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Synthesis of polymeric precursors for the formation of nanocrystalline Ti-C-N/amorphous Si-C-N composites

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The synthesis of trimethylsilyl-substituted poly(titaniumcarbodiimide) as a novel precursor for titanium carbonitride based ceramic materials is described. The precursor and the subsequent processing steps (cross-linking and pyrolysis) are characterized by IR and Raman spectroscopy, thermal gravimetric analysis and simultaneous mass spectroscopy, electron microscopy and powder X-ray diffraction measurements. The novel polymer is formed by the reaction of $TiCl_4$ or $Ti(NEt_2)_4$ with bis(trimethylsilyl)carbodiimide. Subsequent pyrolysis at 1000 °C in argon results in the formation of a ceramic composite material consisting of nanocrystalline TiCN and amorphous SiCN as constituting phases. Using $Ti(NEt_2)_4$ as a starting reagent instead of $TiCl_4$, chlorine contamination of the ceramic material can be avoided. The different molecular vibration modes of the metal–nitrogen, metal–carbon and nitrogen–carbon bonds in poly(titaniumcarbodiimides) with trimethylsilyl substituents were calculated using quantum mechanical methods, providing a comprehensive understanding of the measured spectra. Copyright © 2001 John Wiley & Sons, Ltd.

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INTRODUCTION

Superhard two-component nanocomposite systems consisting of nanocrystalline TiN and amorphous Si_3N_4 as well as TiC_xN_{1-x} $(0 \geq x \geq 1)$ phases have been obtained frequently as thin layers by chemical and physical vapor deposition techniques with hardnesses of about 20 to 40 GPa and 70 GPa respectively.[1–3] In particular, titanium carbonitride is frequently used for wear-resistant protecting layers on cemented carbides. Polycrystalline titanium carbonitride TiC_xN_{1-x} is usually obtained from a mixture of the binary compounds[4] or by the reaction of titanium carbide with nitrogen at temperatures around 1800 °C.[5] Depending on the carbon/nitrogen ratio, TiC_xN_{1-x} changes its color from golden for low carbon contents to brown for low nitrogen contents. Therefore, titanium carbonitride is applied as scratch-resistant protective coatings on watches and jewellery.[1]

In this paper we report on the syntheses and characterizations of carbon-rich titanium carbonitride powders by the polymer-to-ceramic transformation[6–8] of a novel titanium carbodiimide polymer. This process includes (i) the synthesis of organoelement polymers or oligomers, (ii) chemical or thermal cross-linking of these polymers or oligomers, and (iii) pyrolytic transformation of the cross-linked polymer into the desired ceramic

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materials. A variety of review articles report on the main advantages and drawbacks of this ceramic synthesis route.[9–12] In analogy to the well-established syntheses of silicon carbodiimide polymers by reacting tetrachlorosilane (Eqn [1]) or di- or tri-chloromethylsilanes Me_xSiCl_{4-x} $(0 \leq x \leq 2)$ with bis(trimethylsilyl)carbodiimide $Me_3Si\text{-}NCN\text{-}SiMe_3$,[13–15] tetrachlorotitanium was used in the present work as the starting material.

$$n\mathrm{SiCl_4} + 2n\mathrm{Me_3SiN{=}C{=}NSiMe_3} \longrightarrow [\mathrm{Si(NCN)_2}]_n + 4n\mathrm{Me_3SiCl} \qquad [1]$$

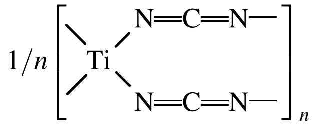
Owing to the higher reactivity of $TiCl_4$ towards bis(trimethylsilyl)carbodiimide, compared with $SiCl_4$, the reaction conditions have to be modified. The substitution of chlorine atoms in the case of $TiCl_4$ with NCNR units proceeds without pyridine as a catalyst; a tedious separation at the end of the reaction can thus be omitted. Tetrahydrofuran (THF) cannot be used as solvent because of the precipitation of the donor complex $TiCl_4{\cdot}2THF$. In order to avoid residual traces of chlorine in the polymeric product, an excess of bis(trimethylsilyl)carbodiimide is used. An alternative strategy is to apply tetrakis(diethylamino)titanium instead of $TiCl_4$ as a starting material. Contamination with chlorine in the polymeric product is thus excluded. Reaction conditions for the synthesis and characterization of the Ti–C–N precursor by IR absorption and Raman spectroscopy, and of the ceramic material by powder X-ray diffraction (XRD) are discussed. The experimentally observed IR and Raman spectra are interpreted on the basis of quantum mechanical and force calculations using the semi-empirical PM3(tm) method.[16–19]

