

INVESTIGATIONS ON NITRIDE-BONDED SiC CERAMICS PRODUCED FROM THIXOTROPIC CASTABLES

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ABSTRACT

Owing to a high temperature resistance combined with a high resistance against abrasion and chemical attack, nitride-bonded SiC-based ceramics (NSiC) are often employed as refractory materials in highly corrosive settings. To produce complex-shaped NSiC ceramics, a thixotropic no cement mass was developed allowing to cast semi-finished products which transform during a heat-treatment in a nitrogen gas atmosphere into the desired refractory materials. During this nitridation process, the silicon metal of the castable reacts with nitrogen to form silicon nitrides, which account for the tight binding of adjacent SiC grains in the burnt ceramics.

In this work, the effect of different grain size distributions of silicon and alumina powders added into the thixotropic castable is studied with respect to resulting changes in the phase composition of the NSiC ceramics. Furthermore, the influences of the grain size distributions of these additives on the material strength and the open porosity of the NSiC ceramics are also discussed.

1. INTRODUCTION

Nitride-bonded SiC-based (NSiC) ceramics are employed in numerous high-temperature applications.¹ Typically, the semi-finished products of these ceramics are densified during a ramming process. Ramming is, however, a quite labor-demanding production method which causes high levels of noise and which seems not well suited to produce delicately shaped semi-finished products. An alternative approach could be the

vibrocasting of green bodies from a thixotropic mass. To improve the flowability of the thixotropic mass, calcined alumina can be added into the mixture. As Al₂O₃ is known to facilitate the sintering of silicon nitrides, the addition of alumina presumably also increases the amounts of nitride phases.

Problematic is, however, the simultaneous presence of alumina and silicon powder in the aqueous suspension. Through the contact of alumina with water the pH value increases, promoting a reaction of the silicon powder with water. As a result, an ebullition of the slurry might occur. The effects of the reaction can be diminished by attaining a neutral pH value of the slurry or by reducing the specific surface area of the silicon through enlarging the average grain size of the silicon powder. How the addition of silicon and calcined alumina with different grain size distributions affects the nitridation of the thixotropic castables is investigated in this work.

2. MATERIALS AND METHODS

Thixotropic SiC-based no cement masses were prepared by blending dry mixtures of raw materials with 7 wt% water. The dry mixtures contained about 78 wt% SiC, 15 wt% Si powder, 5 wt% calcined alumina and 2 wt% silica (Tab. 1). Silicon powders in three different grain size distributions (possessing an average grain size diameter of 75 μm or a grain size with a maximum value of 250 and 500 μm, respectively) were added into the mixtures. The samples were named according to their content of fine-grained (F), coarse-grained (C) or very coarse-grained (V) Si powders in the

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dry mixtures (Tab. 1). While the dry mixtures of sample 15F, 15C and 10F5V contained multimodal calcined alumina with a specific surface area of 4.1 g/m², the alumina added in sample 10F5V' was bimodal possessing a specific surface area of 3.0 g/m².

The thixotropic masses were used to cast standard sample bars (230 mm × 54 mm × 64 mm). After drying at 110 °C, preheating at 500 °C and nitridation at 1450 °C, the cold modulus of rupture (CMOR) and the cold crushing strength (CCS) of the bars were probed employing a testing machine of Form+Test. The open porosities of the samples were determined applying the Archimedes' principle.

Tab. 1: Amounts of raw materials combined to dry mixtures. Values are given in wt%.

	SiC	silica	alumina (4.1 m ² /g)	alumina (3.0 m ² /g)	Si (d150 = 75 μm)	Si (0 - 250 μm)	Si (0 - 500 μm)
15F	78	2	5	0	15	0	0
15C	78	2	5	0	0	15	0
10F5V	78	2	5	0	10	0	5
10F5V'	78	2	0	5	10	0	5

Powder X-ray diffraction (XRD) patterns were measured in reflection mode (Bragg-Brentano geometry) on ground pieces of the nitrided samples employing a PANalytical X'pert³ diffractometer. The measurements were conducted with CuKα₁ radiation for a scattering angle 2θ ranging from 5 to 70 deg (Fig. 1).

