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Aerosol-assisted synthesis of SiC-based nanopowders from organosilicon precursor systems

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Thermally-driven decomposition of various organosilicon derivatives under a neutral gas atmosphere constitutes a reliable way for the preparation of carbon/silicon carbide C/SiC composites (modified carbon materials) in the nanosized range. The two-stage aerosol-assisted synthesis method appears to be especially well suited to fabricate such materials while offering spherical particle morphology with tailored particle size capability. In this method, in the first stage an aerosol mist is generated from a liquid precursor system and transported in a neutral gas stream to a pre-heated ceramic tube reactor where complex physical and chemical changes take place resulting in the formation of solid particles collected on an exit filter. The raw product is usually pyrolyzed in the second stage at appropriately high temperatures to complete the anticipated removal of residual oxygen if excess C is present *via* carbothermal reduction. In this study, preliminary results on the target C/SiC composites prepared with the aerosol method from selected organosilicon precursors are presented. The precursors included hexamethyldisiloxane, tetramethoxysilane, and silicone oil (poly(dimethylsiloxane)) and its ethanol solutions. In the first stage, the aerosols were subject to decomposition at 1200 ºC under an Ar flow and raw products containing SiO_xC_y/SiO_2 and free C of varied proportions were produced. In the second stage, the raw powders were pyrolyzed at 1650 ºC for 1 h under an Ar flow. The presence of a sufficient excess of free C in the raw product should lead in principle to efficient carbothermal reduction processes and conversion of SiO_xC_y/SiO_2 to SiC in a composite system with the remaining free carbon, if any; otherwise, SiC/SiO_2 or even $SiC/SiO_2/Si$ composites can be produced.

Key words: *silicon carbide; C/SiC; composite; aerosol; nanocrystalline material*

1. Introduction

Due to many advantageous properties, silicon carbide SiC has found numerous applications in ceramics and electronics. In recent years, many expectations have

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rested with specific properties of nanocrystalline forms of SiC. For example, a plausible combination of quantum size effect and donor sites has resulted in nano-SiC emitting in the blue range which may have great potentials in optoelectronics [1]. Also, an attractive optical behaviour has been detected in nano-SiC dispersed in photopolymer matrices [2, 3]. Pure and doped SiC powders have been probed as dielectrics at microwave frequencies of 4–18 GHz to appraise their insulating properties and absorption of electromagnetic waves [4]. On the application side in ceramics, high thermal and mechanical resistance of SiC resulted in its utilization as a valuable component in various composite systems. In the case of carbons, SiC is frequently considered as the component of choice by advantageously modifying high temperature properties of carbon materials (C/SiC composites) [5, 6].

Classical approaches to the synthesis of SiC usually include reactions of elemental silicon with carbon or carbothermal reduction of SiO_2 with carbon (elemental C or C source derived from *in situ* decomposition of various hydrocarbons). In both cases, due to required high processing temperatures, microcrystalline SiC is produced. The prerequisite mechanical grounding/milling/mixing of solid precursors in such syntheses may be additionally a source of serious contamination of the product. As far as nanocrystalline SiC is concerned, it is commonly prepared via sol-gel processes from resulting organosilicon-derived colloids [7].

In our previous studies on the C/SiC system, we applied homogenized mixtures of a coal tar pitch and silicon precursors such as poly(carbosilane), elemental silicon [8], and poly(dimethylsiloxane) [9]. The final pyrolysis at 1650 ºC was necessary in these systems to produce a prevailing regular polytype of SiC (β-SiC) with 14–24 nm average crystallite sizes mixed with a poorly crystallized turbostratic carbon. In this regard, the utilization of poly(carbosilanes) as single source precursors containing Si–C bonds enabled Yajima et al. preparation of SiC fibres on the commercial scale (Nicalon fibres) [10, 11].

Yet another way to approach the preparation of nanocrystalline powders of SiC or C/SiC composites is the application of the aerosol-assisted synthesis method utilizing neat organosilicon derivatives or their suitable solutions. In this method, upon generation the aerosolized precursor mist is transported in a stream of neutral gas through a pre-heated ceramic tube reactor. In the high temperature zone and under appropriate conditions, complex physical and decomposition reactions take place producing solid particles of spherical morphology that are collected on an exit filter. This raw product is usually subject to a second-step pyrolysis under special conditions (temperature, time, gas atmosphere) to complete the anticipated changes and yield the final product. It is instructive to point out that one of the outstanding features of the aerosol-assisted process is that all reactions take place within very small liquid/solid particles suspended in a gas stream. In favourable cases, this creates more advantageous conditions for processing toward nanosized particles compared to typical one-stage bulk pyrolysis methods.

