INFLUENCE OF A CALCIUM ALUMINATE CEMENT ON THE PROPERTIES OF NITRIDE-BONDED SIC CERAMICS PRODUCED FROM THIXOTROPIC CASTABLES

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Abstract

Large or complex-shaped bodies of nitride-bonded SiC-based ceramics can successfully be produced from thixotropic castables by burning of semi-finished products in a nitrogen atmosphere. To reduce the fragility of the semi-finished products, typically composed to about 90% of silicon carbide and silicon metal, a calcium aluminate cement (CAC) might be admixed in the castables serving as a binder. The presence of calcium-rich phases, however, can result in the formation of calcium silicates during the nitridation and alter drastically the physical properties of the nitride-bonded SiC ceramics.

In this work, the influence of a CAC admixed into thixotropic castables is studied in respect to its effect on the phase composition and the physical properties of nitride-bonded SiC ceramics produced from the castables. To determine the phase composition of the ceramics, quantitative phase analyses were carried out using measured powder X-ray diffraction data. Standardized test methods were applied to measure the cold modulus of rupture (CMOR) and the cold crushing strength (CCS) of the nitrided samples. The microstructures of the samples were investigated by scanning electron microscopy. Additionally, water vapor oxidation tests were undertaken to probe the oxidation resistance of the samples.

Introduction

For the refractory production, thixotropic masses are widely used. Often these masses contain small amounts of a calcium aluminate cement (CAC) to increasing the green strength of the semi-finished products. For masses containing several percentages of both silicon powder and silicon dioxide, respectively, an addition of calcium-rich phases seems, however, to be problematic as calcium silicates might form at high temperatures, and because the occurrence of these silicates in SiC ceramics is generally associated with a lowering of the high-temperature performance of the ceramics [1].

Due to a low sinterability of SiC, the nitridation of SiC-based ceramics can be used as an alternative approach to establish a binding between SiC grains mediated by silicon nitride and oxynitride phases. Silicon nitride can crystalize in two modification, termed α - and β -Si₃N₄. Both modifications can incorporate Al and O atoms by a formal substitution of Si and N atoms, respectively, resulting in the formation of a compound called SiAlON. The composition of the SiAlONs might be expressed as Si_{3-x}Al_xO_xN_{4-x} (with x standing for the Al and O content, respectively).

In the α -SiAlON, a certain amount of Si atoms can be formally replaced through the same number of Al atoms by balancing electroneutrality by accommodating Ca atoms on empty sites in the crystal structure [1-4]. As this cation exchange results in an increase of the thermal stability of the α -SiAlON phase, the presence of calcium atoms in some ceramics can even be advantageous for their high-temperature resistance, depending on the phases which form.

The phase formation during the nitridation process is essentially influenced by the choice of the precursor materials, the bulk composition of the ceramics, a possible pre-treatment of the materials, and the conditions prevailing during the nitridation [5, 6]. Whether calcium silicate phases do form during the nitridation of the semi-finished products or not and which are the effects of the admixed CAC regarding to the properties of the ceramics is scope of this work.

Experimental

Sample preparation

SiC raw materials with different grain size distributions, fine grinded Si powder, SiO₂ powder, a commercially available calcium aluminate cement (CAC) and small amounts of other ingredients were combined to dry mixtures. In these mixtures, the sum of the contents of SiC and CAC was balanced to a value of 84 wt% for each sample, the contents of Si, SiO₂ and the other ingredients were 9 w%, 2 wt% and 5 wt%, respectively. The CAC used for the experiments is mainly composed of krotite (CaO·Al₂O₃ or CA) and grossite (CaO·2Al₂O₃ or CA₂) with phase contents of ~95 and ~4 wt%, respectively. It was added into the castables in amounts of 0.5, 1.0, 2.0 and 4.0 wt%. According to the admixed CAC amount, the samples were termed NC, 1C, 2C and 4C. The thixotropic masses were prepared by blending the dry mixtures with 7 wt% water and casted to sample bars (54 mm \times $64 \text{ mm} \times 230 \text{ mm}$). To evaporate chemically bound water, the bars were dried for 24 hours at 110°C and then tempered for another 5 hours at 500°C. For nitridation, the samples were burned for several days at 1450°C in a nitrogen atmosphere.

