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Coating of plasma-processed nanosized powders

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Abstract

The homogeneous Si_3N_4/SiC nanocomposites with sintering additives of alumina and yttria have been prepared by plasma technique and combining plasma technique with chemical deposition of oxides. The powders have been characterized by XRD, TEM, Photon Correlation Spectroscopy and electrokinetic titration method. Both preparation routes allow us to produce coated particles with bimodal particle size distribution and average particle size in the range of 40–70 nm, but their surface characteristics and phase composition are different. The surface characteristics of Si_3N_4/SiC and Si_3N_4/SiC–Al_2O_3–Y_2O_3 nanocomposites prepared by plasma technique are similar to pure Si_3N_4 nanoparticles. The chemical deposition of oxides on the Si_3N_4/SiC nanoparticles leads to surface characteristics similar to pure alumina. The influence of the peculiarities of the prepared nanocomposites on their processing have been proved by hot pressing.

Keywords: Hot pressing; Microstructure; Nanocomposites; Powders-chemical preparation; Powders-gas phase reaction; Si_3N_4/SiC

1. Introduction

Silicon carbide/nitride based nanocomposites due to their hardness, mechanical strength, good corrosion and oxidation resistance at elevated temperature are promising candidates for high-temperature application.[1–3] and manufacture ceramic matrix composites.[4,5] However, mechanical and physical characteristics of ceramics strongly depend on their microstructure, determined by sintering regime, particle size, and homogeneity of raw powder and distribution of sintering aids.

The aids occupying the particles surface are of interest in the case of nanosized particles because of their high surface energy leading to formation of agglomerates. Different coating techniques have been studied intensively for the past few years. The surface modification improves the colloidal and casting characteristics and subsequently the properties of ceramic material.

The aim of the present work is the preparation of highly homogeneous Si_3N_4/SiC nanocomposites with sintering aids (Al_2O_3, Y_2O_3) by simultaneous evaporation of raw materials in an inductively coupled plasma flow as well as by chemical deposition of Al_2O_3 and Y_2O_3 on the Si_3N_4/SiC nanosized powders and comparison of their characterization. In this connection the specificity of plasma technique is discussed in comparison with a simple chemical precipitation from solutions containing metallic salts.

2. Experimental

2.1. Plasma chemical synthesis

The nanosize Si_3N_4/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[6] consists of a 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 collection of powder. The flow rate of the plasma-forming gas nitrogen is 7.6–8.0 $m^3.h^{-1}$ and the feed rate of raw powders is 0.9 $kg.h^{-1}$.

The raw powders of Si, or the calculated fractions of Si, Al_2O_3, Y_2O_3 are premixed and introduced into the 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 is reached by varying the particle size and their injection rate, feeding rate, plasma velocity and temperature. The formation of

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products, their particle size, chemical and phase composition are controlled by introduction of the ammonia and hydrocarbon into the reaction chamber.

2.2. Chemical deposition

The nanosized Si_3N_4/SiC particles produced by plasma chemical synthesis 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 calcinations in argon atmosphere. The flow chart of the procedure is displayed in Fig. 1.

2.3. Powder characterization

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 the BET argon adsorption–desorption method.

The crystallite size $d_{cryst.}$ of SiC is calculated from XRD data by using the Scherrer formula. The average particle size d is calculated from the specific surface area assuming spherical form of particles as well as determined by TEM and Photon Correlation Spectroscopy (PCS) studies.

The surface characteristics of prepared nanocomposites are determined by electrokinetic titration of powder suspension. A computer-controlled system, which combines *Zetamaster S* of *Malvern Instruments Ltd.*, *Mettler* autotitrator *DL21* and ultrasonic equipment, is used. This experimental technique allows determination of zeta potential-pH dependence, mean size and size distribution of the particles under study.

