

Preparation of Si₃N₄/SiC Based Nanocomposites

Janis Grabis, Dzidra Jankovica

Institute of Inorganic Chemistry of Riga Technical University, Miera Street 34, Salaspils, LV 2169, Latvia

Abstract

A plasma chemical synthesis has been developed to produce Si₃N₄ nanocomposites with various content of components. The average particle size and crystallite size of SiC is in the range of 30-60 nm and 27-58 nm respectively. The dispersity and phase composition of the produced nanocomposites depends on the concentration of particles in gas flow, growth time of particles and ratio of components.

1 Introduction

Silicon carbide/nitride based nanocomposites due to their hardness, mechanical strength, good corrosion and oxidation resistance at elevated temperature are promising candidate for high-temperature application [1-3] and manufacture metal or ceramic matrix composites [4, 5]. However mechanical and physical characteristics of ceramic strongly depend on microstructure, used sintering method, particle size and homogeneity of raw composite powder. Preparation of homogeneous raw particulate composites is especially actual in the case of nanosized powders because their high surface energy leads to formation of agglomerates.

The aim of the present work was preparation of the highly homogeneous Si₃N₄/SiC nanosized powders and their composites with sintering aids (Al₂O₃, Y₂O₃) or metals (Zn, Cu) by evaporation of raw materials in an inductively coupled plasma flow as well as by chemical deposition of Al₂O₃ or Y₂O₃ on the Si₃N₄/SiC nanosized powders and their characterisation.

2 Experimental procedure

The nanosize Si₃N₄/SiC-based composites have been prepared by evaporation of coarse commercially available powders of chemical elements and their compounds and subsequent condensation of products into a radio frequency inductively coupled nitrogen plasma (ICP). The elaborated experimental apparatus (Fig. 1) consists of radio-frequency (5.28 MHz) oscillator with maximum power of 100 kW, quartz discharge tube with induction coil, raw powder and gas supply systems, water cooled stainless steel reactor and heat exchanger, and cloth filter for collecting of powder. The flow rate of the plasma-forming gas nitrogen is 7.6-8.0 m³h⁻¹ and the feed rate of raw powders is 0.3-1.4 kg·h⁻¹.

The calculated fractions of raw powders of Si, Cu, Zn or Si, Al₂O₃, Y₂O₃ are premixed and introduced into plasma tail through 4 or 8 tubes by carrier gas. Conditions of injection and particle size are determined by theoretical calculations and preliminary experiments. The complete evaporation of raw powders can be reached by varying the particle size and their injection rate, feeding rate, plasma velocity and temperature. The formation of products, their particle size, chemical and phase composition are controlled by introduction the cold nitrogen, ammonia and hydrocarbon into reaction chamber.

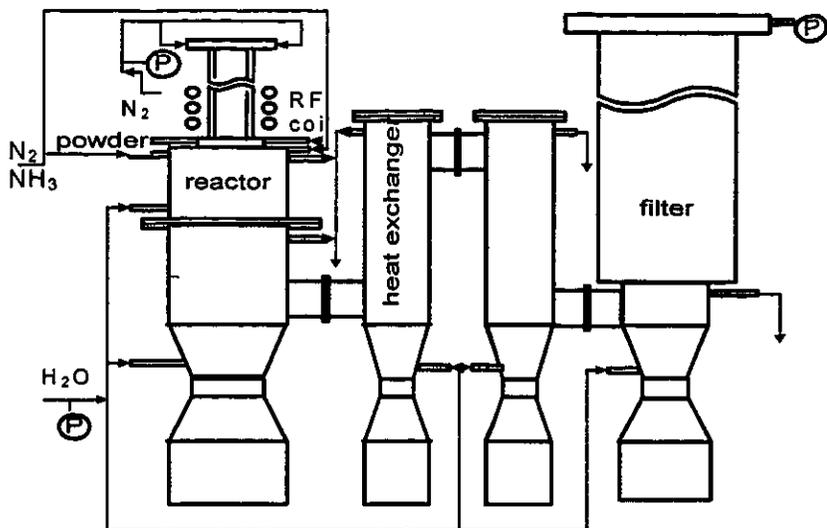


Fig. 1. Schematic view of plasma apparatus.

In order to minimise reduction of oxides by silicon or carbon the $\text{Si}_3\text{N}_4/\text{SiC}$ composites with Al_2O_3 and Y_2O_3 have been prepared also via chemical deposition of aluminium and yttrium hydroxides on nanosized $\text{Si}_3\text{N}_4/\text{SiC}$ particles, produced by plasma chemical synthesis. The nanosized particles are dispersed in ethanol by ultrasonic vibration and then mixed with aluminium and yttrium nitrate solution. The deposition is controlled by adding NH_4OH . The obtained mixture is washed and hydroxides are decomposed by calcination in argon atmosphere.

