DEVELOPMENT OF NITRIDE-BONDED REFRACTORY CERAMICS FROM SIC-BASED, THIXOTROPIC NC CASTABLES

Joachim Angelkort^{*,1}, Natalie Fröse¹, Manfred Knoll¹, Bernd Epstein², Ingo Hofmann²

1 Intocast AG, Westpreußenstraße 30, 47809 Krefeld, Germany 2 VGT-Dyko GmbH, Großalmeroder Str. 18, 37247 Großalmerode, Germany Email:manfred.knoll@intocast.de

Abstract

To complement the production method of SiC-based ceramics fabricated by ramming, a thixotropic no cement (NC) mass was developed allowing for the production of nitride-bonded SiC-ceramics with a complex shape or large size. Nitrided specimens casted from this mass exhibited a similar strength as it can be observed for nitrided specimens of pressed or rammed products. Within this work the properties of nitrided ceramics produced from both a thixotropic and a ramming mass are compared. Moreover, experimental findings derived by electron microscopic studies as well as results of X-ray diffraction investigations on samples of nitride-bonded SiC-ceramic are presented. The influences of some additives on the phase formation during the nitridation and on the resulting microstructure are discussed.

Introduction

Because they possess several outstanding properties, like e.g. a high-temperature resistance combined with a high resistance against corrosion, thermal shock and abrasion, nitride-bonded SiC ceramics are widely used as refractory materials. A comprehensive description of the production of SiC-based ceramics and their applications is given by the publication of Dressler et al. [1]. Generally, the semi-finished products of SiC-based ceramics are produced by ramming or pressing. For the production of delicately shaped ceramics, another well-known production method, the slip casting, is used. To apply this method, usually special casting moulds fabricated of gypsum are employed. These moulds, however, need to be produced in a complex and relatively difficult process, and their drying is energy-demanding. Furthermore, the slip-casting method is applicable for fine-grained slurries only as coarser grains tend to sink down within the slurry. Therefore, a thixotropic no cement SiC-based mass was developed allowing for the production of complex-shaped nitride-bonded ceramics. In this work, the properties of these ceramics are compared to the properties of a ceramic produced from a SiC-based ramming mass.

Within the last years, several investigations have been carried out to scrutinize the catalytic behaviour of different chemical compounds favouring the nitridation of Si and SiC [2-4]. Chen et al. reported e.g. that the degree of nitridation of Si_3N_4 -bonded SiC ceramics can be influenced by tuning the content of carbon black or ferrosilicon in the semi-finished products [2, 3].

At ambient pressure, Si_3N_4 is known to be stable in two modifications, termed α -phase (low-temperature phase) and β -phase (high-temperature phase). By heating, the α -phase irreversibly transforms during a liquid phase reaction into the β -phase causing a densification of nitride-bonded SiC ceramics [1]. Crystals of the β -phase often possess a needle-like crystal shape and can preclude the crack propagation through so-called pull-out and crack-deflection mechanisms exerting an influence on the strength of the ceramics. However, the size and the shape of the crystals of β -Si₃N₄ formed during the nitridation depend on a multitude of parameters as e.g. the temperature [4, 5], the heating rate [6], the chemical composition of the melt [7] and the amount of crystal seeds of β -Si₃N₄ present in the ceramics [5, 8]. In this work, also the effects of an admixing of small amount of α -Si₃N₄, β -Si₃N₄ or fine-grained glass on the phase composition, the microstructure and material properties (CMOR, CCS and porosity) of nitrided ceramics produced from thixotropic masses are investigated.

Experimental

Fabrication of SiC-based refractory ceramics from thixotropic no cement masses

Seven thixotropic no cement (NC) masses composed of the same main constituents but differing in small amounts of additives have been produced. The solid main constituents were 87 wt% SiC, 6 wt% silicon, 5 wt% alumina and 2 wt% of a cement-free binder. The additives were glass powder as well as α - and β -Si₃N₄, which were admixed in amounts of 1 or 2 wt% into the SiC-based NC masses.

The dry mixtures were blended with a small amount of water. The resulting thixotropic masses were used to produce semi-finished products shaped to standard bars (54 mm \times 64 mm \times 230 mm). After drying (24 h at 110°C), the bars were burned for 5 h at 500°C to remove chemically bound water. Nitridation of the bars was accomplished by a firing for several days under nitrogen atmosphere at 1450°C in a kiln.

Fabrication of SiC-based refractory ceramics from a ramming mass

A ramming mass was prepared by mixing 76-85 wt% SiC, 6-12 wt% silicon, 1 wt% SiO₂, 6 wt% clay and 2 wt% special ingredients with water. To determine the bending and the crushing strength of the nitride-bonded SiC ceramic fabricated from this mass, a rectangular bar (54 mm \times 64 mm \times 230 mm) was rammed, nitrided and used for fracture tests.

