Nanoproceses in polymer-derived Si–O–C ceramics: Electronmicroscopic observations and reaction kinetics

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Nickel acetate doped poly(methylphenylsilsesquioxane) with and without silicon filler loading was pyrolysed in argon atmosphere between 800 and 1500 °C. The ceramic residues were investigated with specific view of the nanoaggregates formed in pores during the polymer-to-ceramic conversion. After pyrolysis at 900 °C carbon nanotubes as well as nanowires with a crystalline SiC core and an amorphous SiO$_2$ shell were found in Si filler-free and Si filler-loaded samples, respectively. The evolution of the microstructure and the composition of these carbon nanotubes and SiC/SiO$_2$ nanowires were studied by HREM, SEM, EELS, EFTEM and evolved gas analysis.

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1 Introduction

Polymer-derived ceramics have gained growing interest due to their unique combination of low temperature processing, versatile shaping, and the capabilities of property tailoring via microstructure and composition design [1–3]. Manufacturing of these materials can be carried out from preceramic polymers based on poly(silanes), -(carbosilanes), -(silazanes), -(borosilazanes) and -(siloxanes) or mixtures thereof. Processing of preceramic polymers into ceramic products involves shaping of a low viscous polymer precursor, subsequent curing, and pyrolysis at temperatures above 800 °C. Due to a pronounced density difference between the polymer (1–1.2 g/cm$^3$) and the ceramic phases (2–3 g/cm$^3$), a shrinkage of up to 70 vol.% may occur which gives rise for extended porosity formation or even cracking in the pyrolysed ceramic residue material. Manufacturing of bulk components from preceramic polymers, however, is facilitated when the polymer is loaded with a filler powder, typically in the range of 30–50 vol.%. Inert as well as reactive filler powders such as Al$_2$O$_3$, SiC, B$_4$C, Si$_3$N$_4$, Ti, Cr, Mo, B, MoSi$_2$ were successfully demonstrated to reduce the polymer-to-ceramic shrinkage [4].

The pyrolysis of plain poly(organosilsesquioxanes) in inert atmosphere in the temperature range up to 1100 °C results in the formation of a silicon oxycarbide glass, which is in a metastable state consisting nominally of SiC, SiO$_2$ and C (free carbon). The release of hydrocarbons, water and hydrogen, an accompanying process, usually starts with the beginning of the polymer decomposition typically at ~400 °C and is almost completed at ~1000 °C. Water and ethanol is generated during crosslinking reactions in the temperature range from 200 to 400 °C, while benzene is released in the temperature range...
between 420 and 600 °C, methane between 700 and 1000 °C, and hydrogen between 500 and 1000 °C, respectively.

Nanotubes and nanowires in the Si–C–O system are promising candidates for electronic devices operating at high temperature, high power, and high frequency, due to their unique combination of electronic, chemical, thermal and mechanical properties [5]. The fabrication of Si–C–O nanowires was demonstrated by thermal activation of reaction systems consisting of SiO$_2$/Si in the presence of a carbon source (graphite or hydrocarbon; C$_3$H$_8$) without [6, 7] and with transition metal additives as catalyst [8, 9] at temperatures between 1250 and 1800 °C. A further method is the conversion of SiC powder in the presence of transition metals (cobalt, iron) in the temperature range from 1300 to 1700 °C [10, 11].

The fabrication of nanowires with core/shell structure was demonstrated in the system SiC/BN where SiC nanofibers were coated with boron nitride in a separate thermal treatment [12], and in the system SiC/SiO$_2$ where an amorphous SiO$_2$ layer was formed simultaneously [13].

In [14] the in situ formation of SiC nanorods in the Si–C–N preceramic polymer system was demonstrated in the presence of FeCl$_2$ as catalyst at 1700 °C. However, no work is known with respect to in situ growth of SiC/SiO$_2$ nanowires for the fabrication of composite materials in the preceramic polymer system Si–O–C.