The chemical and phase compositions of prepared powders are determined by conventional chemical and X-ray powder diffraction analysis. The specific surface area of powders is determined by BET argon adsorption-desorption method.

The crystallite size d_{cryst} of SiC is calculated from the XRD data by using Scherrer formula. The average particle size d is calculated from the specific surface area assuming spherical form of particles.

3 Results and discussion

The characteristics of typical prepared by both routes $\text{Si}_3\text{N}_4/\text{SiC}$ based nanocomposites are shown in table 1. All products except nanocomposites with Cu are stable but handling of the powders under air leads to a considerable uptake of oxygen and moisture which depending on specific surface area of powders reaches 3–6 wt.%. The Cu containing nanocomposites are pyrophoric and are collected in solution of stearic acid and hexane.

Content of $\text{Si}_3\text{N}_4/\text{SiC}$ based nanocomposites depends on ratio of hydrocarbon and silicon in the plasma flow. By varying the ratio the $\text{Si}_3\text{N}_4/\text{SiC}$ nanocomposites with SiC content up to 85 wt% could be prepared in nitrogen plasma without admixture of carbon. The further increase of hydrocarbon and silicon ratio increases content of SiC up to 90 wt.%, but product contains 3–5 wt.% of carbon admixture.

According to the XRD analysis the main phases of the prepared nanocomposites are β -SiC and α -, β - Si_3N_4 as well as traces of silicon (0.5–0.8 wt.%). The diffraction maxima of β -SiC on the XRD patterns are strong, but maxima α -, β - Si_3N_4 are very weak and are detectable only if the content of silicon nitride is higher as 40wt.%. The weak, broad maxima of α -, β - Si_3N_4 and increased amorphous background on the XRD patterns indicate on the low degree of silicon nitride crystallinity. Obviously low formation temperature of silicon nitride with respect to SiC and high cooling rate of products limit the growth time of particles and prevent their crystallisation.

From XRD and chemical analysis follow that in the system of $\text{Si}_3\text{N}_4/\text{SiC}$ -Cu or Zn besides above-mentioned phases only Cu or Zn is presented and there is not remarkable chemical interaction among components at least for content of metals less than 10 wt.%.

No	Content of components, wt. %	XRD	SSA, m ² .g ⁻¹	d, nm	d _{cryst} SiC, nm	Method
1	Si ₃ N ₄ /SiC 30	β-SiC, α-, β-Si ₃ N ₄ , Si(tr.)	44	43	32	plasma synthesis chemical
2	Si ₃ N ₄ /SiC 50	β-SiC, α-, β-Si ₃ N ₄ , Si(tr.)	38	49	37	plasma synthesis chemical
3	Si ₃ N ₄ /SiC 80	β-SiC, Si(tr.)	30.1	62	42	plasma synthesis chemical
4	Si ₃ N ₄ /SiC-Cu 70 6	β-SiC, Cu	31.2	55	58	plasma synthesis chemical
5	Si ₃ N ₄ /SiC-Zn 75 10	β-SiC, Zn	32.1	52	56	plasma synthesis chemical
6	Si ₃ N ₄ /SiC-Al ₂ O ₃ -Y ₂ O ₃ 75 4 4	β-SiC, Si(tr.), YSi ₂ (tr.)	32.7	57	37	plasma synthesis chemical
7	Si ₃ N ₄ /SiC-Al ₂ O ₃ 80 5,6	β-SiC, Si(tr.)	52.4	34	29	plasma synthesis of Si ₃ N ₄ /SiC with chemical deposition of Al ₂ O ₃
8	Si ₃ N ₄ /SiC-Y ₂ O ₃ 80 3,2	β-SiC, Si(tr.)	50.8	32	27	plasma synthesis of Si ₃ N ₄ /SiC with chemical deposition of Y ₂ O ₃
9	Si ₃ N ₄ /SiC-Al ₂ O ₃ -Y ₂ O ₃ 80 5,6 3,2	β-SiC, Si(tr.)	50.1	34	27	plasma synthesis of Si ₃ N ₄ /SiC with chemical deposition of Al ₂ O ₃ , Y ₂ O ₃
The content of components was calculated from date of chemical analysis without considering interaction of components or reduction of oxides.						

Table 1. Characteristics of typical prepared nanosized composites.

