

SYNTHESIS OF HIGH PURITY Si_3N_4 AND SiC POWDERS BY CVD METHOD

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Fine, sub-micrometer, amorphous powders of SiC and Si_3N_4 have been prepared from SiH_4 - NH_3 and C_2H_2 - SiH_4 gaseous systems respectively, in tubular flow reactor. The Si_3N_4 powder prepared at 1373 K and NH_3/SiH_4 molar ratio of 11.5 is near stoichiometric in composition, isometric in morphology and the particle size is in range of 50 - 150 nm. The particle size of SiC powder prepared at 1373 K and $\text{SiH}_4/\text{C}_2\text{H}_2$ molar ratio of 2:1 was from the interval 10 to 100 nm. Recrystallization of these powders at 1853 K did not change substantially the particle size distribution and confirmed the Si_3N_4 and SiC as major compounds respectively. The content of metal impurities as Al, Cr, Cu and Fe in the presented powders is one order of magnitude lower compared to the commercially available powders prepared by other methods.

INTRODUCTION

In the last years the production of new ceramic materials with defined mechanical and physical properties is a great challenge to the materials scientist. Interest in the preparation of nano-powders is increasing since nanoscale powders can be used to produce fine-grained homogeneous materials with unique properties. SiC nanosized powder is the main reinforcement of ceramic nanocomposite materials. Significant improvements in strength and toughness have been reported for Al_2O_3 - SiC [1]. Elevated strength values were found for Si_3N_4 - SiC nanocomposites [2]. Silicon nitride as well as silicon carbide have a high heat-stability, hardness and wear resistance, oxidation resistance and corrosion resistance. Therefore, it could be expected that a combination of both materials in one Si_3N_4 - SiC nanocomposite should bring an improvement of material properties comparing to the properties of individual composite components. The main processing routes for preparation of Si_3N_4 and SiC powders are: carbothermic reduction of silica or silane by carbon and subsequent nitridation by N_2 or NH_3 , thermal chemical vapor deposition (CVD) [3], plasma CVD (PCVD) [4] and polymer

pyrolysis [5]. Hajo et al. reported the preparation of Si_3N_4 - SiC composite powder by CVD [6]. This composite powders have fine dispersions, nanometer size, uniformly present in the matrix. Composite Si_3N_4 - SiC powder can be prepared through a co-deposition process using several sources of gases simultaneously. The produced particles are ultrafine and consist of different components mixed on atomic, molecular or nano-sized level.

The aim of the present work was the synthesis of ultrafine Si_3N_4 and SiC powders by thermal CVD process. The effect of temperature (Si_3N_4 powder), and ratio of starting gases $\text{SiH}_4/\text{C}_2\text{H}_2$ (SiC powder) on the product particle size, morphology and quality have been investigated on a laboratory scale.

EXPERIMENTAL PART

Powders synthesis

Silane (15 wt.% in N_2) of the electronic grade (99.99 wt.%), ammonia (99.9 wt.%) and acetylene (99.5 wt.%) were used as the reactants in all described experi-

ments. The experimental set-up used for the synthesis of ceramic SiC and Si₃N₄ powders is described in detail in [7]. Reactant gases flowed through a vertical tubular hot-wall reactor consisting of a vertically oriented alumina ceramic tube placed in a molybdenum resistance furnace. The gas pressure of reactants in the reactor was kept at 110 kPa. The gas flow rate of reactants, 1000 cm³ min⁻¹ and 1270 cm³ min⁻¹ for SiC and Si₃N₄ respectively, was controlled by Brooks model 5850TR mass flow meter and the gases were mixed in a co-axially designed gas input in the cold zone of the furnace in order to avoid their decomposition prior to mixing. The temperature in a reaction zone was controlled by the type B platinum thermocouple with the accuracy ±10 K. The homogeneous reaction zone in the reactor was 10 cm. The synthesis conditions are listed in table 1.

Powders characterization

The morphology, shape and particle size distribution of the powders were studied by scanning electron microscopy (SEM) JEOL JSM-35 at magnifications 10 000 and 20 000. Powders were dispersed in oil dispersant and then glued to the sample holder. The powder was covered by gold. The mean particle size was determined from the micrographs by measuring the particle diameter. Each value was evaluated from 500 random selected measurements.