The present work deals with a novel method for the direct in situ formation of carbon nanotubes and silicon carbide/silicon oxide (SiC/SiO$_2$) nanowires from transition metal catalyst and silicon loaded pre-ceramic polymers of the poly(organosilsesquioxane) type. The nanotubes and nanowires were formed in the pores and/or cracks of the polymer derived ceramic after pyrolysis in the temperature range from 900 to 1500 °C in inert atmosphere. This method is supposed to be suitable for the in situ fabrication of composite materials with tailored mechanical and electrical properties at comparatively low temperatures.

The main emphasis of the paper is on the microstructural and nanochemical characterization of the nanotubes and nanowires with the objective of understanding and controlling of their formation depending on silicon filler and transition metal doping and on pyrolysis conditions.

## 2 Experimental

### 2.1 Sample preparation

Nickel acetate tetrahydrate (Ni(ac)$_2$·4H$_2$O, Merck KGaA) was dissolved in ethanol and added rapidly to an alcoholic solution of poly(methylphenylsilsesquioxane) with the general formula \[\left[\left(\text{C}_6\text{H}_5\right)_{0.62}\left(\text{CH}_3\right)_{0.31}(\text{OR})_{0.07}\text{SiO}_{1.5}\right]_n\] (Silres H44, Wacker Chemie, with \(n = 20\)). After heating up to 60 °C, the solvent was removed by vacuum evaporation at 1.75 × 10$^4$ Pa over 24 hours. Silicon powder with a particle size of \(d_{50} = 8 \mu\text{m}\) (Si-1016, ABCR GmbH & Co KG, Karlsruhe) was added, and the volume fraction H44:Si was adjusted to 6:4 and 8:2 corresponding to samples with 3 wt% and 10 wt%/20 wt% nickel, respectively. A melt mixing device equipped with Banbury rotors was used to prepare 100 g batches by mixing for 20 min at 80 °C (polymer melt) with a rotational speed of 120 rpm. The feedstock mixture was held at a temperature of 200 °C for 4 h to allow curing reactions. During this procedure foaming takes place [15]. The crosslinked samples were cut into pieces and pyrolysed in an electrically heated graphite furnace at 800 to 1500 °C for 1 h at maximum temperature. A heating and cooling rate of 3 K min$^{-1}$ was applied.

### 2.2 Characterization

The bulk phase composition and morphology were characterised by powder diffraction X-ray analysis using monochromated CuK$_\alpha$ radiation (Dilfrac 500, Siemens AG), and by scanning electron microscopy (SEM), respectively. The latter was performed with a JEOL 6340F operating at 5.0 kV. Microstructural and nanochemical information on the in situ formed structures, esp. catalyst particles, nanotubes and nanowires, were obtained by high resolution electron microscopy (HREM), energy-filtered transmission electron microscopy (EFTEM), electron energy-loss spectroscopy (EELS), esp. energy-loss near-edge
structures (ELNES) [16–19]. A Philips CM 20 FEG field emission electron microscope (TEM/STEM) operated at 200 kV, equipped with a Gatan Imaging Filter (GIF 200), mounted below the microscope column, was used. Filtered images were digitally recorded by a slow-scan CCD camera within the GIF 200. For image processing the Gatan Digital Micrograph and ELP software, loaded on a Power Macintosh 7200/75, were employed.

The EELS method allows to estimate the species and concentration of the chemical elements with a spatial resolution limited by the diameter of the measuring probe (≈2 nm). Moreover, by analysing the ELNES of the relevant ionisation edges, it is possible to characterise the chemical bonding state of individual elements with the same local resolution. The ELNES features are caused by excitations of core-shell electrons into unoccupied states above the Fermi level, and thus, the measured intensities give information on the partial local density of states which is representative of the bonding state of the atom. The characteristic ELNES details are the edge onset as well as the shape, the position, and the intensity of individual peaks. The energy filtered TEM enables element imaging as well as chemical-bond specific mapping. For the electron microscopic investigations cross sectional specimens were prepared, including thinning by ion milling.