Qualitative phase analyses were carried out using the computer program HighScore from Malvern Panalytical and database entries of the ICDD (International Centre of Diffraction

Data). Peaks in the diffraction patterns were attributed to reflections of two structure polytypes of moissanite (moissanite-4H and moissanite-6H), corundum, α- and β-Si₃N₄, sinoite (Si₂N₂O), silicon and tungsten carbide (abrasion of the mill). Semi-quantitative phase analyses were performed utilizing HighScore and database entries of the COD² (Fig. 1, Tab. 2).

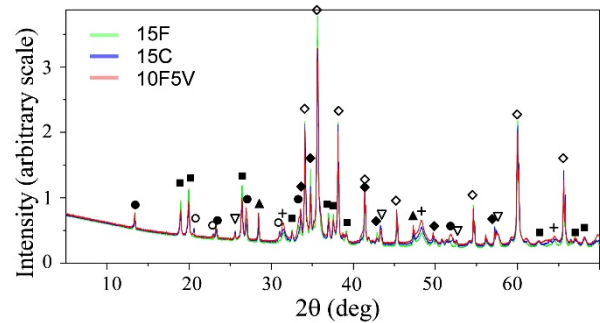


Fig. 1 XRD patterns measured on NSiC samples. Symbols on peaks indicate intensity contributions of phases listed in Tab. 2.

Tab. 2: Origin of crystal structure data used in the phase analysis. Symbols of phases identify peaks in Fig 1.

phase	origin	ID	symbol
silicon oxy nitride	COD	2100737	■
moissanite (6H)	COD	9010158	◇
moissanite (4H)	reference 3		◆
corundum	COD	9009672	▽
α-silicon nitride	COD	1001239	○
β-silicon nitride	COD	1001247	●
silicon	COD	9013108	▲
tungsten carbide	COD	1501588	+

For moissanite-4H, no database entry was found in the COD. To consider this polytype in the phase analyses, crystal structure data of moissanite-4H derived from Bauer³ were inserted in HighScore.

The microstructures of the samples were investigated by scanning electron microscopy (SEM) using a Hitachi TM3000 microscope. Element distributions of selected chemical elements were mapped by using energy dispersive X-ray spectroscopy (EDX).

The oxidation resistance of the NSiC ceramics was probed in a water vapor oxidation test following the standard routine ASTM C863. During the tests, pieces of the NSiC ceramics were exposed to water vapor at 1000°C for 500 hours. The oxidation resistances of the samples are assessed by changes in the weight, volume and porosity.

3. RESULTS AND DISCUSSION

As a result of the nitridation process, the weight of the sample bars increased by about 8 wt%. The bending strengths of the NSiC samples were found to range between 12.5 to 27 MPa (Tab. 3) with the highest value belonging to sample 15F, whose dry mixture contained 15 wt% of the fine-grained Si powder. Although the bending strength of NSiC ceramics are typically higher if the semi-finished products were produced by ramming, bending strengths of 40 MPa and more might also be achieved by nitridation of thixotropic castables if the SiAlON phases form large amounts of elongated crystals with a high aspect ratio.⁴ The compressing strength of the sample bars were higher than the maximal strength attainable by the used testing machine (240 MPa).

The open porosity of sample 15C (15.8 Vol.%) was found to be remarkably higher than the open porosity of 15F (13.8 Vol.%) and 10F5V (13.2 Vol.%), respectively. This observation indicates a lower densification of sample 15C during the nitridation compared to the other samples.

Tab. 3: Selected physical properties of nitrided samples.

	CMOR [MPa]	CCS [MPa]	Porosity [Vol%]
15F	26.9	>240	13.8
15C	12.5	>240	15.8
10F5V	20.8	>240	13.2
10F5V'	18.3	>240	13.7

In all NiSiC samples, unreacted Si metal was found (Fig. 2). It can be assumed that the phase amount of unreacted silicon increases with an increase of the average grain size of the used silicon powder.