The suspension is prepared by dispersing 250 mg of the powder in 50 ml of water applying ultrasonic vibration and mechanical stirring simultaneously. After aging for 72 h the sample is subjected to a short ultrasonic pretreatment and 2 ml of the suspension are placed into the titration vessel containing 200 ml of 0.01 N KCl solution and then titrated with 0.1 N KOH and HCl solution from the natural pH 5.5 to 11 or 2 respectively.

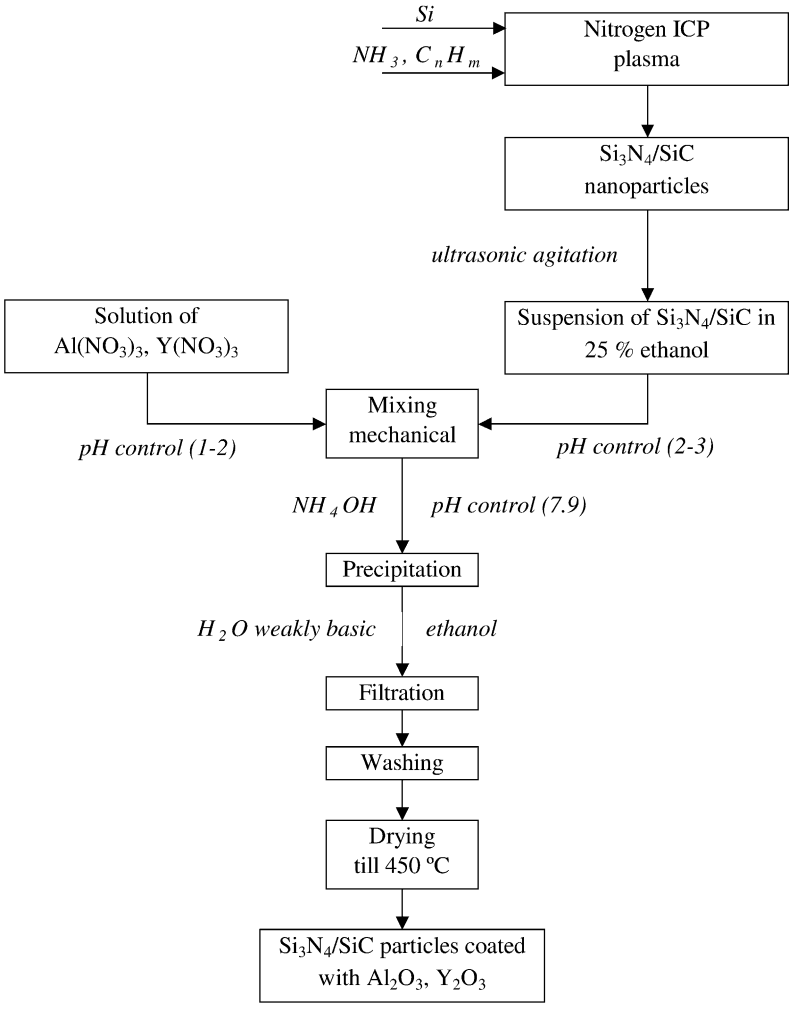

Fig. 1. Flow chart for the preparation of Si_3N_4/SiC particles coated with Al_2O_3 and Y_2O_3.

The isoelectric point (IEP) is determined as an intersection point of the titration curve with abscissa.

The particle size distribution is examined by PCS. The main measuring parameters are as follows: the number of prepared samples—10; the number or repeated measurements (subruns)—10; automatic sample measurement duration; the size of aperture 200 μm; the correlator setting in log mode, the number of channels—128; the cumulant calculation of the light scattering mean size (mean cumulative size); size distribution analysis method—CONTIN. Microsoft Excel data sort facilities are used to analyze the totality of submeasurement size data and to find out the best credible size distribution.