The thermogravimetric (TG) analysis of crosslinked and ground samples was accomplished using a thermobalance (STA 409, Netzsch GmbH) in argon atmosphere up to 1000 °C. Analyses of evolving gases were carried out by coupling the STA 409 with a mass spectrometer of the type ThermoCube MSC 200 (Balzers). The heater inlet was 115 °C, the capillary temperature 150 °C, and the heating rate amounted to 10 °C/min.

3 Results and discussion

3.1 Preceramic polymer decomposition

For nickel acetate and silicon filler/nickel acetate loaded preceramic polymers significant changes in the decomposition behavior compared to Ni-free samples were observed. Figures 1a and b show the TG and
DTG (first derivatives) curves of the decomposition behaviour of plain poly(methylphenylsilsesquioxane) H44, nickel acetate loaded, and silicon filler/nickel acetate loaded poly(methylphenylsilsesquioxane). The highest weight loss was observed in the H44 sample having a value of 24.5 wt%. In the nickel-doped and in the Si-filler-loaded/nickel-doped samples the weight loss decreased significantly having values of 17.8 wt% and 5.7 wt% after pyrolysis at 1000 °C, respectively.

The first derivatives (rates of weight loss) reveal that the peak intensities are significantly changed, and the peak locations are shifted, indicating a change of the nature and temperature range of the released gaseous species caused by the nickel particles which apparently act as highly effective heterogeneous catalysts.

3.2 Nickel acetate-doped poly(methylphenylsilsesquioxane)

The pyrolysis of plain poly(methylphenylsilsesquioxane) H44 in the temperature range of 1000 °C results in an amorphous Si–O–C residue. At higher temperatures crystalization results in the formation of SiC, C and SiO$_2$. During pyrolysis of Ni(ac)$_2$·4H$_2$O loaded H44 silicone resin, however, the formation of Ni-containing nanoparticles in the polymer-derived ceramic matrix was observed. The carbon-to-hydrogen molar ratio of the Ni-containing samples is significantly higher compared to the Ni-free samples, and the formation of turbostratic carbon in the polymer-derived ceramic matrix was verified already at 700 °C [20]. Furthermore, starting at 850 °C, the pyrolysis results in the formation of multiwall carbon nanotubes (MWCNTs) in the pores of the polymer derived ceramic matrix having a diameter range of 100 µm–5 mm. The SEM image, Fig. 2, demonstrates the coverage of such a pore surface with C-nanotubes. With increasing pyrolysis temperature the number of C-nanotubes also increases.

The HREM image, Fig. 3, shows a nickel silicide particle in the Si–O–C matrix (center) surrounded by atomic stackings of turbostratic graphite. Another nickel silicide particle (lower left) initiated the growth of a small C-nanotube. The particles in the heads of such nanotubes can always be identified as nickel silicide by ELNES measurements (cf. Figs. 4a, c). In addition, Fig. 4a demonstrates together with the corresponding EEL spectra (Fig. 4b) that the nanotube consists of carbon with a hollow inner structure (reduction of the C–K peak intensities in the central region of the nanotube).

A percolating network of turbostratic graphite ribbons was formed in Ni-loaded polymer-derived ceramic matrices at significantly lower temperature compared to reports for Ni-free systems [21]. This result suggests that the hydrogen plays an important role during the devitrification and recrystallization of the polymer-derived ceramic matrix for the following reason: Obviously, remnants of hydrogen bonded to the amorphous carbon, which was formed during pyrolysis, have a stabilizing effect on the amorphous matrix and avoid the graphite formation in nickel-free samples. The addition of dehydrogenation-active transition metals (e.g. nickel) leads to a reduction of the hydrogen content and to a decrease of the starting temperature for the formation of turbostratic carbon by some hundred degrees. This forma-
Fig. 3  HREM image of the ceramic matrix with a nickel silicide particle surrounded by turbostratic graphite (center) and a C-nanotube with nickel silicide head (lower left), grown in a nickel acetate-doped H44 sample after pyrolysis in Ar atmosphere at 1200 °C.