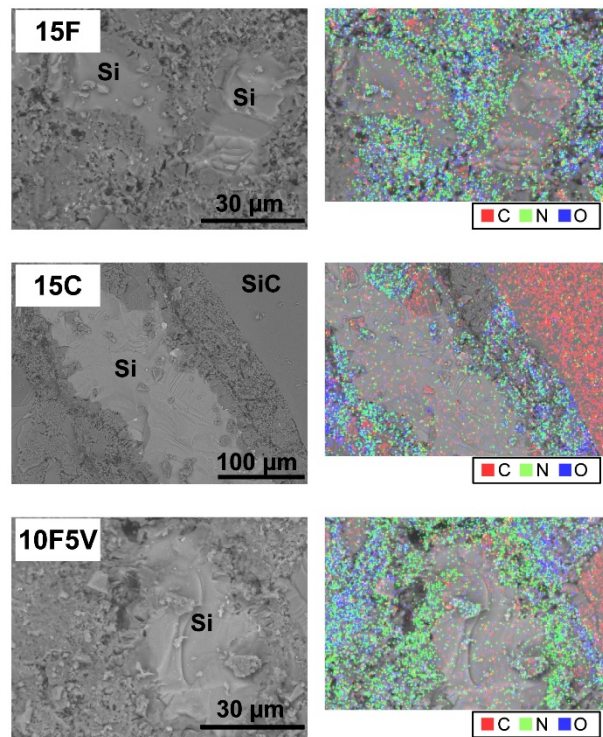


Fig. 2: SEM images of NSiC samples (left), element distributions mapped by EDX for the chemical elements C, N and O (right).

A relatively low amount of silicon determined for sample 10F5V' probably results from an uneven distribution of the silicon content in the sample bars with higher values in the center and lower values at the surface.

The SiC contents of the samples given in Tab. 4 represent the sum of the phase amounts of moissanite-4H and moissanite-6H. The SiC amounts range between 71 and 76 wt% with a noticeably higher value found for 15C than for the other samples (Tab. 4). This circumstance could be caused by a solid solution of SiC in the oxynitride and nitride phases with a larger tendency occurring for samples with a larger amount of nitride phases.

Tab. 4: Phase compositions of nitrated samples, values in wt%.

	SiC	Si ₂ N ₂ O	Al ₂ O ₃	α-Si ₃ N ₄	β-Si ₃ N ₄	Si	others
15F	71.4	18.2	3.0	0.1	5.6	0.7	1.0
15C	75.9	10.5	2.5	2.7	6.2	1.0	1.3
10F5V	70.9	12.6	2.3	0.3	10.4	1.3	2.1
10F5V'	70.8	13.0	2.9	0.4	11.2	0.3	1.4

In the NSiC samples, the phase amount of the oxynitride phase was determined to be ~10 to 18 wt% with the highest value found for sample 15F (Tab. 4). The total amounts of oxynitride and nitride phases is higher in sample 15F (23.9 wt%) and 10F5V (22.9 wt%) than in 15C (19.4 wt%). This lower value for sample 15C seems to be consistent with the higher porosity and the lower strength development in the sample and can be interpreted as a poorer densification of the sample during nitridation compared to the others.

A decrease of the original corundum content (5 wt% in the dry mixtures) to between 2.3 and 3 wt% after nitridation might be related to an uptake of aluminum in SiAlON phases. Al₂O₃ is often used as sintering agent in the production of SiAlON ceramics, in which it can be incorporated in amounts of several weight percent.⁵ By EDX analysis carried out on some nitrogen-rich areas in the vicinity of

silicon grains, predominantly composed of silicon and nitrogen, the aluminum content was estimated to be ~5 wt%.

As finer Al₂O₃ particles can be better incorporated in the SiAlON phases, the use of multimodal alumina (surface area 4.0 m²/g) results in a more even distribution of aluminum in the NSiC ceramic (sample 10F5V, Fig. 3) than through employing bimodal alumina (surface area 3.1 m²/g).

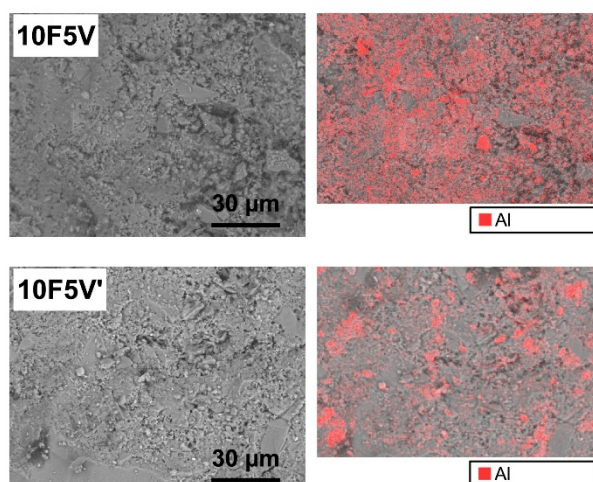


Fig. 3: SEM images of NSiC samples (left) and mapped distribution of Al atoms (right).