EXPERIMENTAL

Syntheses of polytitaniumcarbodiimides

According to the idealized reaction sequences (Eqns [2] and [3]), the preceramic polymeric titaniumcarbodiimides **1** and **2** are obtained by the reaction of bis(trimethylsilyl)carbodiimide with either titanium tetrachloride or tetrakis(diethylamino)titanium:

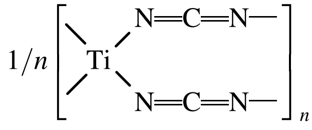
$$\mathrm{TiCl_4} + 2\mathrm{Me_3SiN{=}C{=}NSiMe_3} \longrightarrow$$



$$\frac{1}{n}\left[\mathrm{Ti(N{=}C{=}N)_2}\right]_n + 4\mathrm{Me_3SiCl} \qquad [2]$$

1

$$\mathrm{Ti(NEt_2)_4} + 2\mathrm{Me_3SiN{=}C{=}NSiMe_3} \longrightarrow$$



$$\frac{1}{n}\left[\mathrm{Ti(N{=}C{=}N)_2}\right]_n + 4\mathrm{Me_3SiNEt_2} \qquad [3]$$

2

As will be discussed later, the polymeric structures **1** and **2** contain trimethylsilyl endgroups. In addition, polymer **2** is characterized by terminating diethylamino groups. All reactions were performed in pre-heated glass vessels in an anhydrous stream of argon. Titanium tetrachloride (Fluka) was used after prior distillation, tetrakis(diethylamino)titanium was synthesized according to literature procedures,[20,21] bis(trimethylsilyl)carbodiimide was prepared from cyanoguanidine (Fluka) and hexamethyldisilazane (Fluka) was prepared as described elsewhere.[22] Toluene was distilled from a sodium/potassium alloy.

For the preparation of poly(titaniumcarbodiimide) according to Eqn [2], 205 ml (0.90 mol) of bis(trimethylsilyl)carbodiimide was cooled to 0 °C in an appropriate reaction vessel connected with a reflux condenser. A solution of 16.5 ml (0.15 mol) of titanium tetrachloride in 100 ml of toluene was added dropwise while stirring and cooling. During the addition of $TiCl_4$ an orange precipitate was formed. The reaction mixture was stirred at 0 °C for 6 h and for 8 h at room temperature. After 5 h refluxing of the dark red reaction mixture, the liquid components chlorotrimethylsilane, toluene and excess bis(trimethylsilyl)carbodiimide were removed under reduced pressure. Additional drying of the dark red solid at 170 °C *in vacuo* yielded 27.45 g of a fine powder. The polymeric powder was subsequently cross-linked at 300 °C for 1 h under argon atmosphere and for 30 min *in vacuo*. Cross-linking proceeds *via* polycondensation under separation of bis(trimethylsilyl)carbodiimide. After cooling to room temperature, 18.23 g (73%, based on $TiCl_4$) of a dark red powder were obtained. Elemental analysis data (weight%) are as follows: Ti, 28.9; Si, 5.1; N, 33.4; C, 23.7; H, 1.3; O, 6.0; Cl, 1.6. The ideal composition of $Ti(NCN)_2$ is as follows: Ti, 37.4; N, 43.8; C, 18.8. Deviations from the ideal formula can be explained by residual chlorine and trimethylsilylcarbodiimide substituents.

For the preparation of poly(titaniumcarbodiimide) according to Eqn [3], 8.0 ml (22.2 mmol) of tetrakis(diethylamino)titanium was added dropwise to 11.1 ml (48.7 mmol) of bis(trimethylsilyl)carbodiimide at room temperature while stirring in a three-necked flask with a reflux condenser and a dropping funnel. Subsequently, the reaction mixture was heated at 160 °C for 16 h. A dark green viscous liquid was obtained and the by-product trimethylsilyl(diethylamine) was distilled off at 130 °C. At this synthetic stage, a lower degree of cross-linking may lead to the formation of a liquid instead of a solid. The residue was cross-linked at 300 °C for 1 h under argon atmosphere and for 30 min *in vacuo*. After cooling to room temperature, 3.04 g (81%, based on $Ti(NEt_2)_4$) of a brown powder were obtained. Elemental analysis data (weight%) are as follows: Ti, 31.0; Si, 5.6; N, 26.6; C, 31.2; H, 3.5; O, 2.1. Deviations from the ideal formula can be explained by residual diethylamine and trimethylsilylcarbodiimide substituents.

