the low wall-thickness achievable by stereolithography is a limiting factor for the use of such technology. Therefore, increasing the wall thickness of ceramic parts with good properties would expand the fields in which the advantages of stereolithography can be brought to produce silicon nitride parts. This work is an experimental study of the debinding of silicon nitride parts obtained by stereolithography. Thanks to an optimization of the debinding cycle relying on TGA analysis, defectless parts with a wall-thickness of up to 11 mm were obtained, resulting in parts of 9 mm after sintering. The mechanical properties, as well as the thermal properties were measured, showing values close to dense silicon nitride obtained through conventional methods.

N_2 10K/min



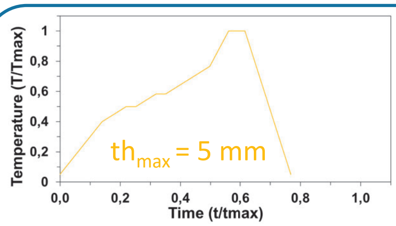
Air 10K/min

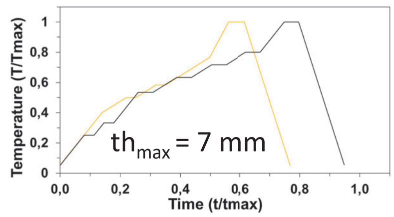


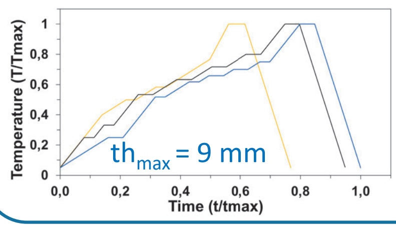
Debinding experiments were performed on **cubes** of size ranging **from 5 to 15 mm.** Based on the TGA under N_2 a debinding profile was built, with significant improvements compared to the industrial cycle achieving a critical wall-thickness of 7 mm, compared to a critical wall-thickness of 5 mm before.

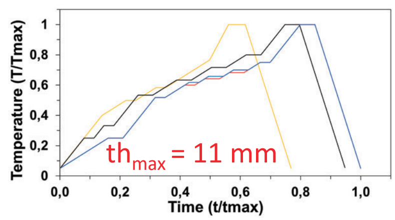
Exothermicity promotes the creation of cracks, therefore a **nitrogen atmosphere** will be used for debinding experiments.

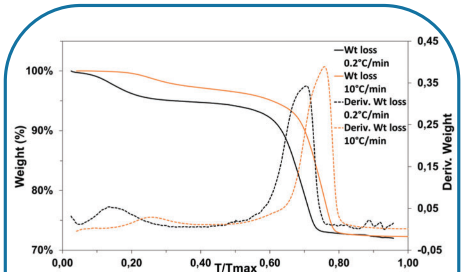
However, the total mass loss is higher under air than nitrogen. This is because the oxygen contained in air is necessary to form carbon dioxide with trapped carbon compounds. During the final step of debinding, air will be introduced to achieve a complete removal of polymers. This is mandatory to avoid pollution during sintering, especially for silicon nitride where silicon carbide could be generated.



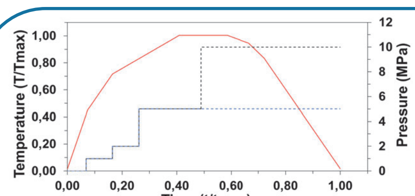


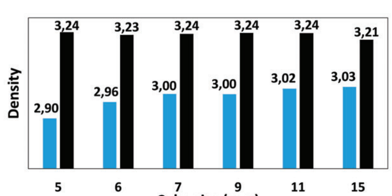




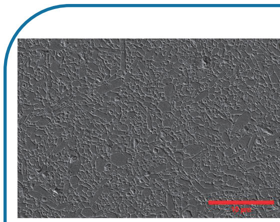


An unconventional TGA at 0,2°C/min, a heating rate close to the one during debinding, has exhibited temperature shifts compared to the TGA at 10°C/min. Adjustments on the debinding cycle were made accordingly, and have yielded a critical wall-thickness of **9 mm** in a first time, before an improvement to **11 mm** after several tries involving minor tweaks on dwelling temperatures.





Sintering of as-debound parts was performed in HIP. A first batch had the nitrogen pressure constant, while a second batch had the pressure being doubled during the dwelling. The latter has yielded parts of higher and more consistant densities. A skin effect is suggested to explain the densities varying with cube size in the first batch.



Rod-shape grains, as expected after sintering

Flexural strength of 393 MPa : lower than expected for Si_3N_4

	92% density	99% density
Hardness (Gpa)	13,95	15,57
Fracture toughness (Mpa.m^1/2)	9,18	10,25

Analyzing thoroughly the TGA carried out on as-printed samples and placing the dwellings accordingly during debinding helped to reduce the risk of cracking and delamination. Performing a TGA at a heating rate close to the one of the debinding was a key step. This method made possible the increase of critical wall-thickness from 5 to 11 mm, for which defectless parts can be obtained after debinding and sintering. Hardness and fracture toughness were found in the usual range for silicon nitride but flexural strength was lower. These findings may enhance the way of using stereolithography for ceramic structural parts. Other parameters such as paste composition or uncured monomers rate were not studied in this work and could help to further increase the critical wall-thickness.