Chemical bonds present in the amorphous powder product were identified by Fourier transform-infrared spectroscopy (FTIR) using spectrometer Nicolet Magna 750 and KBr pressed disc technique [8]. Thermogravimetry (TG) in air/nitrogen atmosphere was used for the determination of the free carbon and estimation of its content in SiC powders. X-ray diffraction (XRD) (Stoe STADIP) was used for the qualitative analysis of main phases in the powder products after crystallization at 1853 K for 2 h in argon. Nitrogen content in the synthesized Si₃N₄ and SiC powders were determined by

titrimetric Kjeldahl method [9]. The elemental analysis of silicon (exclusively for Si₃N₄) was done by neutron activation analysis and oxygen was determined by LECO TC-136.

Throughout analytical experiments, high purity water (18.2 MOhm), prepared by a Ultra CLEAR UV system (Hamburg, Germany), was used and all the plastic-ware employed was carefully cleaned by immersing into warm 0.5 mol l⁻¹ nitric acid. Commercially available ASTASOL (Analytika, Prague, Czech Republic) aqueous standard solutions of 1 mg ml⁻¹ Al, Cr, Cu and Fe, respectively, were used for calibration.

Content of technologically important trace impurities (Al, Cr, Cu and Fe) in the synthesized powder samples was determined by the electrothermal atomic absorption spectrometry employing Perkin-Elmer 4110 ZL spectrometer equipped with the Zeeman effect background correction system, transversally heated graphite furnace with integrated platform and AS 72 autosampler. Hollow cathode lamps of respective elements were used as specific radiation source. Integrated absorbance values were evaluated in quantification procedure. Due to the chemical resistance of the prepared ceramic powders, slurry sampling was advantageously applied for introduction of powder samples into the atomizer. For this purpose, recently described methods [10, 11] were modified. Typically, a sample portion of 0.1 g was admixed into 9.5 ml of high purity water and 0.5 ml of reagent grade ethanol, yielding the 1 % (w/v) suspension. Addition of ethanol was necessary in order to increase the wettability of hydrophobic powders. In advance, blank of the dispersion medium (ethanol/water) was measured. The mixture was then treated in the ultrasonic bath for 15 minutes in order to disintegrate agglomerates of particles. Finally, sample slurry was continuously mixed by a stirring device [12] and aliquots of 20 µl were dispensed into the furnace by the auto-sampler. Calibration was performed by the standard addition method. Samples were analyzed in triplicate and results were statistically evaluated. Experimental parameters are summarized in table 2.

Table 1. Synthesis conditions.

sample No.	synthesis temperature (K)	molar ratio		product composition
		NH ₃ :SiH ₄	SiH ₄ :C ₂ H ₂	
1	973	11.5	-	Si ₃ N ₄
2	1173	11.5	-	Si ₃ N ₄
3	1373	11.5	-	Si ₃ N ₄
4	1373	-	3 : 1	SiC
5	1373	-	2 : 1	SiC
6	1373	-	1.6 : 1	SiC

Table 2. Experimental parameters.

element	wavelength (nm)	spectral bandpath (nm)	lamp current (mA)	atomization temperature* (K)	standard addition (ng)
Al	309.3	0.7	30	2573	0.1
Cr	357.9	0.7	25	2573	0.1
Cu	324.8	0.7	25	2473	0.2
Fe	248.3	0.2	30	2473	0.2

note: * the same pyrolysis temperature of 1173 K was applied in determination of all elements

RESULTS AND DISCUSSION

Formation of Si_3N_4 powder

In a hot zone of the reactor the following reaction is expected:



During reaction the constant molar ratio of ammonia to silane of 11.5 was kept at three different temperatures (973, 1173, 1373 K) and the total flow rate of gases at $1270 \text{ cm}^3 \text{ min}^{-1}$.