Determination of strengths and porosities of samples

Bending and cold crushing strengths of the nitrided sample bars were probed by applying DIN 51010. The open porosities were determined according to DIN EN 993-1.

X-ray diffraction measurements

Powder X-ray diffraction diagrams were measured on grinded samples of the nitrided ceramics using a X'Pert³ diffractometer from PANalytical (Fig.1). The measurements were carried out in reflection mode (Bragg-Brentano geometry) for a scattering angle 20 ranging from 5 to 70 deg. employing CuK α_1 radiation. Each diffraction pattern was measured within about 90 minutes.

Qualitative and quantitative phase analyses were accomplished by applying the software program HighScore Plus in combination with database entries of the COD (Crystallographic Open Database) [7].

Scanning electron microscopic investigations

Pieces of nitrided samples were fixed on carbon fiber plates and investigated using a TM3000 scanning electron microscope (SEM) of the company Hitachi. To ease differentiation of depicted phases, element distributions of selected chemical elements were determined by energy dispersive X-ray spectroscopy (EDX) and visualized in false color images using the software Quantax (Bruker).

Water vapor oxidation test (ASTM C863)

To compare the extent of oxidation experienced by the nitrided ceramics produced from the CAC-bearing thixotropic castables, water vapor oxidation tests were carried out. For that purpose, parts of the samples, cuboids cut to about 4×4×3 cm³ in size, were exposed to water vapor at 1000°C for 500 hours. Changes in weight, volume and porosity were determined every 100 hours.



Fig.1: XRD patterns measured on nitrides samples.

Results and Discussion

While the nitridation of the samples caused an average weight increase of about $4.7\% \pm 0.1\%$, no significant volume changes were found. The cold modulus of rupture (CMOR) and the cold crushing strength (CCS) determined for the sample bars of the nitrided ceramics change as a function of the amount of calcium aluminate cement (CAC) added into the thixotropic masses. For an increase of the CAC content from 0.5 to 2.0 wt%, the CMOR value of the samples decreases from 18.4 to 14 MPa and the CCS values from 171 to 160 MPa (Tab. 1).

Tab. 1: Selected physical properties of the nitrided samples.

		CMOR [MPa]	CCS [MPa]	porosity [Vol.%]
	NC	18.4	171	16.5
	1C	17.2	162	16.3
	2C	14.0	160	16.9
	4 C	14.2	208	16.2

Sample 4C, however, possesses a CMOR of similar height as sample 2C and a clearly higher CCS (208 MPa) than the other samples. The high CCS value of sample 4C might be caused by the high amount of melt which formed during the nitridation of the sample. Because the liquid phase is of central importance to sinter SiC grains and to promote a transition of α -Si₃N₄ into β -Si₃N₄, its occurrence during the nitridation might be expected to have a strong impact on the strength development of the ceramics. By cooling, the liquid phase forms a crustaceous coating which increases the mechanical stability of the microstructure against compression. While the coating in sample NC, 1C and 2C possess a comparatively rough appearance, the surface of the solidified melt of sample 4C seems to be rather featureless and smooth (Fig. 2). The granular appearance of the coatings in sample NC is mainly caused by a direct neighboring of grains of silicon nitride a few micrometers in size (Figs. 2 and 3). In contrast, small grains of silicon nitride and corundum are enclosed in the coating of sample 2C (Figs. 3 and 4).

Despite a smooth appearing surface, the solidified melt of sample 4C consists of areas differing remarkably in their oxygen and nitrogen concentrations (Fig. 3). Some areas with high oxygen contents also possess high concentrations of aluminum and presumably constitute small crystals of corundum.

According to a decrease of the melting temperature of silicate glasses for increasing CaO contents, an increase of the amount of liquid phase in the nitride-bonded ceramics can be expected to occur quantity-dependently with respect to the addition of the CAC in the thixotropic masses. The high CAC content admixed in the semi-finished product of sample 4C results in a high calcium content of the solidified liquid phase of this sample after nitridation (Fig. 4). The large amount of liquid phase formed in sample 4C is associated with a particularly high crushing strength.



Fig. 2: Images of nitrided samples captured by SEM.



Fig. 3: EDX maps showing element distributions of C, N and O.