Tab. 5: Results of the water vapor oxidation test (500 h).

	weight changes [%]	volume changes [%]	density changes [%]	porosity changes [%]
15C	6.0	12.5	-5.7	-2.2
15F	7.0	14.2	-6.3	4.8
10F5V	5.0	9.2	-3.9	-9.8

Differences in the bending strengths of samples 10F5V and 10F5V' might be caused by a better flowability of the thixotropic mass containing the multimodal alumina. Because the aluminum concentration in SiAlON phases

exerts, however, also an influence on the material strength⁵, the differences might partly be affected by different amounts of aluminum incorporated in the SiAlON phases.

During the water vapor oxidation test, parts of the NSiC ceramics (i.e. mainly nitride phases and fine-grained silicon carbide) are oxidized to silicon dioxide. As consequence of this oxidation process, both the sample weight and the sample volume increase (Tab. 5).

For NSiC ceramics whose green bodies were produced by ramming, a volume change of ~1% or less might be achieved in the oxidation test. The substantially lower oxidation resistance of the ceramics burnt from the thixotropic castables is probably caused by a higher porosity of the SiAlON matrix, allowing a faster penetration of oxygen and water molecules into the intergranular space. Presumably, the oxidation resistance of the ceramics could be improved by increasing the silicon content in the thixotropic castables. In this context, further studies should first clarify whether an ebullition of the thixotropic masses can be avoided by using another solvent than water.

4. CONCLUSIONS

Four thixotropic masses with the same chemical composition but different grain size distributions of added silicon powders and calcined alumina were casted to semi-finished products. The effect of the grain size distributions on the phase composition of the nitrated castables was studied. It was found that a finer grain size in the thixotropic castable is associated with a larger total amount of nitride and oxynitride phases in the NSiC ceramic. A silicon powder with an average grain size of 75 μm was found to be still too coarse-grained to be completely nitrated during the nitridation process. The utilization of a noticeably finer-grained silicon powder, however, is hampered by a reaction between silicon and water leading to an

ebullition of the thixotropic mass during hardening.

The calcined alumina added into the thixotropic masses was either bimodal (surface area 3.0 m^2/g) or a multimodal (4.1 m^2/g). Atom distribution maps of the NSiC ceramics show that if the multimodal alumina was added, the aluminum was more evenly distributed. The NSiC ceramic burnt from the castable containing the multimodal alumina possessed a significantly higher bending strength than the NSiC ceramic obtained from the sample containing the bimodal alumina.

REFERENCES

1. W. Dressler and R. Riedel "Progress in Silicon-Based Non-Oxide Structural Ceramics.", *Int. J. Refract. Met. Hard Mater.*, **16**, 13-47 (1997).
2. S. Gražulis, A. Daškevič, A. Merkys, D. Chateigner, L. Lutterotti, M. Quirós, N. Serebryanaya, P. Moeck, R. Downs and A. LeBail "Crystallography Open Database (COD): an open-access collection of crystal structures and platform for world-wide collaboration", *Nucleic Acids Res.*, **40**, D420-D427 (2012).
3. A. Bauer "Strukturverfeinerungen von Siliziumkarbid-Polytypen", Dissertation, Friedrich-Schiller-Universität Jena (2003).
4. J. Angelkort, N. Fröse, M. Knoll, B. Epstein and I. Hofmann "Development of nitride-bonded refractory ceramics from SiC-based thixotropic NC castables", *Proceedings of the 62nd International Colloquium on Refractories*, (2019).
5. L. Zhang, C. Zhang, Y. Yun, E. Xu, J. Mu, X. Liu, F. Zhao, H. Yuan, J. Cui and J. Gao "Effects of Z-value on physiochemical and biological properties of β -SiAlONs ceramics", *Ceram. Int.*, in press (2021).