Characterization of Si_3N_4 powder

FTIR spectra of Si_3N_4 powders are shown in figure 1. Although the spectra are similar, small but clear differences are seen in relation to the temperature used for synthesis of the powders. The most intensive band, found in the spectra of all samples in the $937\text{-}960 \text{ cm}^{-1}$ region, is assigned to the asymmetric stretching vibration of Si-N-Si groups [3]. The position of the band increases with the temperature used (figure 1a-c). The symmetric stretching vibration of Si-N-Si groups was observed near 470 cm^{-1} . In addition to the Si-N-Si vibrations the powder prepared at 973 K revealed several small bands of by-products (figure 1a). A broad band near 3400 cm^{-1} consists of contributions of several different absorptions. The Si-NH-Si stretching vibration at 3367 cm^{-1} overlaps the absorptions of Si-NH₂ groups and physically sorbed water molecules. The corresponding bending vibrations appear near 1170, 1545 and

1630 cm^{-1} , respectively. The insert in figure 1 shows decreasing intensity of a band at 2171 cm^{-1} , assigned to Si-H stretching vibration in mono-substituted silan (-SiH₃), with increasing temperature. This fact together with a disappearance of Si-NH-Si and Si-NH₂ bands indicate higher purity of the Si_3N_4 powders prepared at 1173 K and 1373 K (figure 1b, c).

Chemical analysis showed that the nitrogen content of the product prepared at 973 K was $39.9 \pm 0.1 \text{ wt.}\%$ of N₂ which is close to the stoichiometric composition of Si_3N_4 (39.96 wt.% of N₂). Other main constituents were determined as follows: silicium $59.4 \pm 0.1 \text{ wt.}\%$, and oxygen $1.4 \pm 0.1 \text{ wt.}\%$. Reaction (1) does not produce the oxygen rich constituents. The oxygen content in the powder product probably depends on the subsequent reaction of residual silane on the surface of powder with air humidity after handling on the air. The color of the powder was white and powder was amorphous. The product prepared at 973 K was not agglomerated. On the other hand, the refinement of the products was observed with an increase of the reaction temperature, figure 2. The size range and the mean particle size of the Si_3N_4 product are shown in the table 3 with respect to the reaction temperature.

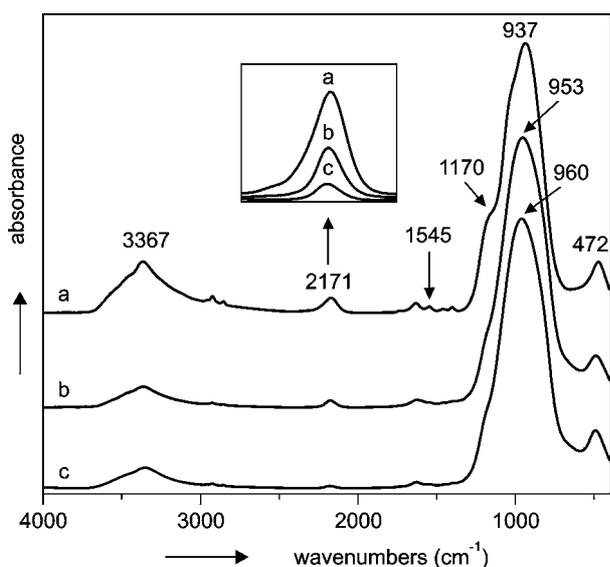


Figure 1. IR spectra of Si_3N_4 powders prepared at 973 K (a), 1173 K (b) and 1373 K (c).