The crystalline phases of the nitride ceramics were identified by powder X-ray diffraction. Peak positions in measured diffractograms were assigned to reflections of moissanite (SiC), sinoite (Si_2N_2O), corundum, α - and β - Si_3N_4, silicon, mullite and anorthite (Fig. 1). The occurrence of broad peaks in the diagrams at a scattering angle 20 of 31.5 and 48.3 deg. were attributed to a slight contamination of the samples with tungsten carbide, which was abraded from parts of the disk mill during sample grinding. As can be seen from the results of the quantitative phase analyses (Tab. 2), the amount of anorthite found in the nitride-bonded ceramics increases with the initial CAC content of the thixotropic masses used to produce the ceramic. While the samples NC and 1C contain ~1 and ~2 wt% of mullite after nitridation, respectively, for samples 2C and 4C the mullite content was found to be zero. This, together with the fact that 2C and 4C contain higher corundum contents than NC and 1C after the nitridation indicates that SiO₂ reacts preferentially with calcium aluminates to anorthite instead with Al₂O₃ to mullite. The SiO₂ in the sample might, however, also react during the nitridation with silicon nitrides to Si_2N_2O causing a lowering of the bending strength of the ceramics [8, 9].

As the fines of the semi-finished products used for our experiments contained considerable amounts of SiC and Ca-rich phases, the SiAION forming during the nitridation might incorporate several atom percent of Ca and C. The values of the lattice parameters of the α -SiAION phase determined in the quantitative phase analyses correspond, however, rather to the values of the pure α -Si₃N₄ than to the values of calcium-rich SiAION given in [2]. Thus, the calcium content of the α -SiAION phase in the samples of the nitride-bonded ceramics is assumed to be low. As the incorporation of calcium atoms in the α -SiAION is restricted to low oxygen contents of the compound [2, 3, 4], a too high oxygen concentration in our ceramics probably precluded the formation of the Ca-SiAION. This is probably also the reason why no clear trend in the change of the α -Si₃N₄ phase content for different CAC contents of the castables could be observed.

Tab. 2: Phase compositions of nitrided samples.

	Moissanite (SiC)	Sinoite (Si ₂ N ₂ O)	Corundum	α -Si ₃ N ₄	β -Si ₃ N ₄	Silicon	Mullite	Anorthite	Tungsten carbide
NC	80.6	9.7	3.8	1.0	2.0	0.8	1.1	0.1	0.9
1C	82.9	7.6	4.0	0.7	1.0	0.7	1.7	0.3	1.1
2 C	73.5	11.3	6.8	1.3	2.8	0.6	0.0	3.2	0.5
4C	75.5	6.5	5.6	0.2	3.2	0.9	0.0	7.8	0.3



Fig. 4: EDX maps showing element distributions of Ca and Al.

To investigate how the oxidation resistance of the nitrided ceramics depend on the initial CAC contents of the samples, water vapor oxidation tests were carried out. During the oxidation test fine grains of SiC as well as parts of the Si_3N_4 and Si_2N_2O in the nitrided samples react with water vapor forming silicon oxide and volatiles. The decrease of the SiC content and the increase of the cristobalite content of the samples seem to be inversely related to their Ca content (Tab. 3). After an oxidation test of 500 h, the amount of SiC in sample NC decreased to 55.7 wt% and the amount of cristobalite increased to 32.6 wt%. For sample 4C, in contrast, the SiC content remains unchanged by the test and its cristobalite content (9.9 wt%) after the test corresponds to the amounts of nitrides and oxynitrides found for the sample before the test (Tab. 2). Since the increase of the CAC content in the thixotropic castables is related with a formation of a higher amount of glassy phase during nitridation, a covering of the SiC grains by the glassy phase probably prevents their oxidation to cristobalite.

During the oxidation test, relative changes in weight, volume, density and porosity of the samples were determined after 100, 200, 300, 400 and 500 hours (Tab. 4). Figure 5 shows the results of table 4 together with lines depicting the trend of the changes graphically.

Due to the oxidation reactions the weight and the volume of the samples were found to increase. As the increase of the relative volume change is larger than the relative weight change, a decrease of the density of the sample results (Fig. 5). The open porosities of the samples were found to decrease drastically during the first 100 hours of the oxidation test, pointing to a fast deposition of SiO₂ in the pores of the sample at the beginning of the oxidation test. For the subsequent periods, an increase of the open porosity is observed, which might be affected by a grain growth allowing likewise the size of cavities to increase.