The diffractograms of Si₃N₄/SiC nanocomposites with oxides prepared by both routs show β-SiC, Si maxima and increased amorphous background. Beside this the XRD analysis indicates presence of YSi₂ in the plasma prepared nanocomposites. It means that at least partial reduction of oxides occurs in the plasma process and it should lead to formation of silicon oxynitride and possibly sialon type phases.

The dispersity of the produced nanocomposites strongly depends on concentration of particles in plasma flow (Fig. 2.). High content of vapours promotes particle growth and as result the specific surface area of product decreases according parabolic law. The concentration of particles higher as 10% increases the content of silicon, possibly due formation of large aggregates by collisions of liquid silicon particles. At the concentration of particles about 10% in nitrogen plasma flow the production rate of nanocomposites is 0.9–1.0 kg per hour.

Dispersity of the products depends also on growth time of particles which is varied by introducing quenching gas into region of vapours or by increasing the velocity of gas flow and product particles. Besides this the dispersity of the product is influenced by the composition of nanocomposite (Fig. 3).

The decreasing specific surface area of Si₃N₄/SiC nanocomposites with content of SiC can be explained by longer growth time of silicon carbide particles formed at higher temperature as silicon nitride. The decrease of the specific surface area of the nanocomposites with Cu or Zn is mainly due

increase of density of particles because change of calculated average particle size with metal content is small.

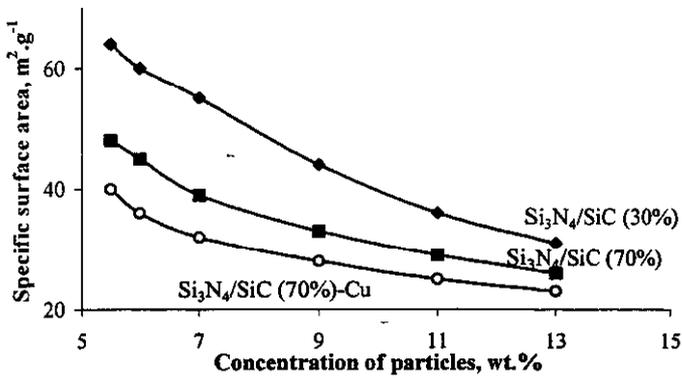


Fig. 2. Dependence of the specific surface area on concentration of particles in gases flow.

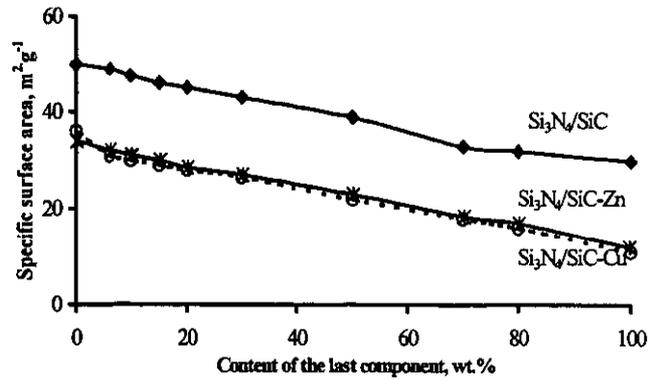


Fig. 3. Dependence of the specific surface area of Si₃N₄/SiC, Si₃N₄/SiC-Zn, Si₃N₄/SiC-Cu on the content of the last component.

From data of Table 1 follows that typical average particle size d of the produced nanocomposites is in the range of 30-60 nm and crystallite size $d_{cryst.}$ of SiC is from 27 nm up to 58 nm. The relatively low difference between calculated average particle size and crystallite size of SiC convinces that degree of agglomeration of particles is not high.

Additional calcination of nanosize composites in vacuum increases average particle size and crystallite size of SiC at temperature above 1200 °C (Fig. 4). The remarkable increase of average particle size of Si₃N₄ /SiC composites starts at 1350-1400 °C, but of composites with Al₂O₃ and Y₂O₃ at 1300 °C because sintering additives promote consolidation of particles. At the same time the increase of crystallite size of SiC with temperature is relatively slow. At 1500 °C the average particle size two times exceeds the crystallite size of SiC in the Si₃N₄/SiC nanocomposites.

