EFFECTS OF HEAT TREATMENT ON THE STRUCTURE OF THERMAL PLASMA SYNTHESIZED SiCN COMPOSITE NANOPOWDERS

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Abstract. SiCN composite nanopowders with different chemical composition and characteristics were synthesized by the RF induction plasma at atmospheric pressure.
Frequently the as-produced powders exhibit a high degree of chemical disorder or structural defects. Because the composition and the microstructure of starting powders have a great influence on the properties of composite ceramics, the changes of chemical composition, crystallization, and morphology of the as-produced powders during heat treatment up to 1500 °C were investigated in detail.

1. INTRODUCTION

Composite nanopowders with high purity, homogenity, and diameter less than 100 nm are of interest in the development of advanced ceramics, new catalysts, electronic devices, *etc*. Generally, the use of conventional methods such as sol gel process, reaction spray technique or milling to generate this type of powders is difficult, very expensive and sometimes even impossible. Recently, silicon carbonitride refractoriness has become of great interest, mainly because of their excellent thermal shock resistance, high strength at high temperature, high fracture toughness, and good oxidation resistance [1].

Silicon carbonitride nanocomposites can be obtained from different methods such as the polymer precursor route [2] or from the sintering of SiCN composite nanopowders [3]. Therefore, in the last few years, increasing activities have been given to the production of nanoscale silicon carbonitride composite powders by various synthesis techniques, such as thermal plasma [4], laser [5], and thermal pyrolysis [6].

One effective method for the synthesis of nanoscale composite powders is the simultaneous gas phase synthesis of the components in a thermal RF induction plasma torch. This route is chemically non-specific, because the typical plasma temperatures (>3000K) allow the decomposition of near-arbitrary precursors. Moreover, high quenching rates (10^4 - 10^8 K/s) are connected with high supersaturations which provide the driving force for the particle condensation and the preparation of nanoscale powders (typically <100nm). In addition it is possible to produce powders containing metastable phases, composites, and multicomponent materials by the rapid quenching of the high temperature reaction system. Thermal plasma technique offers the advantage of a continuous one-step process with potential for mass production so that computer process control can be applied to yield reproducible and uniform powders.

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It is known that the properties of silicon carbonitride nanopowders strongly depend on their microstructure, such as particle size, chemical composition, phases, crystallite size, morphology, specific surface area, structural defects, and chemical disorder. Frequently, these features can be tailored by heat-treatment of the powders. Therefore it is important to get knowledge about the influence of annealing on these features.

In this context the present work is focused on the determination of the thermal behavior of two SiCN composite nanopowder samples with different compositions (C/N ratio in SiCN/1 and SiCN/2 is 0.25 and 0.65, respectively) which were produced by tetramethylsilane (TMS) and ammonia in a RF induction plasma torch.

2. EXPERIMENTAL

The SiCN composite nanopowders were synthesized by the RF induction plasma at atmospheric pressure. The home-made moderate-scale synthesis facility mainly consisted of four components: plasma torch with RF generator, reactor, quenching system, and powder collector. The principle of the reactor has been described previously in detail [7]. The used RF induction plasma torch is of standard design with an air-cooled quartz plasma confinement tube of 50 mm diameter, surrounded by a three-turn induction coil of 30 mm length and 60 mm diameter. The plasma torch was powered by a 5 kW power supply (Steremat, Berlin, model GI5/5D-047) operating at a frequency of 4 MHz. The plasma was operated with Ar and Ar/H_2 as central and sheath gas, respectively. The torch discharged into a water-cooled reactor of stainless steel for reactant injection and mixing. The reactants tetramethylsilane (TMS) and ammonia were injected radial into the flame tail at injection levels 65 mm and 95 mm downstream the induction coil, respectively. The TMS was fed by a peristaltic displacement pump into a stainless steel heating system where it was evaporated at 200 °C and diluted with H_2 carrier gas. The reacting system is quenched by injecting cold gases (Ar) at the exit nozzle of the reactor. Moreover a water-cooled quenching chamber was located after the chemical reactor allowing cooling by gas expansion. It has to be noted, that ammonia acts as quenching gas too by endothermic reactions. The produced composite powders were collected by solid-gas separation on a textile filter, because this filter has proved to be very efficient in collecting the powders. Overall size of the synthesis facility is approximately 100 mm diameter and 500 mm height without the filter. The discharge parameters were kept constant in the experiments. The torch was powered by 3 kW plate power. The ratio of TMS to ammonia was varied.