The oxygen content analyzed for both polymers is due to contamination by manipulation of the materials in air.

Characterization of the polymeric materials

Samples for spectroscopic investigation were prepared in a glove box (Braun MB 150G-I SPS; $O_2 < 1$ ppm; $H_2O < 1$ ppm). IR and Raman spectra were measured on a Perkin–Elmer FT-IR 1750 (KBr pellets) and a Bruker FRA 106 (1.5 mm glass tubes).

Simultaneous thermal analysis (STA) of the synthesized titanium-containing polymers was conducted in combination with mass spectrometry (Netzsch STA 429 and Balzers QMG 420) in the temperature range between 100 and 1450 °C with a heating rate of 5 °C min^{-1} under 0.1 MPa helium atmosphere for **1** and between 20 and 1450 °C with a heating rate of 2 °C min^{-1} under 0.1 MPa helium atmosphere for **2**. Further investigations with corresponding heating rates have to be performed.

Pyrolysis of the titaniumcarbodiimide polymers obtained up to 1000 °C was conducted in a tube furnace (Reetz LOBA/S 50/600) under flowing argon in a quartz Schlenk tube.

XRD measurements of the pyrolyzed powders were performed on a Siemens D 500. The Ti–C–N/Si–C–N powders were investigated by high-resolution transmission electron microscopy (HRTEM) using a Phillips CM 20.

The chemical analysis data were determined at Mikroanalytisches Labor Pascher, 53424 Remagen, Germany.

Quantum chemical and force calculations

Simple clusters with the structure $Ti[{-}N{=}C{=}N{-}TiH_3]_4$ and with terminal trimethylsilyl groups $Ti[{-}N{=}C{=}N{-}Si(CH_3)_3]_4$ were chosen to calculate the IR and Raman spectra of the synthesized compounds. These clusters were submitted an energy minimization using the semi-empirical PM3(tm) method considering all valence electrons, including *d*-electrons.[16,17] These calculations include a geometry optimization of the clusters using the BFGS method.[18] With the known geometry and electronic properties (energy eigenvalues, eigenvectors and atomic charges) a force calculation was performed[19] in order to determine the vibrational and rotational eigenvalues of the clusters. These calculated values were used to interpret the experimentally obtained bands of IR absorption and Raman spectra.

RESULTS AND DISCUSSION

Within this work, two synthetic routes were used to obtain poly(titaniumcarbodiimide) compounds according to the reactions in Eqns [2] and [3]. Bis(trimethylsilyl)carbodiimide reacts with tetrachlorotitanium or tetrakis(diethylamino)titanium to afford the desired polymeric precursors **1** and **2** for ceramization under cleavage of trimethylchlorosilane and trimethylsilyldiethylamine respectively. To avoid chlorine contamination as analyzed in polymer **1**, tetrakis(diethylamino)titanium was used as a starting compound instead of $TiCl_4$. The resulting reaction product is denoted as polymer **2** and can be distinguished from polymer **1** by FT-IR spectroscopy (Fig. 1a).

A comparison of the measured and calculated Raman and FT-IR spectra of the poly(titaniumcarbodiimide) is given in Table 1. The calculated data were derived from simple clusters with the structures $Ti[{-}N{=}C{=}N{-}TiH_3]_4$and $Ti[{-}N{=}C{=}N{-}Si(CH_3)_3]_4$. The Raman spectrum (Fig. 1b, bottom) of poly(titaniumcarbodiimide) **1** annealed at 170 °C shows two characteristic bands of the carbodiimide group at 1423 and 2004 cm^{-1}. The band at 1423 cm^{-1} is caused by the symmetric stretching vibration of the $N{=}C{=}N$ group, whereas the latter is assigned to the antisymmetric stretching vibration and is usually forbidden in Raman spectroscopy. The appearance of this band can be explained by different substituents con-