2.4. Densification of nanocomposites

In order to evaluate the processing behavior of the prepared nanocomposites three batches with close chemical composition have been selected for hot pressing: plasma-prepared Si_3N_4/SiC–Al_2O_3–Y_2O_3 (A), plasma-prepared Si_3N_4/SiC with chemically deposited Al_2O_3 and Y_2O_3 (B) and plasma-prepared Si_3N_4/SiC mechanicaly mixed with nanosized Al_2O_3 and Y_2O_3 (C).

All three batches have been hot pressed at 1850 °C in nitrogen with applied pressure of 30 MPa for 2 h. The density of the materials is measured by the Archimedes method, bending strength—by the three-point method at room temperature and hardness—by Vickers indentation technique (load 1 kg).

3. Results and discussion

The characteristics of typical Si_3N_4/SiC-based nanocomposites prepared by both routes are shown in Table 1. Chemical and phase composition of Si_3N_4/SiC-based nanocomposites depends on the ratio of hydrocarbon and silicon in the plasma flow. By varying the ratio the Si_3N_4/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 the content of SiC up to 90 wt.%, but the 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 40 wt.%. The weak, broad maxima of α-, β-Si_3N_4 and increased amorphous background on the XRD patterns indicate a 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 crystallization. The crystallinity of pure Si_3N_4 powder prepared by the similar plasma technique reaches only 10–60% depending on cooling rate of products and their specific surface area.[6]

The diffractograms of Si_3N_4/SiC nanocomposites with oxides prepared by both routes show β-SiC, traces of Si maxima and increased amorphous background. Besides this, the XRD analysis indicates the presence of YSi_2 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. These compounds produced by plasma technique are X rays amorphous.

Fig. 2 demonstrates the electrokinetic titration curves for Si_3N_4/SiC nanocomposite and for dopped Si_3N_4/SiC nanocomposites produced by different processing routes—plasma chemical and chemical. The kind of information obtained by the surface titration is sensitive to the surface composition as the nature and number of the charged groups at the surface governs the pH dependence on zeta potential primly. Some conclusions can be drawn from the titration curves presented in Fig. 2. Si_3N_4/SiC nanocomposites produced by plasma with and without oxide additives give the similar titration curves evidencing that the introduction of oxides in the plasma jet does not influence the properties of the particle surface. The results show that the surface of chemically treated particles is thoroughly transformed.

Table 1
Characteristics of typical prepared nanosized composites

No.	Content of components (wt.%)			XRD	SSA ($m^2\ g^{-1}$)	d (nm)	$d_{cryst.}$ (SiC, nm)
	SiC	Al	Y				
1	30	–	–	β-SiC, α-, β-Si_3N_4 (tr.), Si (tr.)	44	43	32
2	50	–	–	β-SiC, α-, β-Si_3N_4 (tr.), Si (tr.)	38	49	37
3	80	–	–	β-SiC, Si (tr.)	30.1	62	42
4	75	2.3	3.4	β-SiC, Si (tr.), YSi_2 (tr.)	42.7	57	37
5[a]	70	9	3.6	β-SiC, Si (tr.)	44.6	39	36

[a] Prepared by combining plasma chemical synthesis of Si_3N_4/SiC with chemical deposition.