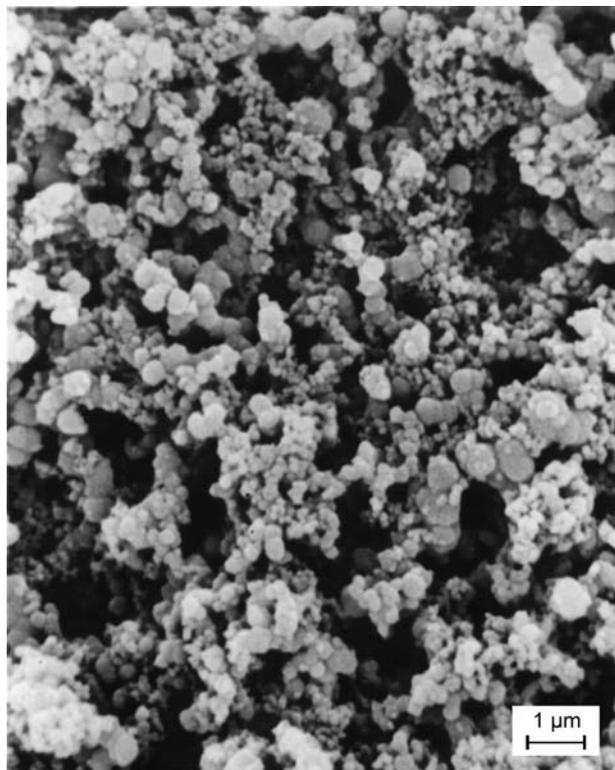


Figure 2. SEM photograph of Si_3N_4 powder prepared: total gas flow rate $1270 \text{ cm}^3 \text{ min}^{-1}$, NH_3 : SiH_4 molar ratio = 11.5, temperature 1373 K.

Table 3. Particle size of Si₃N₄ powders synthesized at the NH₃:SiH₄ ratio of 11.5 and the total flow rate of 1270 cm³min⁻¹.

reaction temperature (K)	particle size range (nm)	mean particle size (nm)
973	100 - 400	250
1173	100 - 300	200
1373	50 - 150	100

The finest Si₃N₄ powder prepared at 1373 K was crystallized at 1853 K for 2 h in argon. From the morphological point of view the crystallization did not cause any substantial changes, the mean particle size remained approx. 100 nm. The XRD measurements confirmed only the presence of α-Si₃N₄ after crystallization.

Metal trace impurities

Content of technologically very important trace impurities (Al, Cr, Cu and Fe) in samples was determined by electrothermal atomic absorption spectrometry. This method enables to determine directly very low concentration of elements in ceramic powders and to reduce very easily the risk of contamination. Limits of detection (LODs) of 0.12, 0.03, 0.04 and 0.05 μg g⁻¹ could be reached for Al, Cr, Cu and Fe, respectively. Analytical results are summarized in table 4.

Samples contained Al, Cr, Cu and Fe at ppm and sub-ppm level, one to two orders of magnitude lower than that of commercially available products [10,11]. No significant relationship was found between the content of a respective element and conditions of powder preparation.

Table 4. Trace impurities content.

reaction temperature (K)	element content mean ± uncertainty* (μg g ⁻¹)			
	Al	Cr	Cu	Fe
973	3.482±0.184	0.463±0.008	0.053±0.006	1.650±0.091
1173	2.828±0.169	0.291±0.003	0.070±0.001	1.587±0.193
1373	1.300±0.077	0.080±0.003	0.244±0.030	1.342±0.082

note: * evaluated according to EURACHEM guidelines [13]

Formation of SiC powder

The synthesis of fine amorphous SiC powder was performed in the same reactor as above, according to the reaction:



Reaction conditions are listed in table 1.

The FTIR spectra of all powders resemble each other indicating that differences in the molar ratio of constituents used for SiC synthesis have minor effect on the spectra of final products. The FTIR spectrum of SiC powder shown in figure 3 has a pronounced absorption band at 842 cm⁻¹, which corresponds to Si-C stretching vibration [3]. The absorption at 3431 and 1627 cm⁻¹ belong to vibration of water molecules adsorbed on the KBr disc. In the 2100 cm⁻¹ region a weak band related to the stretching vibration of triple -C≡C- bond was found in the spectra of all SiC powders (insert in figure 3). The frequency of this absorption depends on the character of the other atoms bonded to carbons, for instance the H₃C-C≡CH absorbs near 2130 cm⁻¹ while H₃Si-C≡CH at 2056 cm⁻¹. The position of the band, found in the spectra of SiC powders in the 2086 to 2103 cm⁻¹ range, indicates the contribution of both C-C≡C and Si-C≡C bonds present in by-products to be present in the SiC powders.