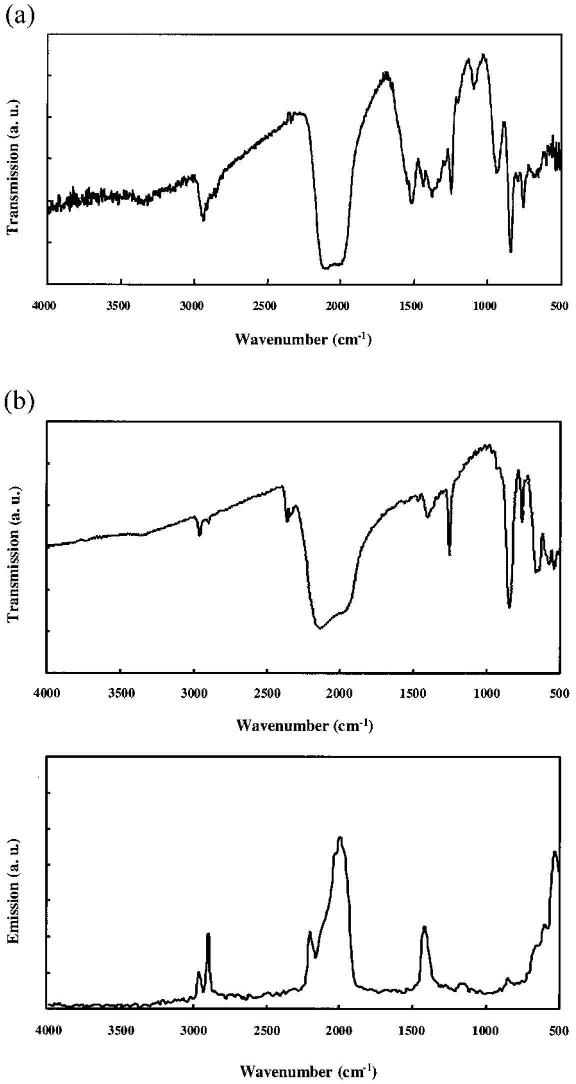
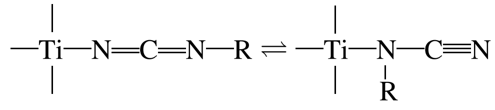


Figure 1 (a) FT-IR spectra of poly(titaniumcarbodiimide) **2**. (b) Raman (bottom) and FT-IR (top) spectra of poly(titaniumcarbodiimide) **1**.

nected to the N=C=N group or by disturbance of the linearity of the carbodiimide unit in the highly cross-linked polymer. CH_3 groups give rise to the bands located at 2965 and 2902 cm^{-1}. Ti—N stretching modes, in addition to the CN vibrations, can be observed between 600 and 500 cm^{-1}. A band due to Ti—N deformations (rocking) is observed at 400 cm^{-1}. Deformational vibrations of the N=C=N group can be correlated to the band at 523 cm^{-1}, and Ti—N deformations occur at 218 cm^{-1}. Raman spectra of polymers **1** and **2** annealed at 300 °C could not be obtained because of the strong absorption of laser light.

The FT-IR spectrum of **1** shown in Fig. 1b (top) exhibits a broad antisymmetric stretching band with high intensity at 2050 cm^{-1}, which is attributed to the N=C=N group. A comparison with the calculated vibrational spectra and the visualization of this vibration using the graphical user interface of the quantum chemical program "Spartan", version 5,[23] shows that the split into different vibration modes is due to a cancellation of the degeneration of the eigenvalues for the antisymmetric stretching vibration. Obviously the coupling of this vibration of different carbodiimide bonds *via* the titanium atom leads to the observed broad and split band.

The sharp band of the deformational Si—CH_3 vibration at 1250 cm^{-1} and the small bands of the C—H vibrations below 3000 cm^{-1} indicate the presence of terminal trimethylsilyl groups. The FT-IR spectrum of poly(titaniumcarbodiimide) (**1**) heat-treated at 300 °C shows a strong carbodiimide band around 2050 cm^{-1}. The formation of the isomeric cyanamide derivative (Eqn [4]) can be excluded, as its characteristic C≡N stretching at about 2400 cm^{-1} could not be detected.



$$-\overset{|}{\underset{|}{\mathrm{Ti}}}-N{=}C{=}N-R \rightleftharpoons -\overset{|}{\underset{|}{\mathrm{Ti}}}-\underset{\underset{R}{|}}{N}-C{\equiv}N \qquad [4]$$