One has to be aware of the fact that thermal decomposition of some organosilicon precursors, especially those containing oxygen, may result in the formation of transient glassy SiO_xC_y phases of variable composition depending on the type of precursor. Furthermore, some by-product carbon clusters are known to be entrapped in such phases. It has been reported that the silicon oxycarbide glasses can be stable up to 1200 ºC [12, 13] while higher temperatures of the order of 1400–1600 ºC result in phase separation and/or progressing carbothermal reduction to yield mostly β-SiC or C/SiC if enough carbon is present while β-SiC/SiO_2 (nanocrystalline or amorphous) [14] or β-SiC/Si are formed in the systems deficient in carbon and rich in silicon [15]. A similar behaviour was noticed in the case of silsesquioxanes where the decomposition of the transient silicon oxycarbides in the 1200–1400 ºC range resulted in the formation of mostly amorphous mixtures of SiC and SiO_2 in addition to small quantities of crystalline SiC and turbostratic graphitic carbon [16].

In this report, preliminary results of the study on the nanocrystalline composite C/SiC powders prepared *via* the two-stage aerosol-assisted method utilizing selected oxygen-bearing organosilicon precursor systems have been discussed. The progress of decomposition and evolution of final products is described, based on the characterization with powder XRD spectroscopy, FT-IR spectroscopy, SEM examination, and carbon content determinations.

2. Experimental

The raw powders were made by the aerosol-assisted synthesis method. The experimental set-up consisted of an ultrasound aerosol generator with the output connected to a ceramic tube reactor, ID = 76 mm, length = 1500 mm, while a fine nylon filter was attached at the air-cooled reactor exit. The reactor was placed in an electric tube furnace routinely preheated to 1200 ºC. The aerosol mist was transported through the reactor in an argon gas stream, 4 dm^3/min, and the solid product was collected on the filter. Neat hexamethyldisiloxane $[(CH_3)_3Si]_2O$ (Aldrich), neat tetramethoxysilane $Si(OCH_3)_4$ (Aldrich), and a 50:50 (by volume) ethanol solution of poly(dimethylsiloxane) $[–O–Si(CH_3)_2–]_n$ (Silikony Polskie, Nowa Sarzyna, Poland) were used as precursors. The raw products were dark brown to black free flowing powders. They were pyrolyzed in the second stage at 1650 ºC for 1 h under an Ar flow. Instrumental characterization methods included the powder XRD determinations (PANanalytical, Model X'Pert Pro, Holland, CuK_α, $\lambda = 1.54060$ Å), FT-IR spectroscopy (Nicolet 380, Thermo Electron Corporation, KBr pellets), and SEM (Hitachi, Model S-4700). In order to evaluate the free carbon contents, mild oxidation of powder samples in air, 700 ºC, 90 min, was carried out and the resulting changes of sample weights were used in calculations assuming $C + O_2 = CO_2\uparrow$ and no significant reactions of the SiC component under applied conditions. In addition, the total carbon contents were evaluated by combustion of powder samples in oxygen at 1300 ºC with detection of CO_2 by an IR analyzer (ACS-40/1350 IR-analyzer, PIE Warsaw, Poland).

3. Results and discussion

A typical morphology of raw powders examined with SEM is displayed in Fig. 1. The powders obtained from hexamethyldisiloxane (a) and ethanol solution of poly(dimethylsiloxane) (b) show a characteristic spherical particle morphology of quite uniform sizes while, occasionally, individual particles tend to be partially fused and agglomerated. Similar spheroidal appearance is shown by the powder from tetramethoxysilane (c) alas with seemingly more deformed particles.