X-ray diffraction measurements and determination of phase compositions

Diffraction patterns of powder samples from the nitrided ceramics were measured using a Panalytical X'Pert³ X-ray diffractometer $(\lambda(Cu_{Ka}), 40 \text{ kV}, 40 \text{ mA})$. Qualitative and quantitative phase analyses were performed by using the computer program HighScore Plus and database entries of the COD [9] (Crystallography Open Database) and ICDD (International Center for Diffraction Data). Peaks in the diffraction patterns were attributed to reflections of the two most common structural polytypes of SiC, i.e. moissanit-4H and moissanit-6H, as well as α - and β -Si₃N₄, silicon oxy nitride (Si₂N₂O), corundum and silicon (Fig. 1, Tab. 1). While the COD contains reflection and crystal structure data of moissanite-6H (ID 9010158), corresponding data for moissanite-4H is missing in this database. Several peaks in the diffraction patterns, however, were identified as reflections of moissanite-4H using a database entry of the ICDD (ID 00-029-1127). To determine also the phase amount of moissanite-4H in the semi-quantitative phase analysis, crystal structural data of moissanite-4H found in

reference [10] were included in Rietveld refinements performed by using Highscore. The calculations converged with final R_p values of ~7-9%.



Fig. 1: X-ray diffraction pattern measured on sample REF. Symbols used in the figure indicate peaks assigned to phases listed in Tab. 1.

Tab.1: Name of phases and ID numbers of used database entries. Shown symbols identify peaks of corresponding phases in Fig 1.

phase	data base	ID number	Symbol
silicon oxy nitride	COD	2100737	
moissanite (6H)	COD	9010158	\diamond
moissanite (4H)	ICDD	0291127	•
corundum	COD	9009672	\bigtriangledown
α-silicon nitride	COD	1001239	0
β-silicon nitride	COD	1001247	•
silicon	COD	9013108	

Electron microscopic investigations

The microstructures of the nitrided ceramics were studied by scanning electron microscopy (SEM). For a better resolution of the area at grain boundaries, the surfaces of the samples were polished. The polishing was accomplished by a manual treatment of the samples using diamond pastes in the decreasing grain sizes 6, 3 and 1 μ m. Through the application of energy dispersive X-ray spectroscopy (EDX), images showing the element distributions of selected chemical elements were recorded (Fig. 2).

Results and Discussion

In the following discourse the properties of nitrided SiC ceramics are compared in respect to their phase composition, cold modulus of rupture (CMOR), cold-crushing strength (CCS) and open porosity to determine how the properties of SiC ceramics can be influenced by the admixing of the different additives. The denomination of the samples produced from thixotropic NC castables reflects the amount of admixed additives, whereas a reference sample into which none of the additives was admixed was termed REF (Tab. 2).

Tab. 2: Overview of the produced thixotropic NC masses.

sample	type and amount of used additives
REF	none
1B	$1 \text{ wt\% } \beta\text{-Si}_3N_4$
2B	$2 wt\% \beta$ -Si ₃ N ₄
1G	1 wt% fine-grained glass
2B2G	2 wt% $\beta\text{-}Si_3N_4\text{,}~2$ wt% fine-grained glass
2A	$2 \text{ wt\% } \alpha \text{-} Si_3N_4$
2A1G	$2 \text{ wt\% } \alpha \text{-} Si_3N_4, 1 \text{ wt\% fine-grained glass}$

In a preliminary test, the phase composition of a bar which had the same original composition as sample REF was determined after heating the sample for 5h to 500°C in air. A quantitative phase analysis indicated the sample to be composed of 73 wt% moissanite-6H, 14 wt% moissanite-4H, 6 wt% silicon, 5 wt% corundum and 2 wt% different phases of small quantities.

Through the nitridation, the phase content of α -Si₃N₄ and β -Si₃N₄ in the sample REF increased to 0.4 and 6.3 wt%, respectively. The content of silicon oxy nitride was found to be 9.3 wt% (Tab. 3). In images of the element distribution measured by EDX, areas with higher nitrogen concentration (Si₃N₄ phases and Si₂N₂O) can be differentiated from areas with higher oxygen concentrations (corundum) and carbon concentrations (SiC). These distributions visualize the phase intergrowth resulting from the nitridation of the SiC-based ceramic (Fig. 2).



Fig. 2: (a) SEM image of the reference sample REF, (b) element distribution for carbon, nitrogen and oxygen.