R = TiR'_3, $SiMe_3$ not observed
R′ = NCNR

However, bonds assigned to terminating trimethylsilyl groups at 1250 and 3000 cm^{-1} are still visible. This finding clearly shows that the composition of the as-synthesized polymer **1** deviates from the idealized form, given in Eqn [1]. Accordingly, chemical bulk analysis gives $\{[Ti(NCN)_2]_3NCNSiMe_3\}_n$ as the formal composition of the heat-treated poly(titaniumcarbodiimide) polymer. This formula reflects that, on average, one trimethylsilylcarbodiimide ligand statistically comes under three titanium centers within the polymeric structure. Owing to the absence of cyanamide structural units, polymer **1** is considered to contain Ti—NCN—Ti units as the backbone structure and Ti—NCN—Si units as terminating groups. Chemical analysis shows that the cross-linked polymer contains 1.57 wt% chlorine impurities.

Two characteristic bands of the carbodiimide group at 2090 and 1445 cm^{-1} are visible in the spectrum of polymer **2**. The occurrence of the latter vibration mode shows that different substituents are

Table 1 Comparison of experimentally observed vibrational modes in Raman and FT-IR spectra (KBr pellets) with calculated eigenvalues of vibrations using PM3(tm) method/force calculation

Vibration		Wavenumber (cm^{-1}) Experimentally found Raman	FT-IR	Calculated PM3/force
Ti—N	Deformation	218		219–228
Ti—NCN—Si	Deformation (non-localized)	400		370–460
—N=C=N—	Deformation	523		535–560
Si—C	Valence (asym.)		650	626–632
Si—N	Valence		780	776
Si—C	Coupled Si—C valence and C—Si—C deformation (rocking)	830	840	864–867
Si—C	Deformation		1250	1300–1320
—N=C=N—	Valence (sym.)	1423		1466–1476
—N=C=N—	Valence (asym.)	2004	2050	2063–2067
		2200		2273
C—H	Valence (asym.)	2902	<3000	3126–3132
C—H	Valence (sym.)	2965		3225–3227

connected to the N=C=N-group or that linearity of the carbodiimide unit is disturbed. The existence of residual terminal trimethylsilyl groups is confirmed by the bands at 2950 and 1254 cm^{-1}. A further hint of the presence of trimethylsilyl groups can be deduced from the Si—N stretching mode at 757 cm^{-1} and a band at 840 cm^{-1} characteristic of Si—C deformation (rocking). The IR spectrum in Fig. 1a shows a broadened band in the 2900 to 3000 cm^{-1} region compared with that of the spectrum in Fig. 1b. Owing to remaining diethylamino groups attached to the titanium atoms in polymer **2**, a broadening and increase in intensity of the aliphatic C—H stretching mode in combination with the occurrence of the aliphatic deformation band at 1380 cm^{-1} is visible. Additional bands of medium intensity can be observed at 1523 cm^{-1} and 943 cm^{-1}, which can be attributed to the symmetric stretching and rocking vibration respectively of the carbodiimide N=C bond.

The FT-IR spectrum of the poly(titaniumcarbodiimide) **2** heat-treated at 300 °C shows a carbodiimide band at 2090 cm^{-1}. Trimethylsilyl groups are still present in the annealed polymer, as analyzed by the bands located at 1267 and 798 cm^{-1}. The elemental analysis of the cross-linked polymer **2** reveals a formal composition of $\{[Ti(NCN)_2]_6[Ti(NEt_2)_2(NCNSiMe_3)_2]\}$.

The transformation of the poly(titaniumcarbodiimides) **1** and **2** into the Ti–C–N/Si–C–N composite ceramics was investigated by thermal gravimetric analysis and simultaneous mass spectroscopy (TGA–MS) (Fig. 2a and b). Polymer **1** was heated with 5 °Cmin^{-1} from room temperature to 1450 °C under helium atmosphere. A mass loss of 43 wt% up to 1000 °C is detected. Between 1000 and 1450 °C the mass is reduced by 9 wt%. During TGA the highest mass loss is found in the temperature range between 320 and 750 °C. MS of the volatile species evolved in this temperature range indicate the formation of methane ($m/z = 16$) and HCN^+ ($m/z = 27$). The evolution of hydrogen ($m/z = 2$) starts above 320 °C and reaches its maximum at 613 °C. The formation of nitrogen ($m/z = 28$) is detected in the temperature range between 450 and 900 °C (see Fig. 2a). Between 350 and 590 °C acetonitrile and/or methylisonitrile ($m/z = 41$) are found with lower intensity. The fragmentation products C_2N^+ ($m/z = 38$), $CHCN^+$ ($m/z = 39$) and CH_2CN^+ ($m/z = 40$) also appear in this temperature range. At higher temperatures a minor amount of organic nitrile fragments (CH_3CN^+, $C_2H_5CN^+$ and $C_3H_5CN^+$) were analyzed, exclusively.