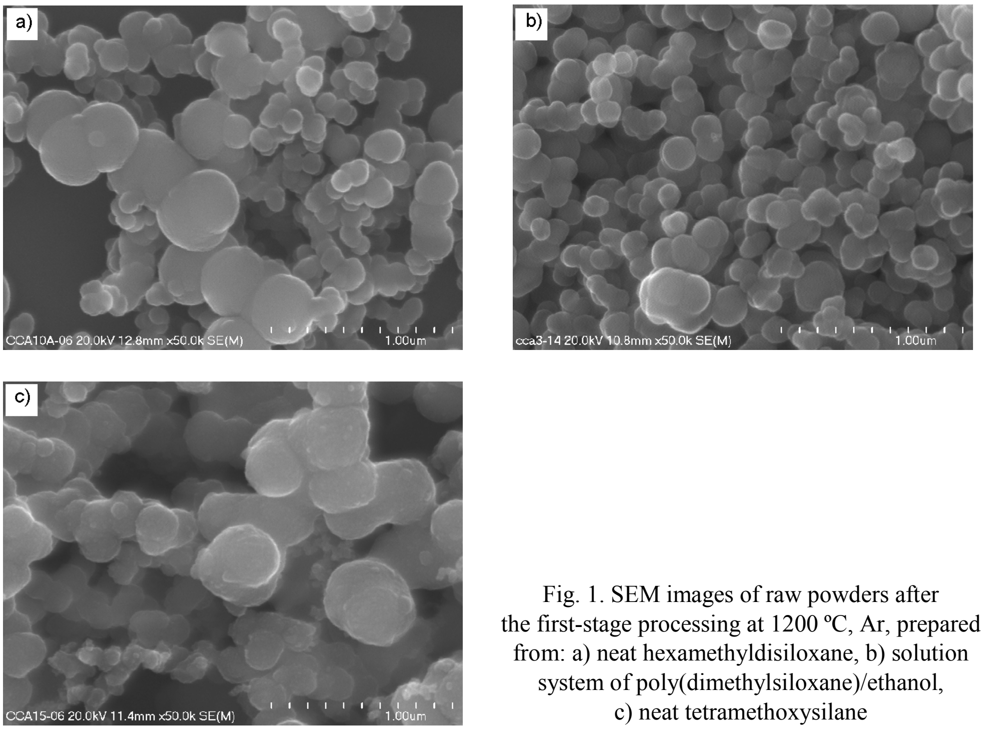

Fig. 1. SEM images of raw powders after the first-stage processing at 1200 ºC, Ar, prepared from: a) neat hexamethyldisiloxane, b) solution system of poly(dimethylsiloxane)/ethanol, c) neat tetramethoxysilane

The prevailing spherical shape of the particles stems from both the characteristics of the aerosol generation step and dynamics of the following decomposition/polymerization processes. In this regard, in the initial stage spherical droplets in the mist are introduced into the preheated reactor to undergo thermochemically induced changes. If a precursor solution is used, the evaporation of the solvent and precipitation of the precursor that may possibly collapse into a smaller-diameter sphere first take place. In the case of all our precursors, the progressing decomposition of the neat precursor is associated with continuing polymerization processes occurring mainly from the outer layers toward the core of the spheres and resulting in time-dependent increasing viscosities while preserving the overall shape of stiffened particles. Some incidental impacts and possible bursting events, the latter due to developed hindrances in volatiles evolution from the core, may cause particle deformation at this stage, too. At a certain point, the polymerization and accompanying carbothermal reduction processes eventually result in solidification of individual particles or particle agglomerates.

The particle morphology "imprinted" in the first stage is found to be, generally, preserved after the subsequent second-stage pyrolysis at 1650 °C under an Ar flow. The molecular-scale or micro-scale carbothermal reduction, phase separation, and crystallization phenomena taking place during the pyrolysis do not appear to influence the overall macrosized particle shape and diameter (typically, up to several micrometers). It is worth pointing out that relatively large SiC crystallites with well developed facets were occasionally observed among the prevailing spheres, the former indicative of recrystallization/growth phenomena taking place locally under advantageous conditions. Also, in the final product from tetramethoxysilane some severely fused agglomerates were detected that were absent in the raw powder and this supported a partial melting and fusing of the particles during the final pyrolysis. Small quantities of whiskers were additionally observed in this product, possibly resulting from the gas phase reaction of the type:

$$SiO_{(g)} + 3CO_{(g)} \rightarrow SiC + 2CO_2$$

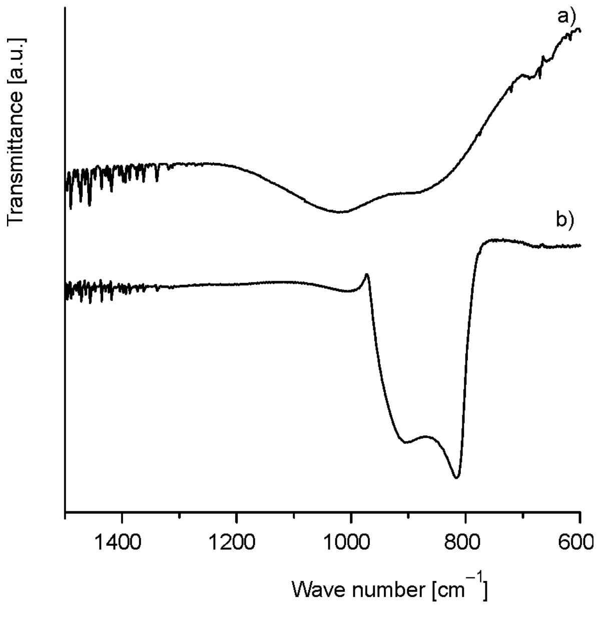

Fig. 2. FT-IR spectra for products prepared from neat hexamethyldisiloxane (KBr pellets): a) raw powder after first-stage processing at 1200 °C, Ar, b) final powder after second-stage pyrolysis at 1650 °C, Ar

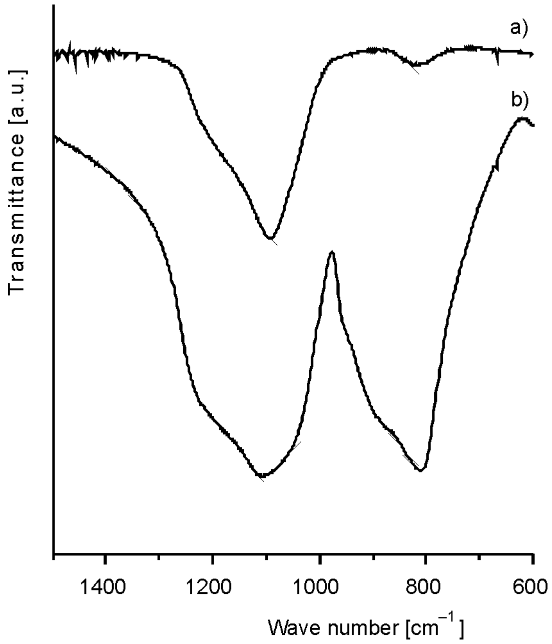

Fig. 3. FT-IR spectra of products prepared from neat tetramethoxysilane (KBr pellets): a) raw powder after first-stage processing at 1200 °C, Ar, b) final powder after second-stage pyrolysis at 1650 °C, Ar

Figures 2 and 3 present FT-IR spectra of the products prepared from hexamethyldisiloxane and tetramethoxysilane, respectively. In each case, the spectrum a) was collected for the raw product and spectrum b) for the final product in the system. Both spectra for the raw products appear to be similar to each other in the characteristic spectral ranges, i.e., they contain absorption bands associated with Si–O bonds (stretching mode at ca. 1060 cm^{-1}) and Si–C bonds (stretching mode at ca. 850 cm^{-1}). On the other hand, the respective IR spectra of the final products after the pyrolysis at 1650 °C point out to their different chemical make-up. In the case of the powder from hexamethyldisiloxane (Fig. 2b), there are exclusively absorptions related to Si–C bonds while for the powder from tetramethoxysilane (Fig. 3b) Si–O bonds seem to persist and can be linked to some silica SiO_2. The latter is further corroborated by the powder XRD determinations (*vide infra*). The presence of silica indicates a deficiency of carbon in the raw product of which definite excess is inevitable for carbothermal reduction to occur in the second stage. The excess C affects the extent of oxygen removal from SiO_xC_y/SiO_2 in the form of volatile carbon oxides (carbon as oxygen scavenger) and, therefore, creates right conditions for the formation of the target SiC or C/SiC products.

The XRD patterns of the powders prepared from hexamethyldisiloxane are shown in Fig. 4, the diffractogram a) is recorded for the raw powder and diffractogram b) for the final product. The diffractogram a) is typical of the prevailingly amorphous material. The very broad halo at $2\theta \approx 25°$ can be interpreted as related to small quantities of disordered graphitic carbon structures and that at $2\theta \approx 35^\circ$ can likely be linked to emerging nanocrystalline β-SiC. On the other hand, the most intense peaks in the pattern b) are assigned to the major regular phase of β-SiC (average crystallite size of 32 nm as determined from the Scherrer equation) and the remaining small intensity peaks are associated with the minor hexagonal α-SiC polytype. No broad features typical of turbostratic carbon are seen here (within the detection limits of the powder XRD method) that, to be recalled, was detected in the raw powder in this system. This observation is consistent with the most of the free carbon being consumed in the carbothermal reduction of SiO_xC_y/SiO_2 during the second-stage pyrolysis. In this regard, low temperature oxidation of the final powder showed some 7.7 wt. % of free C to be compared with 9.5 wt. % of free C in the raw powder. The presence in the product of such a small proportion of turbostratic carbon, possibly, resulted in broadening of the low intensity diffraction peaks due to C beyond detection limits of the XRD method.