For the ceramic produced from the ramming mass (termed RAMMED), the amounts of α -Si₃N₄, β -Si₃N₄ and Si₂N₂O were quantified to be 3.0, 3.2 and 13.5 wt%, respectively (Tab. 3). While the β -Si₃N₄ contents in the samples REF and RAMMED are of similar height, the sample RAMMED possesses higher values for the α -Si₃N₄ and Si₂N₂O content (Tab. 3).

As sintering aid, 5 wt% of alumina were added into the thixotropic castables effecting also a decrease of the activation energy required for the α -to- β phase transition of Si₃N₄ [5]. Differences in the content of corundum found in the samples may result from an incorporation of Al₂O₃ in β -Si₃N₄ by forming sialones or the formation of Al₂O₃-containing melts. A differing of the amount of SiC-H6 and SiC-H4 in the samples (Tab. 3) is probably caused by small variations of the phase contents of the polytypes in the raw material.

The samples into which 2 wt% of α -Si₃N₄ was admixed (samples 2A and 2A1G), contained after the nitridation about 5 wt% α -Si₃N₄ and a significantly smaller amount of β -Si₃N₄ than the reference sample REF. Conversely, samples into which small amounts of β -Si₃N₄ were admixed (samples 1B and 2B) contained

about 10 wt% β -Si₃N₄ after nitridation and small amounts of α -Si₃N₄. The admixing of small amounts of α - and β -Si₃N₄ thus favours the formation of the corresponding phases during the nitridation process consistent with a faster crystal growth through the presence of crystal nuclei. The possibility to direct the phase formation by the admixing of nucleating agents seems to be a simple way to optimize the material properties of the nitridebonded ceramics.

Tab. 3: Phase compositions in wt% for different nitrided samples.

	C-H6	C-H4	O_2N_2O	rundum	$\rm Si_3N_4$	${\rm Si_3N_4}$	hers
	Si	Si	S	c0	α-	β-	ot
REF	66.5	12.6	9.3	3.6	0.4	6.3	1.4
1B	67.1	9.4	8.0	4.3	0.4	10.0	0.8
2B	61.6	13.7	8.3	3.8	0.7	10.8	1.1
1G	65.0	14.1	12.8	4.8	0.4	1.2	1.7
2B2G	61.5	15.1	13.3	3.8	0.6	4.6	1.1
2A	67.0	10.1	7.9	4.4	5.0	4.5	1.1
2A1G	66.8	9.6	10.1	4.6	4.6	3.1	1.2
RAMMED	61.5	11.9	14.9	0.0	3.4	7.7	0.7

standard uncertainties of listed values are smaller than 1.0 wt%

According to numerous reports in the literature, crystals of pure β -Si₃N₄ possess a needle-like crystal shape and their formation in SiC ceramics is supposed to increase the bending strength of the material by a so-called pull-out mechanism, which pertains the bridging of cracks by crystals embedded in the matrix of the ceramic [1, 7, 8]. Indeed, samples B1 and B2, which contained the highest amounts of β -Si₃N₄, also possess the highest bending strengths found for the ceramics produced from the thixotropic masses (Tab. 4).

Tab. 4: Material properties determined for different samples.

sample	CCS [MPa]	CMOR [MPa]	Porosity [Vol.%]
REF	197	34.6	14.6
1B	187	47.7	15.0
2B	181	41.2	15.5
1G	224	34.5	15.2
2B2G	198	26.2	15.3
2A	189	34.1	15.0
2A1G	189	37.9	16.3
RAMMED	>250	51.8	14.4

s. u. of values for the CCS (CMOR) are smaller 5 MPa (2MPa) and of values for the porosities smaller 1Vol.%, respectively

The formation of β -Si₃N₄ as a function of the number of crystal nuclei and the coexistence of the α - and the β -phase of Si₃N₄ in samples 2A and RAMMED indicate that β -Si₃N₄ can form under the experimental conditions which were used by us to nitride SiC ceramics through both a growth of crystal nuclei and a phase transition from α - to β -Si₃N₄.

The rate constant for the α -to- β phase transition of Si₃N₄ was determined experimentally by Bučevac et al. for hot-pressed samples (40 MPa, 1500°C < T < 1600°C) [5]. Through extrapolation of their data to a temperature of 1450°C, the value of the rate

constant is expected to be ~0.0025 /min. According to this value, roughly the half of the initial α -Si₃N₄ content should transform into β -Si₃N₄ under a 40 MPa load within approximately 4.5 h. As no load pressure was used during the nitridation of our samples, the reactivity of Si₃N₄ is apparently diminished in such a degree that high amounts of α -Si₃N₄ can coexist with β -Si₃N₄ (samples 2A and 2A1G) for the time of nitridation. However, as witnesses the phase composition of sample RAMMED (Tab. 3), even without the addition of the sintering aid Al₂O₃ and crystal nuclei of β -Si₃N₄ a high amount of α -Si₃N₄ can transform into β -Si₃N₄ if the sample is highly densified.