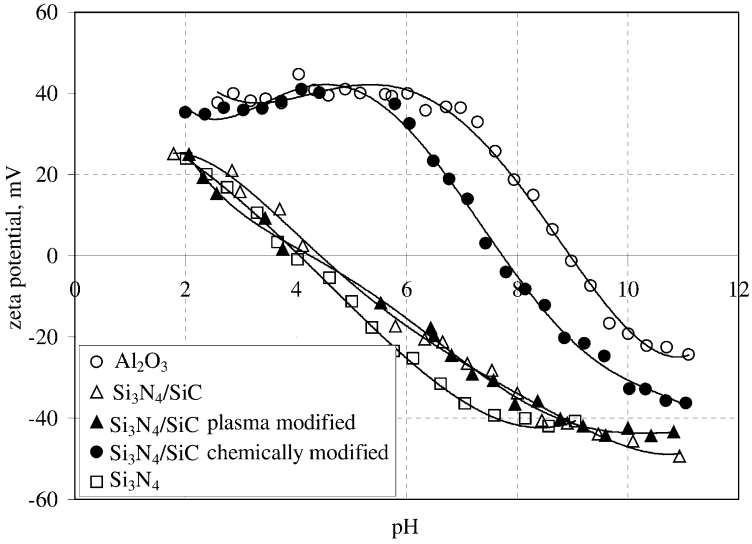

Fig. 2. Electrokinetic titration curves for dopped Si_3N_4/SiC nanocomposites produced by different processing routes and for plasma-prepared Al_2O_3 and Si_3N_4.

The IEP is shifted from pH 4.4 for initial powder to pH 7.75 for the chemically treated one, zeta potential reaching a high positive value. Obviously, the coverage with oxides changes the surface electrokinetic properties. As is seen from the location and shape of the curves, Al_2O_3 dominates on the chemically treated Si_3N_4/SiC nanocomposite surface.

The established surface characteristics of the plasma prepared nanocomposites and chemically treated nanoparticles can be explained regarding the formatting feature of compounds in the plasma flow. It is well known that the microstructure of nanocomposites prepared from vapor phase in plasma flow with gradually decreasing temperature strongly depends on formation or condensation temperature of components.[6] The component formed at the higher temperature can act as nuclei for condensation of the other component. In the system Si_3N_4/SiC–Al_2O_3–Y_2O_3 the essential difference of condensation temperatures of Y_2O_3 (4300 °C), Al_2O_3 (3000 °C) and formation temperatures of SiC (2830 °C), Si_3N_4 (1900 °C) leads to formation of nanoparticles with complex microstructure. The nucleus of Al_2O_3 and Y_2O_3 can be enclosed in the layer of SiC and Si_3N_4 as well of Si_2ON_2 regarding partial reduction of oxides by silicon. As a result the plasma prepared Si_3N_4/SiC nanocomposite dopped with oxides has similar to Si_3N_4/SiC or Si_3N_4 surface characteristics determined mainly by the presence of Si_3N_4 on the surface (see Fig. 2), as well as various Si_3N_4/SiC composites reveal similar electrokinetic surface properties regardless of the SiC content changing in the large scale (Table 1).

Fig. 3 plots the particle size distribution by number and by volume for Si_3N_4/SiC and dopped Si_3N_4/SiC nanocomposite powders obtained in plasma and for the chemically modified sample. The distribution curves by number exhibit long "tail" towards the big particles. It indicates the existence of a small amount of large particles. The particle size distribution by volume is bimodal for all powders under study. As can be seen the shape of size distribution curves for Si_3N_4/SiC nanocomposite powders produced by plasma and later chemically modified is generally similar. It confirms that the chemical process—precipitation and subsequent heating—uniformly coats all particles in the size spectra. The maximum of size distribution peak by number is increased from 45 nm for Si_3N_4/SiC powder to 70 nm for the modified one. Both maximums are close to the theoretical particle size value calculated from the specific surface area data (Table 1).

The TEM investigations of plasma prepared Si_3N_4/SiC nanocomposite confirm the presence of large particles. The sample besides small nanoparticles with a size

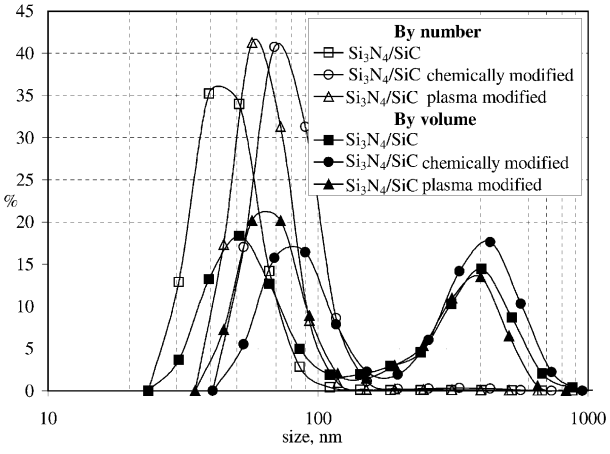

Fig. 3. The best credible particle size distributions measured by Zetamaster S. Calculation method CONTIN.

of 10–50 nm contains particles with a size up to some hundred nm (Figs. 4 and 5).