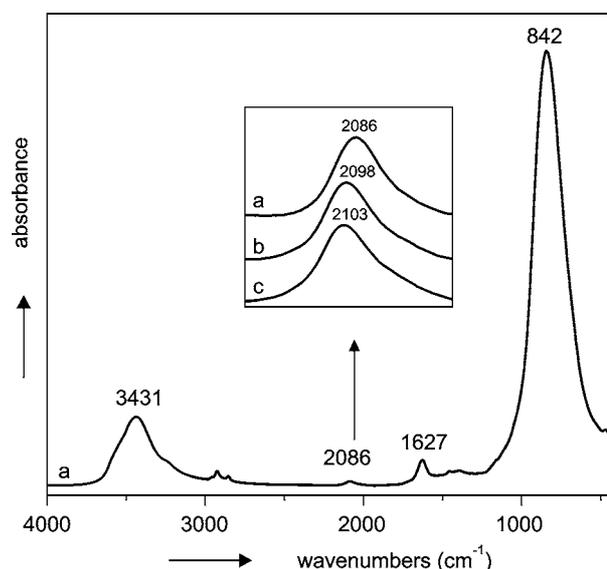


Figure 3. IR spectra of SiC powders prepared: temperature 1373 K, molar ratio of initial constituents 3:1 (a), 2:1 (b) and 1.6:1 (c).

The prepared SiC powders, generally consisted of spherical solid loosely agglomerated amorphous particles. From the morphological point of view, the temperature 1373 K is considered as the optimum [7], powder particles are equiaxial and quasispherical, figure 4. The mean particle size and the particle size ranges of the powders synthesized according to the reaction (2) at 1373 K are listed in the table 5.

The XRD pattern of this powder after crystallization at 1853 K for 2 h in Ar confirmed the β-SiC as the major phase. The particle size distribution was not changed after crystallization.

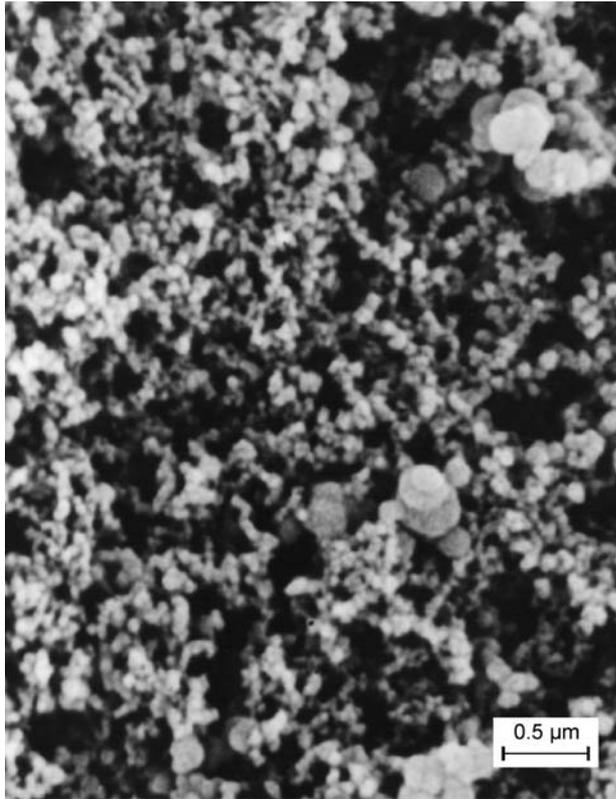


Figure 4. SEM photograph of SiC powder prepared: total gas flow rate 1000 cm³ min⁻¹, SiH₄ : C₂H₂ molar ratio 2:1, temperature 1373 K.

Table 5. Particle size of SiC powders synthesized at the temperature of 1373 K and the total flow rate 1000 cm³ min⁻¹.

molar ratio SiH ₄ : C ₂ H ₂	particle size range (nm)	mean particle size (nm)
3 : 1	50 - 200	100
2 : 1	10 - 100	50
1.6 : 1	10 - 100	50

TG analysis curve of SiC powder indicated a weight loss at about 873 K in air, related to the oxidation of free carbon, e.g. see figure 5. As documented in table 6, the amount of the free carbon varies according to the reaction conditions.