The thermal decomposition of poly(titaniumcarbodiimide) **2** up to 1450 °C gives a total ceramic yield of 55 wt%. Analysis of the weight change versus temperature by TGA–MS shows three seperate steps (Fig. 2b). The main ceramization reaction proceeds at $T = 300$–450 °C with a loss of H_2^+, HCN^+, N_2^+, NH_3^+ (H_2^+ and NH_3^+ are not shown in Fig. 2b), acetonitrile (CH_3CN^+) and a fragmentation product of hexamethyldisiloxane ($m/z = 147$, $(CH_3)_2SiO—Si(CH_3)_3^+$), which are

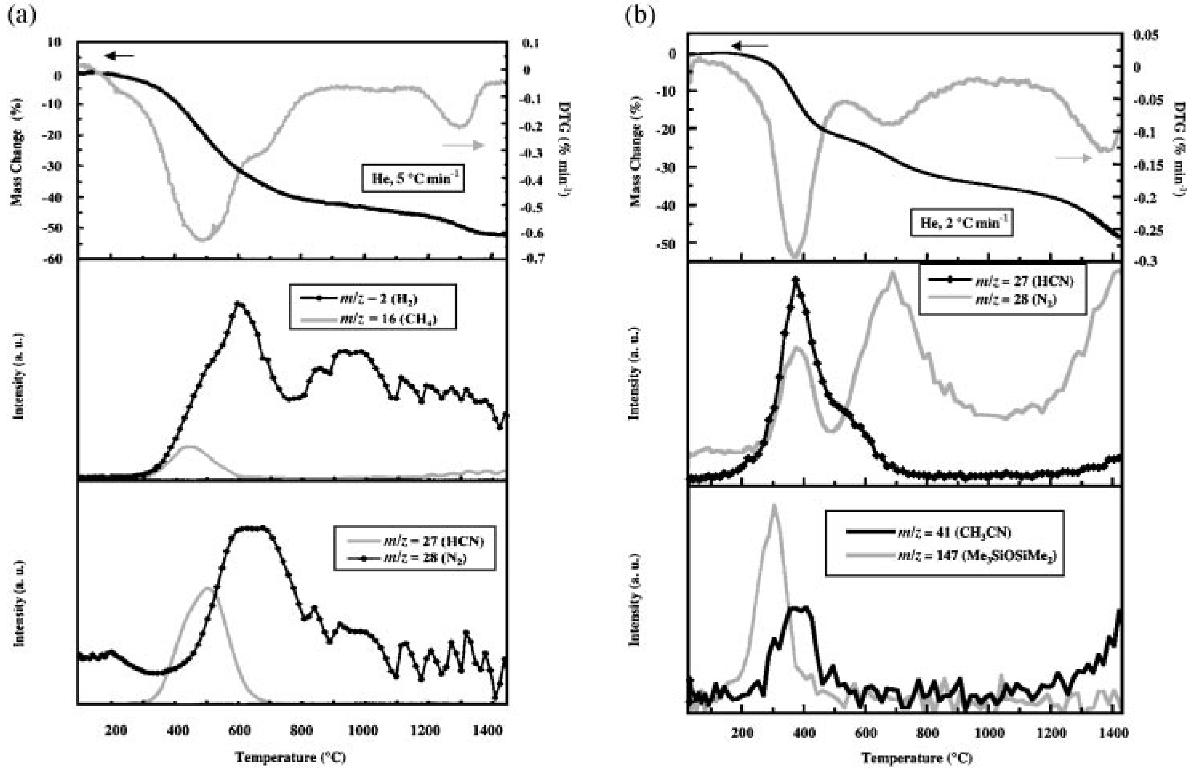


Figure 2 (a) TGA of the titaniumcarbodiimide polymer **1**. Weight loss versus temperature is shown and the data are obtained by heating under stationary 0.1 MPa helium in graphite crucibles. The species detected by simultaneous MS in different temperature regions are shown on the lower diagrams. (b) TGA of the titaniumcarbodiimide polymer **2**. The species detected by simultaneous MS in different temperature regions are shown on the lower diagram.

identified unambiguously by simultaneous MS. In the second step, between 620 and 750 °C, the mass change is mainly due to the formation of N_2^+. Finally, $(CN)_2^+$ ($m/z = 52$) CN^+ ($m/z = 26$), CO^+ ($m/z = 28$) and SiO^+ ($m/z = 44$) evolve between 1250 and 1400 °C (see Fig. 2b). The formation of SiO^+ and CO^+ is attributed to oxygen contamination in the Ti–Si–C–N material investigated. The outgassing of N_2^+ and HCN^+ is one order of magnitude higher than that of CH_3CN^+, $(CN)_2^+$ and $(CH_3)_2SiOSi(CH_3)_3^+$.