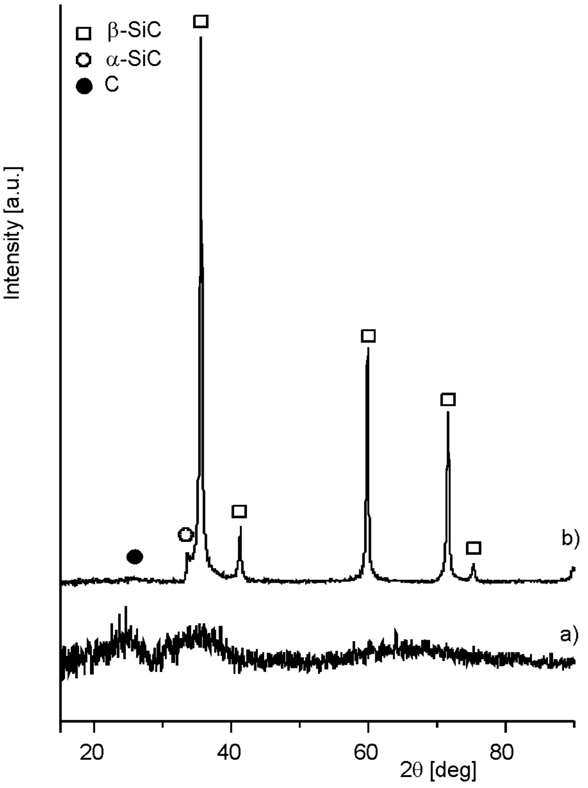

Fig. 4. Powder XRD patterns for products prepared from neat hexamethyldisiloxane: a) raw powder after first-stage processing at 1200 °C, Ar, b) final powder after second-stage pyrolysis at 1650 °C, Ar

Figure 5 contains the XRD patterns for the raw product (a) and final product (b) in the poly(dimethylsiloxane)/ethanol system. The diffractogram a) shows only three broad halos at 2θ equal approximately to 25, 43, and 80° characteristic of the turbostratic graphitic domains. This corresponds well with significant quantities of free C available in the raw product from the thermal cracking of ethanol; the excess carbon was analyzed in the product at 85.5 wt. % and the total carbon at 94.9 wt. %.

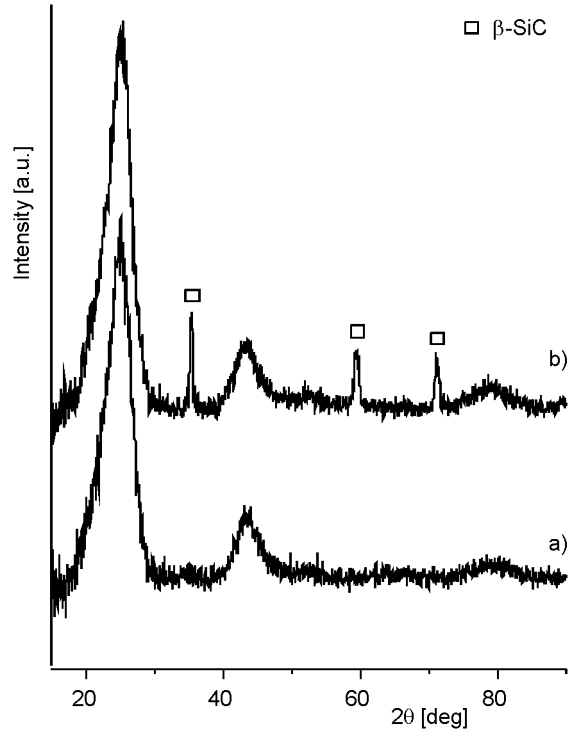

Fig. 5. Powder XRD patterns for products prepared from the solution system of poly(dimethylsiloxane)/ethanol: a) raw powder after first-stage processing at 1200 °C, Ar, b) final powder after second-stage pyrolysis at 1650 °C, Ar

The diffractogram b) for the pyrolyzed powder also shows the peaks for turbostratic carbon and the widths of the peaks appear to be very similar to those in the diffractogram a). This kind of behaviour suggests that the additional pyrolysis at 1650 °C does not result in a detectable increase of crystalline ordering of carbon in this powder. In addition to the carbon phase, the peaks due to the minor phase of β-SiC (average crystallite size of 9 nm) are also seen. Free carbon in the final powder was found at 73.5 wt. % and the total carbon at 94.5 wt. % supporting only small nonetheless detectable extent of carbothermal reduction during the second-stage pyrolysis in this system with a large excess of free carbon.