Fig. 4  HREM image (a) and EEL spectra of a carbon nanotube (b) with a nickel silicide particle head (corresponding ELNES shown in (c)), grown in the pore of Ni acetate-doped H44 after pyrolysis in Ar at 1200 °C.
tion of graphitic carbon strongly reduces the electrical resistance: After pyrolysis at all temperatures the Ni-loaded samples exhibit an electrical resistance which is by about three orders of magnitude lower compared to the Ni-free samples after pyrolysis at the same temperature [20].

The gas phase reaction yielding C-nanotubes can be expressed schematically by Eq. (1), where nickel silicide nanoparticles act as nuclei for the C-nanotube growth process at the surface of the pores:

\[
\text{C}_x\text{H}_y(\text{gas}) \overset{\text{Ni, Ar atmosphere}}{\rightarrow} \text{C}_x\text{CNT} + \frac{y}{2} \text{H}_2. \quad (1)
\]

3.3 Nickel acetate-doped poly(methylphenylsilsesquioxane) loaded with Si filler

Analogous to the foregoing case of nickel acetate doped H44 silicone resin without silicon filler, also during pyrolysis of the silicon filler loaded system, nickel silicide nanoparticles are formed in the Si–O–C matrix. The precipitation of turbostratic graphitic carbon within the matrix was verified at the lowest pyrolysis temperature of 800 °C. With growing pyrolysis temperature and nickel concentration the volume fraction of turbostratic graphite increases.

Silicon carbide is formed, starting already at 1000 °C, in the polymer-derived ceramic matrix as verified by XRD [22]. Figure 5 shows a matrix region with a nickel silicide particle surrounded by several atomic planes of carbon having a spacing of 0.36 nm as known for turbostratic graphite, and a precipitation of silicon carbide (upper left). Nickel acetate doped and silicon filler loaded poly(methylphenylsilsesquioxane) also was found to host nanosized fibre-like aggregates in the pore space of the polymer-derived Si–O–C matrix as demonstrated in Fig. 6. In contrast to the filler-free case, where carbon nanotubes occurred, nanowires with a crystalline core and an amorphous shell were observed. The crystalline nature of the nanowire core, having a lattice spacing of 0.25 nm, which corresponds to the (111) lattice planes of cubic \( \beta \)-SiC, was proven by HREM (Fig. 7).

Further information about the chemical composition of the nanowire (Fig. 8a) was obtained from EFTEM images for silicon, oxygen and carbon, presented in the mappings of Fig. 8b. The photometric profiles of the Si, O, and C element distribution along the indicated lines across the fibre diameter (cf. Fig. 8c) reveal that the highest silicon and carbon concentrations are located in the core, whereas oxygen and some silicon is found in the shell, thus clearly showing that the nanowire is composed of a SiC core and a SiO\(_x\) shell.

Fig. 5 HREM image of a nickel silicide particle (lower right), surrounded by turbostratic graphite, and a SiC precipitation (upper left) in a Ni doped/Si loaded H44 sample (20% Ni) after pyrolysis in Ar at 1000 °C.
As demonstrated in Fig. 9, this result is approved by the ELNES details, measured across the fibres: Fig. 9a presents the EEL spectra taken along the line shown in Fig. 9b with a point-to-point distance of about 1.5 nm. Selective enlargements of the ELNES features of the Si-L edge are presented in Fig. 9c. The upper curve, found in the spectra of the core region, exhibits a peak at 105 eV which is a characteristic attribute of the carbidic bonding of Si, whereas the shell regions show the typical ELNES features of the oxidic silicon bonding with peaks at 108 eV and 115 eV, presented in the lower curve of Fig. 9c. The increasing intensities with approaching the central region in Fig. 9a are caused by the correspondingly growing thickness of the transmitted volume of the nanowire.
The total diameters of the SiC/SiO$_2$-nanowires are in the range of 10 to 100 nm, where the mean values are nearly independent of the pyrolysis temperature. Concerning the core-to-shell ratio, however, EELS and HREM measurements suggest an increasing ratio with rising pyrolysis temperature.