Bulk pyrolysis experiments with polymer **1** were carried out in order to examine the structure of the ceramic material. The cross-linked polymer was heated at 20 °C h^{-1} to 1000 °C and held at this temperature for 4 h under argon atmosphere. The yield of the black powder obtained was nearly 60 wt%. Powder XRD measurements of the pyrolyzed ceramic gave the diffraction pattern shown in Fig. 3. According to an additional Rietveld refinement, the lattice parameter a was determined to be 4.2676(3) Å. A composition of $TiC_{0.32}N_{0.68}$ is derived by application of Vegard's law[24] using the lattice parameter values for pure TiN and TiC and the lattice parameters of various TiC_xN_{1-x} phases.[25] The XRD pattern is in good agreement with that of $TiC_{0.3}N_{0.7}$, as indicated by the lines in Fig. 3. This finding is in good agreement with the work reported by other authors. Accordingly, molecular Ti–Si–C–N precursors have been thermally transformed to nanocrystalline TiN, TiC or TiC_xN_{1-x} phases embedded in an amorphous SiC, Si_xN_y or SiC_xN_y matrix.[2,3,26–28] To our knowledge, a crystalline silicon-containing TiC_xN_{1-x} material has not been observed so far. The average crystallite size τ is estimated to be 12–13 nm by the line broadening β according to the Scherrer equation [$\tau = (K\lambda)/(\beta \cos \theta)$, where K is the shape factor (0.9), λ is the wavelength, and θ is the diffraction angle].

The elemental composition of the pyrolyzed ceramic material obtained from polymer **1** is

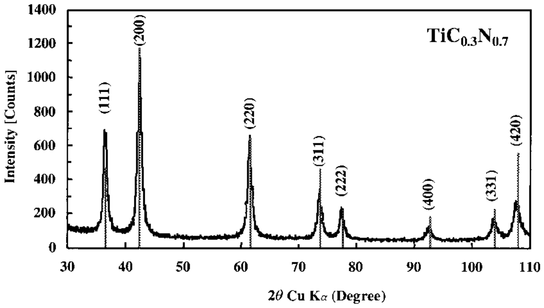


Figure 3 XRD pattern of the poly(titaniumcarbodiimide) heat-treated at 1000 °C for 4 h under argon. All reflections can be assigned to $TiC_{0.3}N_{0.7}$. Bars indicate the published intensities and 2θ values of a crystalline $TiC_{0.3}N_{0.7}$ sample.[25].

determined to be $Ti_{1.0}C_{1.8}N_{1.2}Si_{0.3}$ from the chemical analysis. Assuming that all titanium atoms have been crystallized as $TiC_{0.3}N_{0.7}$, carbon-rich amorphous silicon carbonitride is considered to be the remaining phase. HRTEM investigations of the nanocrystalline titanium carbonitride/amorphous Si–C–N powder obtained after pyrolysis of polymer **1** confirm that the mean Ti–C–N crystallite size is in the above-mentioned range. Figure 4 (left) shows an overview of the titanium carbonitride sample. The nano-sized crystallites are depicted with a higher magnification (right). Larger crystallites are also found. The cubic symmetry of the titanium carbonitride is proved by electron diffraction (Fig. 4, right, bottom). The diffraction image displays the typical pattern of a face-centered cubic phase and is in accordance with the X-ray study. Additionally, HRTEM observations reveal minor amounts of amorphous and graphitic carbon (not shown in Fig. 4).