Annealing experiments of both SiCN nanopowders were performed in alumina furnaces using alumina crucibles. The powders, without pressing, were heat-treated at temperatures up to 1500 °C in an argon gas flow of 500 standard cubic centimetres per minute with a dwell time of one hour and a heating rate of 20 °C/h.

Chemical analysis, Fourier transform infrared spectroscopy (IR), X-ray powder diffraction (XRD), and transmission electron microscopy (TEM) were applied to characterize the powders before and after annealing.

3. RESULTS AND DICUSSION

The synthesized SiCN composite nanopowders were soft and fluffy. The colour of the composites changed from light to dark grey as the N/C ratio in the powders decreased. The mean diameter varies between 10 and 40 nm with a narrow size distribution according to the reaction route. The particles are always smaller than 80 nm. From TEM and HREM (not presented here) it can be seen that most of the particles have a spherical and isometrical shape, whereas angular (mostly hexagonal) structures only appear additionally.

Table 1 reports the evolution of the chemical composition and weight change of the SiCN nanopowders samples during the heat treatment. It can be noticed that the content of carbon and nitrogen only slightly changes during the heat treatment. This can be an indication that no clear structure change appears. The as-produced powders contain around 1 wt.% hydrogen what could be explained by an incomplete dissociation of the precursor. The thermal stability of both samples during annealing is similar. The weight change could be attributed to evaporation of hydrogen, adsorbed water and unreacted precursors. This is in agreement with XPS investigations according to which nearly the total oxygen content of the powders is located at the surfaces.

Fig. 1 presents the IR spectra of the SiCN nanopowders samples. The spectra of the as-produced samples show a broad featureless absorption between 700 and 1300 cm^{-1} and additionally a smaller absorption centered at 480 cm^{-1}, which are usually attributed to SiCN amorphous structures (Si-N absorption: 900-1000 cm^{-1} and 480 cm^{-1}, Si-C absorption: 850 cm^{-1} [8, 9]). In sample SiCN/1, maximum absorption was observed at 980 cm^{-1}.

Table 1. Evolution of the chemical composition and weight change of the SiCN nanopowders during the heat treatment.

| Sample	Annealing temperature, °C	Chemical analysis, wt.%			Weight change, %
		C	N	H	
SiCN/1	as-produced	6,5	24,9	1,1	0
	1100	5,5	26,9	0,2	-4,9
	1300	5,9	27,2	0	-5,9
	1500	5,3	28,3	0	-10
SiCN/2	as-produced	12,8	19,8	1,0	0
	1100	10,3	17,1	0	-1,6
	1300	11,6	20,3	0	-3,8
	1500	12,7	17,0	0	-11,1

Therefore, in this sample Si atoms seem to be bonded mainly to N atoms. On the other hand in sample SiCN/2 the absorption maximum was shifted to 930 cm^{-1} indicating that more Si–C bonding is containing. In both spectra, a weakly absorption at 1260 cm^{-1} is also observed. It may be attributed to a Si–CH$_3$ deformation vibration [10]. The presence of this Si–CH$_3$ unit may be indicated the incomplete pyrolysis of the TMS. However, this band disappears in the spectra of the annealed samples. This is in agreement with the decrease of the hydrogen during heat treatment. It is to note that the C-N absorp-

tion at 1260 cm^{-1} [11] might be overlapped with that of Si–CH$_3$.

The predominantly similar spectra of the annealed samples up to 1300 °C indicate that no significant evolution of the silicon coordination occurred. Furthermore this means that the samples are thermally stable what the slightly weight change also points out.