The XRD patterns for the raw and final products prepared from tetramethoxysilane are shown in Fig. 6. The broad feature in Fig. 6a at 2θ ranging approximately from 20° to 22° can be assigned to highly amorphous SiO_2 apparently already formed in the first stage at 1200 °C. The final product is composed of the major β-SiC and minor α-SiC phases as well as of some crystobalite SiO_2 as supported by Fig. 6b. Moreover, a small quantity of re-solidified tiny spheres likely to be elemental Si (m.p. 1410 °C) was found in the crucible bottom after product discharge.

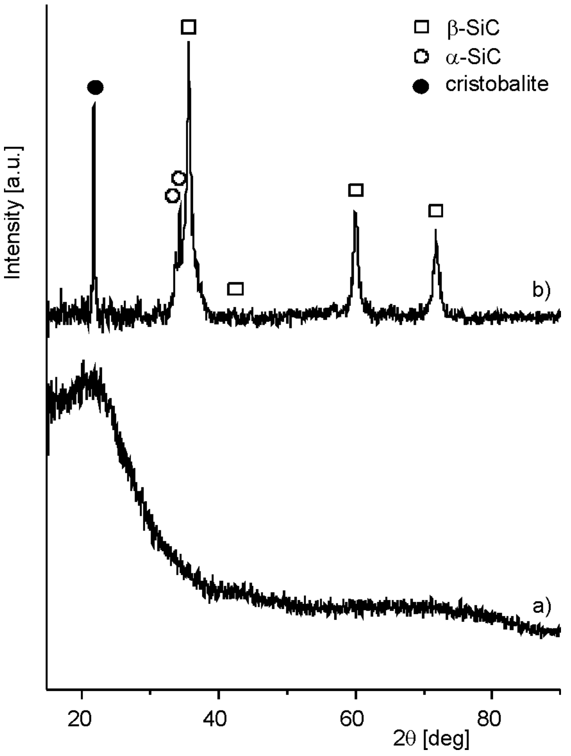

Fig. 6. Powder XRD patterns for products prepared from neat tetramethoxysilane: a) raw powder after first-stage processing at 1200 °C, Ar, b) final powder after second-stage pyrolysis at 1650 °C, Ar

All this has to be confronted with the low temperature determination of free carbon, <1 wt. %, and the total carbon content of mere 7.2 wt. %. Based on that, one can deduce that there is a severe deficiency of carbon in this system, the latter needed for the efficient carbothermal reduction of SiO_2 (and/or SiO_xC_y) to SiC according to the overall reaction $SiO_2 + 2C \rightarrow SiC + CO_2\uparrow$. With the deficiency of carbon, some unreacted SiO_2 may persist and/or even elemental Si may be formed from incomplete reduction/carbidization according to $SiO_2 + C \rightarrow Si + CO_2\uparrow$ as demonstrated in this system.

4. Conclusions

The average crystallite sizes of the SiC-based powder nanocomposites prepared with the aerosol-assisted method from the pool of readily available organosilicon precursors can be reasonably controlled. The method provides the powders with spherical/spheroidal particle morphology of quite uniform sizes and with varying degrees of primary agglomeration, *i.e.*, loose or partially fused spheres.

The utilization of neat hexamethyldisiloxane under applied conditions yields the powder composed of the major β-SiC and minor α-SiC phases and very small quantities of free carbon. It is worth pointing out that this product upon a mild oxidation treatment could be a source of pure nanocrystalline SiC powders.

The use of the solution precursor system of poly(dimethylsiloxane)/ethanol is advantageous for the prevailing formation of β-SiC in the composite system with excess free carbon. There is ample room in this system for adjusting the C/SiC composition by setting up the solvent to precursor ratios within the miscibility range.

Finally, the utilization of neat tetramethoxysilane with, apparently, insufficient available carbon to complete the carbothermal reduction processes yields mixtures of SiC with SiO_2 and elemental Si. From the viewpoint of the target composite C/SiC, in order to remedy the problem of carbon deficiency in this system, one can preferably apply a suitable organic solvent (source of carbon *via* solvent cracking) in the aerosol generation stage or ensure an additional source of carbon during the second-stage pyrolysis. Such options are planned to be explored in the near future.

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