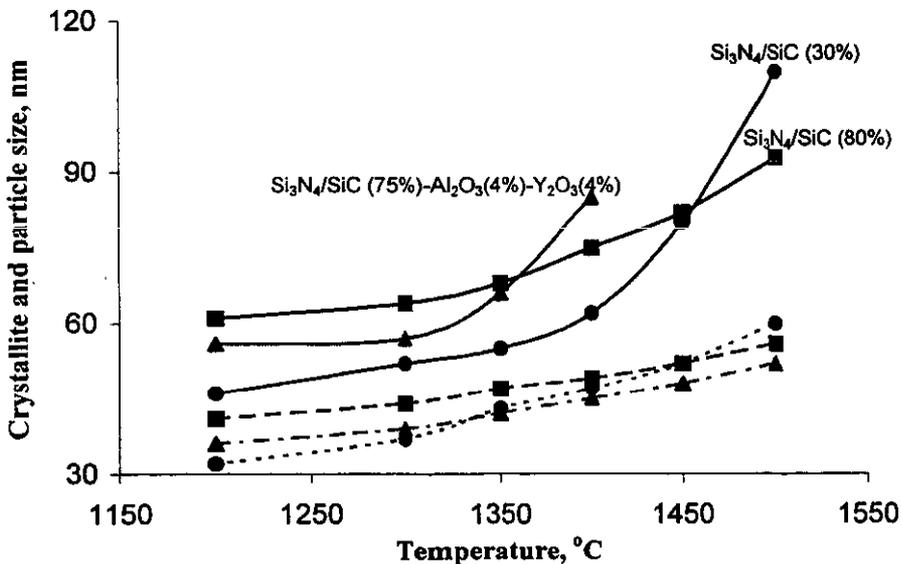


Fig. 4. Dependence of SiC crystallite size (dashed lines) and calculated average particle size (solid lines) of composites on calcination temperature in vacuum.

For Si₃N₄ /SiC- Al₂O₃-Y₂O₃ nanocomposites the difference is yet higher indicating that presence of aluminium and yttrium compounds limits recrystallisation of SiC. The similar results are obtained

by heat treatment of nanocomposites in argon, only the increase of particle average size and crystallite size of SiC is about 24-30% less.

The heat treatment of powders has influence on phase and chemical composition of nanocomposites (Table 2).

Samples	Phase composition				Method
	1300 °C, vacuum	1400 °C, vacuum	1500 °C, vacuum	1400 °C, argon	
Si ₃ N ₄ /SiC 30	β-SiC, α-, β-Si ₃ N ₄ , Si(tr.)	β-SiC, α-, β-SiC, Si (tr.)	β-SiC	β-SiC, α-, β-Si ₃ N ₄	plasma synthesis
Si ₃ N ₄ /SiC 80	β-SiC, Si(tr.)	β-SiC	β-SiC, Si (tr.)	β-SiC	plasma synthesis
Si ₃ N ₄ /SiC -Cu 70 6	β-SiC, Cu, Si(tr.)	β-SiC, α-, β-Si ₃ N ₄ (tr.), Si(tr.), Cu ₅ Si, Cu ₄ Si	β-SiC, α-, β-Si ₃ N ₄ (tr.), Si, Cu ₅ Si, Cu ₄ Si	β-SiC, α-, β-Si ₃ N ₄ (tr.), Cu ₅ Si, Cu ₄ Si	plasma synthesis
Si ₃ N ₄ /SiC -Al ₂ O ₃ -Y ₂ O ₃ 75 4 4	β-SiC, Si(tr.), YSi ₂	β-SiC, YSi ₂	β-SiC, Si(tr.), YSi ₂ , Al ₂ Y ₄ O ₉	β-SiC	plasma synthesis
Si ₃ N ₄ /SiC -Al ₂ O ₃ -Y ₂ O ₃ 80 5,6 3,2	β-SiC,	β-SiC, Si ₂ ON ₂ (tr.)	-	β-SiC, Si(tr.)	plasma synthesis with chemical deposition

Table 2. Phase composition of calcinated nanocomposites.

Calcination of samples reduced the content of free silicon at temperatures up to 1400°C. At higher temperatures content of silicon increases due to dissociation of silicon nitride in vacuum. There is a little difference between chemical and phase compositions of Si₃N₄/SiC-Al₂O₃-Y₂O₃ nanocomposites produced by single step plasmachemical synthesis and chemical route. From obtained results it is difficult to evaluate advantage of each method. Obviously such evaluation will be possible on the base of results of sintering and testing of materials characteristics.

4 Conclusions

1. The plasma technique could be successfully applied to preparation of Si₃N₄/SiC based nanocomposites with production rate about 1 kg per hour.
2. The average particle size of typical nanocomposites is in the range of 20-60 nm, but crystallite of SiC in the range of 27-58 nm.
3. Dispersity of nanocomposites depends on concentration of particles in gas flow, growth time of particles and ratio of components.

References

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