Table 6. Free carbon in the synthesized SiC powders determined by TG on air for the different silane : acetylene ratio.

molar ratio SiH ₄ : C ₂ H ₂	free carbon content (wt.%)
3 : 1	0.2
2 : 1	1.9
1.6 : 1	4.3

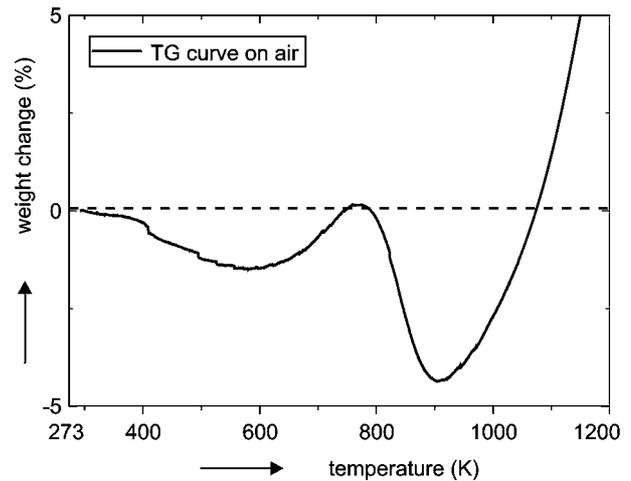


Figure 5. TG curve of SiC powder (prepared at the SiH₄ : C₂H₂ molar ratio of 1.6 : 1) on air.

Analytical measurements performed on these SiC powders are summarized in table 7. Samples contained Al, Cr, Cu and Fe at ppm and sub-ppm level, as it was found also for the Si₃N₄ powders.

Table 7. Content of trace impurities.

molar ratio SiH ₄ : C ₂ H ₂	element content mean ± uncertainty*			
	Al	Cr	Cu	Fe
3 : 1	3.205±0.099	0.125±0.011	0.398±0.038	1.779±0.101
2 : 1	3.635±0.117	0.091±0.003	0.391±0.008	2.459±0.180
1.6 : 1	1.425±0.080	0.164±0.002	0.343±0.074	3.644±0.104

note: * evaluated according to EURACHEM guidelines [13]

CONCLUSION

Fine sub-micrometer amorphous ceramic Si₃N₄ and SiC powders were synthesized by the thermal chemical vapor deposition.

The refinement of the Si₃N₄ powder was observed with increasing of the reaction temperature. The mean particle size of the Si₃N₄ powder was 100 nm at temperature of 1373 K.

Equiaxial and quasispherical SiC powder with the mean particle size of 50 nm was prepared in the SiH₄-C₂H₂ system with the molar ratio of 2:1 at a temperature of 1373 K.

The residual free carbon was observed in the SiC product. The carbon content rose with the increasing amount of C₂H₂ in the gas mixture. The lowest amount of carbon (0.2 wt.%) was observed at the SiH₄ : C₂H₂ molar ratio of 3 : 1.

The metallic impurities in both synthesized Si₃N₄ and SiC powders were < 1 µg g⁻¹ for Cu and Cr and < 4 µg g⁻¹ for Fe and Al.

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PRÍPRAVA VYSOKOČISTÝCH PRÁŠKOV Si₃N₄ A SiC METÓDOU CVD

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V rúrkovom prietochnom reaktore boli pripravené, jemnozrnné submikrónové amorfné prášky Si₃N₄ a SiC, z plynných reakčných zmesí: SiH₄-NH₃ a C₂H₂-SiH₄. Veľkosť častíc stechiometrického, kubického Si₃N₄ prášku, pripraveného pri teplote 1373 K a molárnom pomere plynov NH₃ / SiH₄ = 11.5 dosahovala 50-150 nm. Častice SiC prášku pripraveného pri teplote 1373 K a molárnom pomere plynov C₂H₂/SiH₄ = 2 dosahovali veľkosť 10-100 nm. Rekryštalizáciou pripravených práškov Si₃N₄ a SiC pri teplote 1853 K sa v nich potvrdila prítomnosť Si₃N₄ a SiC ako majoritných zložiek, pričom nedošlo k podstatnej zmene v rozdelení veľkosti častíc.

Obsah sledovaných kovových nečistôt: Al, Cr, Cu a Fe v pripravených práškoch v porovnaní s komerčnými práškami pripravenými inými metódami je o jeden rád nižší.