Because the phase transition from the α - into the β -Si₃N₄ involves the precipitation of crystals of the β -phase from a melt [5-7], it seems interesting to investigate whether the admixing of finegrained glass into thixotropic castables would change the phase compositions of the samples during nitridation.

Although the sample 2B2G, which was seeded with 2 wt% β -Si₃N₄, contains a considerable amount of β -Si₃N₄ (4.6 wt%), the samples into which glass was added (samples 1G, 2B2G and 2A1G) possess much smaller amounts of the β -Si₃N₄ than the reference sample REF. Concomitantly, the amounts of Si₂N₂O in these samples are higher than in sample REF. The addition of the glass powder seems to perturb the transformation of α - to β -Si₃N₄ by the nitridation of the SiO₂-rich melt. Lee et al. reported that the increase of the Si_2N_2O content by the addition of SiO_2 in nitride-bonded SiC ceramics does also affect the shape of the β -Si₃N₄ crystals and by this eventually the porosity of the ceramics [7]. Although no clear correlation of an increase of the porosity with increasing Si₂N₂O contents can be found by comparing the values listed in Tabs. 3 and 4, the presence of the SiO₂-rich melt apparently exerts a higher influence on the formation of β -Si₃N₄ than on the formation of α -Si₃N₄. By comparing the phase contents of the samples 2A and 2AG1, it can be noticed that sample 2AG1, the sample into which the glass powder was admixed, possesses a ~10% smaller value of the α -Si₃N₄ content and a ~30% smaller value of the β -Si₃N₄ content, respectively. In sample G1 the β -Si₃N₄ content is even ~80% smaller than in the reference sample REF.

The ceramics produced from the thixotropic NC masses possessed bending strengths (CMOR) of 25 to 50 MPa, cold crushing strengths (CCS) of 130 to 230 MPa and open porosities ranging from 14.6 to 16.5 Vol% (Tab. 4). For the sample RAMMED, the ceramic produced from the ramming mass, the bending strength was determined to be 51.8 MPa, the CCS was found to be larger than 250 MPa and the open porosity to be 14.4 Vol% . Compared to the other samples of Tab. 4, sample RAMMED possesses therefore the highest values for CMOR and CCS as well as the lowest value found for the open porosity. The values of CMOR and CCS of the ceramics produced from the thixotropic masses, however, can apparently be optimized by a proper choice of additives resulting in strengths almost as high as these of the sample RAMMED.

To visualize the influence of the phase contents of α -Si₃N₄, β -Si₃N₄ and Si₂N₂O on the material strength of the ceramics produced from the thixotropic masses, CMOR and CCS values were plotted against the three phase amounts in Fig. 3. For changes in the α -Si₃N₄ contents, no clear trend of the CMOR and CCS values can be recognized. Increasing phase contents of β -Si₃N₄, however, are associated with an increase of the CMOR value and a decrease of the CCS value of the samples. A correlation of the bending strength with the β -Si₃N₄ content of the samples can be possibly attributed to the described pull-out effect [1, 7, 8]. A decrease in the cold-crushing strength for increasing β -Si₃N₄ contents might be caused by an increase of the porosity through the growth of elongated β -Si₃N₄ crystals. Increases in the Si₂N₂O content of the samples are found to be accompanied by a decrease of the CMOR value and an increase of the CCS value (Fig. 3). These trends are caused by the decrease of the β -Si₃N₄ content for an increase of the Si₂N₂O content, but possibly also reflect, in parts, a lowering of the aspect ratios of the β -Si₃N₄ crystals by increasing the phase amount of Si₂N₂O as it was observed by Lee et al. [7].



Fig. 3: Values of CMOR and CCS plotted against the α -Si₃N₄, β -Si₃N₄ and Si₂N₂O phase contents of the samples.

Conclusion

An addition of small amounts of α -Si₃N₄, β -Si₃N₄ or fine-grained glass in SiC-based NC thixotropic masses influences the phase

formation during the nitridation of the ceramics. The modulus of rupture of the nitrided ceramics increased significantly if small amount of β -Si₃N₄ were admixed into the thixotropic masses. Conversely, if fine-grained glass was employed as an additive, the nitridation of the ceramics resulted in a formation of lower Si₃N₄ and higher Si₂N₂O contents affecting a decrease of the bending strength of the samples.

The experimental findings also testify that thixotropic NC masses can successfully be used to produce nitride-bonded SiC ceramics of similar strengths as they can be produced from the nitridation of ramming masses. The application of thixotropic NC SiC masses therefore offers an elegant and effective way to produce nitride-bonded ceramics possessing a complex shape.

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