Tab. 3: Phase compositions after 500 h of oxidation test.

	Moissanite (SiC)	Sinoite (Si ₂ N ₂ O)	Cristobalite	Quartz	Corundum	α -Si ₃ N ₄	β -Si ₃ N ₄	Mullite	Anorthite	Tungsten carbide
NC	55.7	0.6	32.6	2.0	3.4	0.4	0.8	4.6	0.0	0.1
1C	62.2	0.7	23.8	1.5	2.2	0.7	0.6	5.0	0.9	0.4
2 C	73.3	0.7	14.0	3.2	4.0	1.0	0.5	0.3	2.1	0.9
4C	75.5	0.4	9.9	2.2	4.2	0.6	0.1	0.0	6.4	0.6

Tab. 4: Changes of selected properties during the oxidation test.

	100 h	200 h	300 h	400 h	500 h				
weight changes [%]									
NC	2.6	3.5	4.2	5.0	5.7				
1C	2.7	3.7	3.9	5.4	6.3				
2C	2.0	2.9	3.6	4.3	5.2				
4C	1.4	2.1	2.7	3.4	4.4				
volume changes [%]									
NC	3.1	5.2	7.2	9.5	12.1				
1C	3.1	5.8	7.9	11.3	14.5				
2C	2.5	3.9	5.9	7.0	9.8				
4C	2.4	4.1	5.7	7.8	10.8				
density changes [%]									
NC	- 0.5	- 1.6	-2.8	- 4.1	- 5.7				
1C	-0.4	-2.0	- 3.7	- 5.3	- 6.7				
2C	-0.4	- 1.0	-2.2	-2.5	-4.2				
4C	- 1.0	- 1.9	-2.9	- 4.1	- 5.8				
porosity changes [%]									
NC	-23.3	- 16.6	- 13.3	- 9.0	-4.5				
1C	-20.7	-25.4	- 7.8	- 5.1	- 3.2				
2C	- 16.4	- 16.2	- 12.5	- 13.1	- 8.5				
4C	-9.4	- 6.8	-2.0	2.3	7.2				

For the ceramics 2C and 4C, whose castables contained 2 and 4 wt% of the CAC, respectively, smaller changes of the weight



Fig. 5: Changes of selected properties during the oxidation test.

and volume are found than for the samples NC and 1C (Fig. 5). As the amount of glassy phase is clearly higher in sample 2C and 4C than in NC and 1C, probably the lower weight and volume changes might be attributed to the effect of the glassy phase to hamper the reaction of SiC grains with water vapor.

Consistently, for sample 4C, containing the highest amount of glassy phase, the smallest decrease of the open porosity was found during the oxidation test underlining once more the implication of the glassy phase in respect to the oxidation resistance of the nitride-bonded ceramics.

The α -to- β phase transition of Si₃N₄ is associated with a liquid phase reaction during which α -Si₃N₄ is resorbed by the melt and crystals of β -Si₃N₄ precipitate. As sample 4C contains a high amount of glassy phase, its high β -Si₃N₄ content relative to the α -Si₃N₄ amount in the sample and a lacking of well-developed Si₃N₄ crystals might be indications for the β -Si₃N₄ crystals to reside in the glassy phase possessing grain sizes below the micrometer scale.

Conclusions

In this work, the effect of admixing 0.5 to 4 wt% of a calcium-aluminate cement (CAC) into SiC-based thixotropic masses was studied in terms of its influence on the properties of nitridebonded ceramics produced from these masses. Material strengths determined for samples of the nitride-bonded SiC ceramics exhibit quantity-dependent changes in response to the different CAC-contents of the semi-finished products. The amount of liquid phase forming during nitridation strongly influences the phase composition, material strengths and the oxidation resistance of the nitride-bonded ceramics. In the sample produced from the thixotropic castable containing 4 wt% of the CAC, a particularly high amount of glassy phase developed during nitridation. A low bending strength found for this ceramic as well as a higher crushing strength and a higher oxidation resistance of this sample compared to the other samples is attributed to the occurrence of the glassy phase.

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