Therefore both preparation routes allow us to obtaining uniform Si_3N_4/SiC nanocomposites dopped with sintering additives, but their surface characteristics differ strongly.

Density and mechanical parameters of manufactured materials depend on the preparation route of nanocomposites (Table 2). The lowest values of density and mechanical properties are obtained for the hot pressed samples of mechanically premixed nanopowders. It can be explained by more uniform distribution of the oxide dopants in the batches A and B. Microstructures of hot pressed powders are very similar and grain size for all materials reaches 0.1–1 μm (Fig. 6). These results exhibit a remarkable grain growth during sintering and prove that the presence of oxides on the surface of Si_3N_4/SiC particles has small influence on this process.

Table 2
Parameters of hot pressed at 1850 °C nanocomposites

Samples	Density (g/cm^3)	σ_{20° (MPa)	E_{20° (GPa)	HV (GPa)
A	3.06	548±33	327±11	18,8
B	3.16	609±30	374±10	17,4
C	2.99	517±46	302±16	17,1

In general, determined parameters show some advantage of nanocomposites prepared by single step plasma synthesis or by two step route including plasma synthesis and subsequent chemical deposition over mechanical mixture of the nanosized powders. Obviously, the further improvement of the material parameters

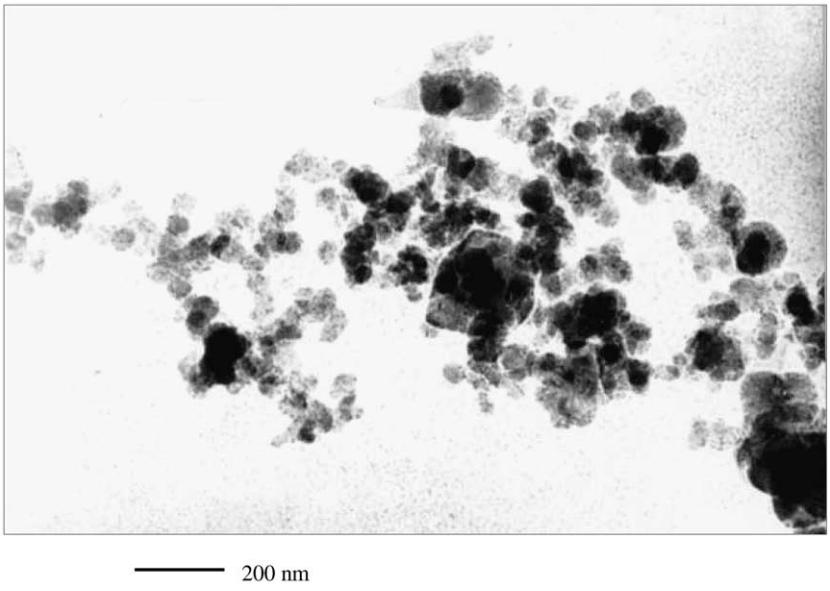

Fig. 4. Micrograph of Si_3N_4/SiC nanocomposite produced by plasma technique.