Most of the SiC/SiO$_2$ nanowires formed in the temperature range between 900 and 1200 °C showed a catalyst particle in their tip similar to those found in the C-nanotubes (cf. Figs. 3 and 4a). These observations suggest a vapour-liquid-solid (VLS) growth mechanism in the above mentioned temperature range, analogous to the VLS growth of $\beta$-SiC nanorods synthesized by hot-filament chemical vapour deposition with iron or nickel particles as catalysts [23, 24].

The following steps of the reaction kinetics should be of relevance for the SiC/SiO$_2$ nanowire formation:

During crosslinking and polymer decomposition hydrocarbons, water and hydrogen are released, analogous to the case of Si filler-free samples (cf. Section 3.2). In samples loaded additionally with silicon filler, however, the reaction of the silicon with the silicodioxid of the matrix results in the formation of gaseous SiO according to Eq. (2):

$$\text{Si}(s) + \text{SiO}_2(s) \rightarrow 2\text{SiO}(g) \ .$$

The hydrocarbons, e.g. CH$_4$, and the SiO released into the pores of the material can react in a further step to form SiC, H$_2$, and CO, according to Eqs. (3) and (4),

$$\text{SiO}(g) + \text{CH}_4(g) \rightarrow \text{SiC} + \text{H}_2\text{O}(g) + \text{H}_2(g) \quad (3)$$
$$\text{SiO}(g) + 2\text{CH}_4(g) \rightarrow \text{SiC} + \text{CO}(g) + 4\text{H}_2(g) \quad (4)$$

resulting in the growth of SiC nanowires via the VLS mechanism with nickel silicide nanoparticles as nuclei. The released water may react with the SiC nanowire surface to form the silica shell, as described in
Eq. (5):
\[
\text{SiC} + 3\text{H}_2\text{O}(g) \rightarrow \text{SiO}_2 + 3\text{H}_2(g) + \text{CO}(g) .
\]

The details of the SiC/SiO\(_2\) nanowire formation may be illustrated by the scheme, presented in Fig. 10: In a first step, turbostratic graphite is formed in the Si–C–O matrix by a nickel assisted catalytic process according to the HREM observation shown in Fig. 5. Then it can be assumed that the fibre formation from the SiO and hydrocarbon atmosphere in the pores will be initiated by the terminating reactive ends of the atomic planes of the graphite bands (I), analogous to the role of graphite in the microprocesses of metal dusting in iron and iron-nickel alloys [25, 26]. Thereafter, further growth of the nanoaggregates will be catalysed by nickel particles at their tip (II), i.e., a VLS mechanism proceeds as described above, finally followed by the SiO\(_2\) shell formation.

4 Conclusions

During the pyrolysis of nickel acetate doped poly(methylphenylsilsesquioxane) with and without silicon filler loading the formation of nickel silicide nanoparticles in the polymer-derived ceramic matrix results in dehydrogenation activities and growth processes of nano-ensembles as revealed by thermogravimetric measurements and by high resolution and analytical electron microscopy. The formation of turbostratic graphitic carbon in the polymer derived ceramic matrix was verified already at 800 °C.

Multiwall carbon nanotubes were formed in the pore space of nickel acetate doped poly(methylphenylsilsesquioxane) without silicon filler loading from the gaseous decomposition products during the organic-to-inorganic transformation. The pyrolysis of silicon filler loaded samples, however, resulted in the formation of crystalline nanowires in the pores of the polymer-derived ceramic matrix, in the temperature range from 900 to 1500 °C. HREM, EELS (ELNES) and EFTEM analyses revealed these nanowires to consist of a silicon carbide core and a SiO\(_2\) shell.

The formation processes of the observed nanotubes and nanowires include a heterogeneously catalyzed VLS mechanism and the reactivity of the free ending atomic planes of the precipitated graphite bands.

The described method of the \textit{in situ} formation of nanotubes and nanowires in the Si–C–O system and its reaction kinetics seem to have the potential for a processing route of novel polymer derived nanofibre or nanowire reinforced SiC microcomposite materials with tailored mechanical and electrical properties at comparably low temperatures.
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