Taking into account the formal composition of the starting poly(titaniumcarbodiimide), $\{[Ti(NCN)_2]_3NCNSiMe_3\}_n$, the titanium/silicon ratio does not change during the polymer-to-ceramic conversion. The polymer gives off low volatile

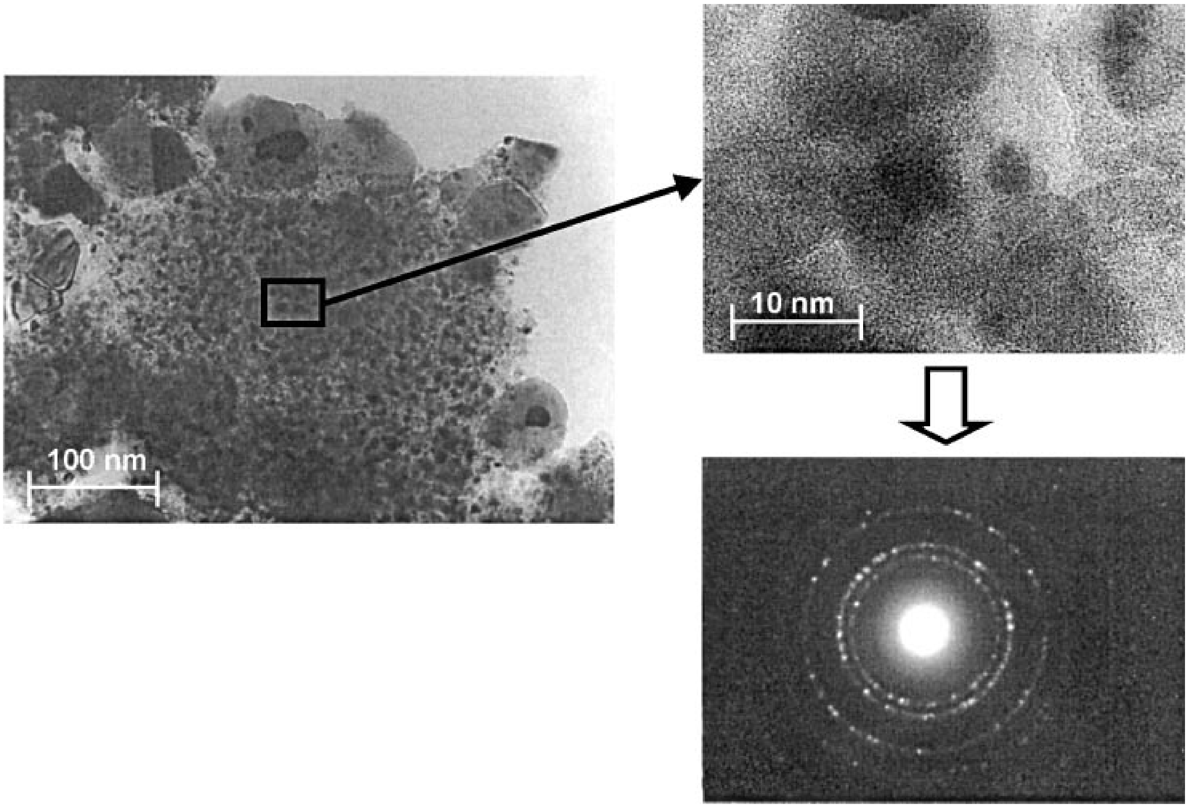


Figure 4 Transmission electron micrographs and electron diffraction of the poly(titaniumcarbodiimide)-derived TiCN phase. Left: overview; right: HRTEM (top), and electron diffraction (bottom) images.

carbon species and elemental nitrogen, as discussed above (Fig. 2a), and successively partitions into polycrystalline titanium carbonitride and amorphous silicon carbonitride. According to *in situ* powder XRD between room temperature and 1000 °C, no intermediate crystalline phases besides that of $TiC_{0.3}N_{0.7}$ are formed.

CONCLUSION

Polymeric titanium carbodiimides containing terminating trimethylsilyl or diethylamino groups are accessible by the reaction of tetrachlorotitanium or tetrakis(diethylamino)titanium with bis(trimethylsilyl)carbodiimide. In anolgy to hydrolysis or aminolysis of metal chlorides, the aforementioned reaction is denoted as carbodiimidolysis. The side products formed are Me_3SiCl or Me_3SiNEt_2, and these can be distilled off from the reaction mixture. This one-step and salt-free synthesis route opens the door to an economic preparation of novel titanium polymers, as has been worked out recently for poly(organosilyl)carbodiimides.[15,29] The titanium polymers are suitable for the polymer-to-ceramic conversion and give crystalline titanium carbonitride embedded in an amorphous silicon carbonitride matrix after pyrolysis at 1000 °C in protective atmospheres.

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