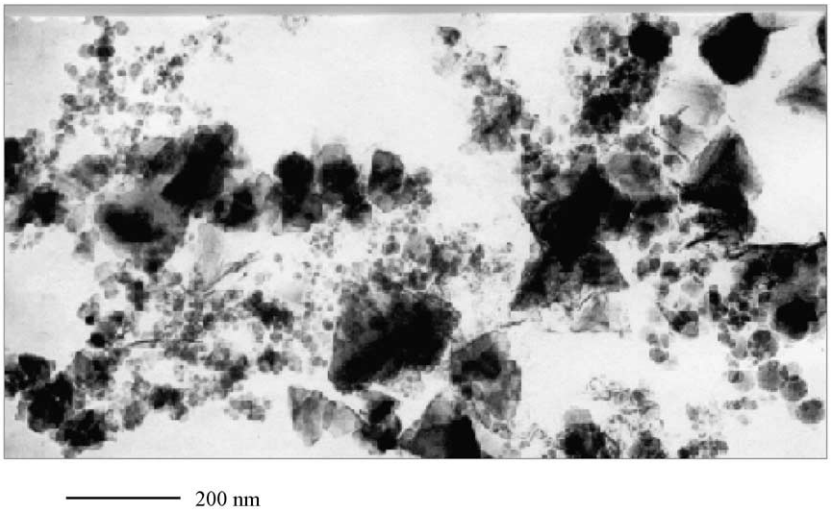

Fig. 5. Micrograph of Si_3N_4/SiC dopped with Al_2O_3 and Y_2O_3 nanocomposite produced by plasma technique.

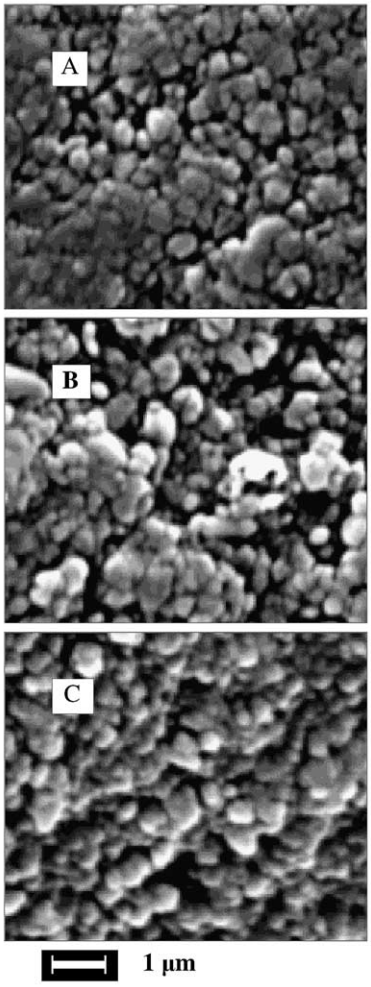

Fig. 6. Microstructure of chemically etched materials: A, B and C.

demands the optimization of the amount of oxide dopants and hot pressing conditions.

4. Conclusions

1. Evaporation of silicon, alumina and yttria powders in nitrogen plasma in the presence of hydrocarbons as well as chemical deposition of oxides on Si_3N_4/SiC nanoparticles allows to obtain nanocomposites with complex microstructure, but their surface characteristics strongly depend on preparation route.
2. Microstructure of the plasma prepared Si_3N_4/SiC and Si_3N_4/SiC nanocomposites dopped with oxides depends on the formation or condensation temperatures of components and therefore Si_3N_4—component with the lowest formation temperature, determines the surface characteristics of the particles.
3. Coated particles with surface characteristics similar to alumina can be obtained combining the preparation of Si_3N_4/SiC nanocomposites by plasma technique and chemical deposition of the oxides from the solution.
4. Crystallite size of the basic component of nanocomposites—SiC is in the range of 32–42 nm, calculated average particle size is in the range of 39–62 nm, but powder has bimodal particle size distribution including particles with size up to some hundred nm.
5. Microstructure and grain size of hot pressed[7,8] nanocomposites prepared by both routes are similar, but chemical deposition of oxide dopants on the surface of Si_3N_4/SiC particles leads to the improvement of the strength of the bulk material with respect to the materials prepared by plasma synthesis and especially by mechanical mixing of the components.

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