Otherwise annealing of the samples at temperature of 1500 °C shows a strongly influence on the IR absorptions. The IR spectra are composed of sharp bands attributed to the presence of crystallized struc-
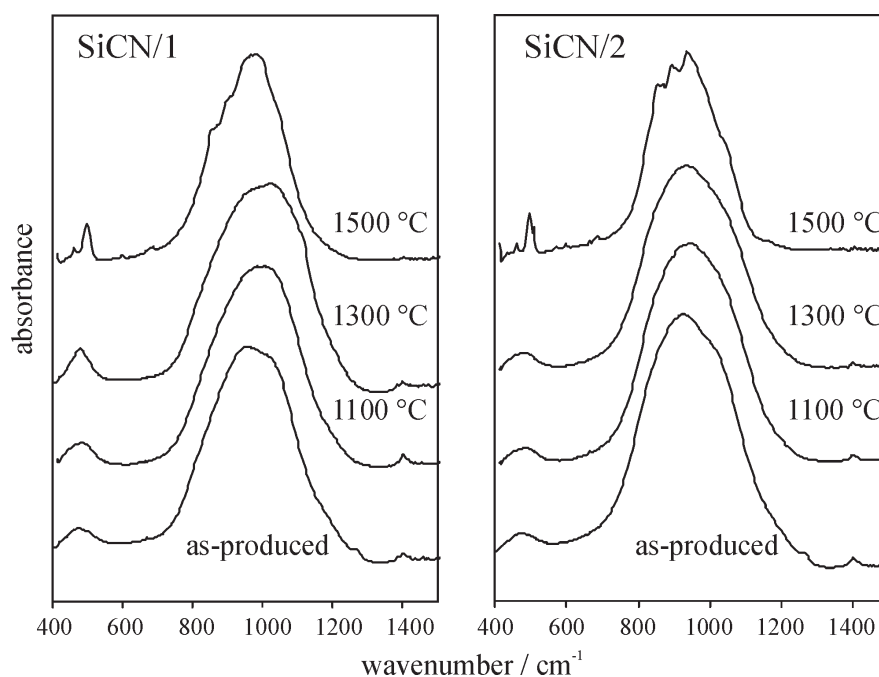
Fig. 1. Infrared spectra of the as-produced and annealed SiCN composite nanopowders.
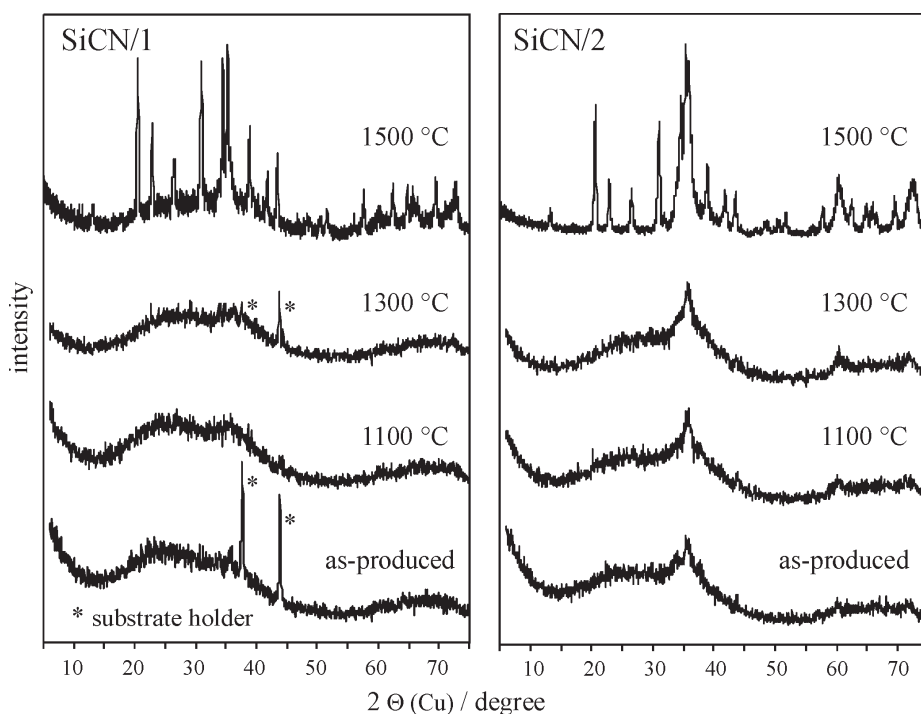
Fig. 2. X-ray diffraction patterns of the as-produced and annealed SiCN composite nanopowders.

tures besides amorphous phases. The main crystallized phase is α-Si$_3$N$_4$ [8] but the shoulder at 830 cm^{-1} indicates the presence of SiC. It has to be remarked that the sample SiCN/2 is more crystallized than sample SiCN/1, especially the content of α-Si$_3$N$_4$ is higher. XRD (see later) proves unambiguously the presence of α-Si$_3$N$_4$ and β-SiC in both samples.

Furthermore it is necessary to note that IR and NMR (not presented here) indicate no evidence for the presence of Si–O structures in the as-produced or heat treated samples.

Fig. 2 shows the XRD diagrams of samples SICN/1 und SICN/2. The X-ray powder diffraction patterns of the as-produced sample SiCN/1 did not show any diffraction peaks, demonstrating that the material exhibits a complete amorphous structure. In contrast the as-produced sample SiCN/2 contained a little amount of crystalline SiC in a predominantly amorphous matrix. Annealing of the samples up to temperature of 1300 °C did not show any influence on the phase composition, which was also confirmed by the IR investigations.

On the other hand, heat treatment at 1500 °C led to a significant increase of the crystallinity in both samples whereas sample SiCN/2 had a higher degree of crystallinity than sample SiCN/1. The main

peaks in the diffraction patterns are corresponding to α-Si$_3$N$_4$. Phase identification was achieved by matching the measured patterns against stick patterns from the JCPDS database (α/β-Si$_3$N$_4$ 410360/ 331160, α/β-SiC 291131 / 291129). The samples could be composed of α-Si$_3$N$_4$, β-Si$_3$N$_4$, α-SiC, and β-SiC; but neither any crystalline Si carbon nor oxygen containing compounds were detectable by XRD in the SiCN nanopowders.

With the models of α-Si$_3$N$_4$, β-Si$_3$N$_4$, α-SiC, and β-SiC, the X-ray diagrams are calculated and fitted to the experimental intensities by trial and error method. The obtained diagrams are directly comparable with the experimental diagrams.

The diffraction pattern of SiCN/1 shows sharp and well-defined reflections. The peaks correspond to α-Si$_3$N$_4$. Furthermore the diagram contains the intensities of β-SiC and an amorphous background. The ratio (weight fractions) of α-Si$_3$N$_4$/β-SiC amounts to 6. The background could consist of mixed tetrahedral SiC$_x$N$_{4-x}$ unit ($1 \leq x \leq 3$) [12-14]. The ^{29}Si NMR-Spectra of SiCN/1 references to SiC$_x$N$_{4-x}$ units and could explain the X-ray background.

Fig. 3 represents the reduced radial distribution functions (DRDF) of sample SiCN/1 calculated from wide-angle X-ray scatterings (WAXS). The diagrams show the absence of long range order for $r > 4$Å.
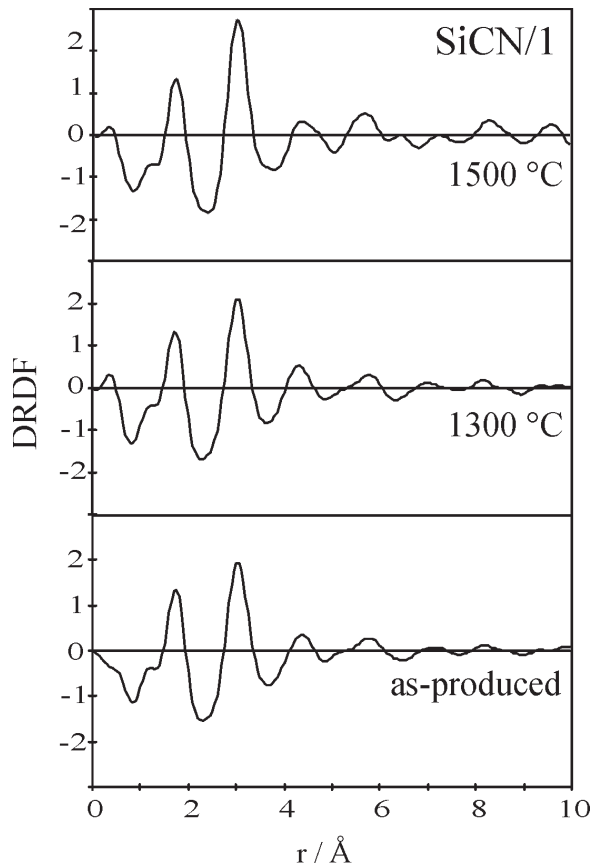
Fig. 3. Reduced radial distribution function of the as-produced and annealed sample SiCN/1 {DRDF(r)=$4\pi r^2$[$\rho(r) - \rho_0$]}.

The near range order improves with the temperature and a displacement of the first peak can not be observed.

The diffraction pattern of SiCN/2 annealed at 1500 °C also shows well-defined peaks. The powder consists of partial crystalline powder of α-Si_3N_4, β-SiC and amorphous α-SiC in the ratio (weight fraction) of 3:1:2 in contrast to SiCN/1.

4. CONCLUSION

The thermal RF induction plasma process is well suitable for producing SiCN composite nanopowders. The chemical composition as well as the morphology of nanoscale SiCN composites can be controlled by processing. So, plasmachemical powder processing can be designed to attain multiple microstructure-property objectives and consequently plasma nanopowders can be tailored to the specific requirements for different applications.

The as-produced SiCN composite nanopowders synthesized from TMS and ammonia are mainly amorphous, sometimes β-SiC is also available. The nanopowders are thermally stable up to 1300 °C in argon atmosphere without remarkable change in phase, chemical composition, and morphology. Annealing above 1300 °C leads to nanostructered powders, containing considerable amounts of α-Si_3N_4 as well as β-SiC.

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