JOURNAL OF MATERIALS SCIENCE 16 (1981) 1349–1355

Synthesis of a polytitanocarbosilane and its conversion into inorganic compounds

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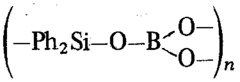
The novel polytitanocarbosilane, formed by the cross-linking of polycarbosilane with titanium tetra-alkoxide, was synthesized to examine the process of converting a multi-element organometallic polymer into an inorganic compound. The chemical structure of this polymer was investigated by the techniques of infra-red spectroscopy (IR), gel permeation chromatography (GPC), number average molecular weight measurements and ^{29}Si nuclear magnetic resonance (NMR) measurements. The pyrolysis products in N_2 gas at 1400° C and 1700° C were the microcrystalline and crystalline states of silicon carbide and titanium carbide, respectively.

1. Introduction

From a polycarbosilane, a high tensile strength continuous SiC fibre [1–3] and a high flexural strength sintered SiC body [4, 5] have been successfully produced by heat treatment. A polyborodiphenylsiloxane [6], was useful as a binder in the SiC body, in addition to the polycarbosilane.

In the process of converting these oraganometallic polymers into inorganic compounds, during the heat-treatment in N_2 gas, polycarbosilane is converted into β-SiC at above 1500° C and polyborodiphenylsiloxane is converted into β-SiC and B_4C at 1700° C: heating these organometallic polymers produces ceramics such as SiC or B_4C, and so these polymers are very useful as precursors of heat-resistant ceramic materials. Through further investigations on organometallic polymers, a novel polytitanocarbosilane has been found which can be converted, by pyrolysis in an atmosphere of inert gas or non-oxidizing gas, into the mixture of silicon carbide and titanium carbide in a high yield. The synthesis method, the chemical structure and the pyrolysis of this organometallic polymer have been studied. These results are reported here.

2. Experimental procedure

The new polytitanacarbosilane (PTC) was synthesized as follows. Polydimethylsilane (250 g), $-Me_2Si-_n$ [7], synthesized by dechlorination of dimethyldichlorosilane with sodium metal in xylene under N_2 gas and polyborodiphenylsiloxane (9.07 g),  $\left(-Ph_2Si{-}O{-}B\begin{smallmatrix}O-\\O-\end{smallmatrix}\right)_n$ [6], synthesized, in turn, from boric acid, $B(OH)_3$, and diphenyldichlorosilane were mixed and heated to 350° C under N_2 gas in a 2 l quartz reaction vessel equipped with a reflux tube, and polymerized for 10 h. The reaction product was concentrated at 320° C for 1 h in a stream of N_2 gas to produce 175 g of the polycarbosilane (PC) with a number average molecular weight of 950. 40.0 g of PC and 28.4 g of titanium tetrabutoxide were mixed with 400 ml of xylene to form a homogeneous solution. The

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solution was reacted under reflux at 130° C for 1 h, with stirring, in an atmoshpere of N_2 gas. After the refluxing reaction, the temperature was raised to 220° C and the xylene solvent was distilled off. The polymerization was carried out at 220° C for 30 min to form PTC with a number average molecular weight of 1674. PTC is a polymer which melts when heated at a temperature above 200° C. It is also soluble in organic solvents such as benzene, toluene, xylene and tetrahydrofuran.

To investigate the effect of the above heat treatment on PC itself during the synthesis of PTC, PC was heat treated without titanium tetrabutoxide by the same method as that used for synthesis of PTC. The characteristics of a number average molecular weight, the infra-red (IR) spectrum and the gel permeation chromatogram of this heat-treated PC scarcely changed in comparison with those of the untreated PC.

Specimens were measured using the following. IR spectra were measured with a Hitachi 285 grating infra-red spectrometer by the KBr pellet method. Number average molecular weights M_n, were measured with a Hitachi 117 molecular measurement apparatus by vapour pressure osmometry (VPO) in benzene solution, using benzil as the standard material. Gel permeation chromatograms (GPC) were taken with a Hitachi HCL-635A with A-803 Shodex packing and tetrahydrofuran eluent at a flow rate at room temperature of 1 ml min^{-1}. Thermal gravimetric (TG) analysis was carried out using a Rigaku Micro TG-DTA (high-temperature type) machine by raising the temperature at 5° C min^{-1} up to 1400° C in a N_2 flow of 50 cm^3 min^{-1}. ^{29}Si nuclear magnetic resonance (NMR) spectra were measured with JEOL JNM-FX60 high resolution FT NMR spectrometer at 19 MHz, at room temperature, in $CDCl_3$ solutions. X-ray powder diffraction patterns were recorded with a Rigaku X-ray diffractometer using CuKα radiation with a Ni-filter.

Chemical analysis of PTC and pyrolyzed PTC were made for six elements: Si (by a gravimetric method), Ti (by a colorimetric method), C (by a combustion volumetric method), and O, H, and N (by gas analysis).

3. Results and discussion

3.1. The chemical structure of PTC

Fig. 1a and b show the GPC of PTC and PC, respectively. The PTC trace, in Fig. 1a, shows the new broad peak at 7 to 14 ml of elution volume not seen in the trace of PC, shown in Fig. 1b. Furthermore, in the peaks at 17.3 ml of elution volume seen in the traces for PTC and PC, the height of this peak is smaller in the PTC trace than it is in the PC trace. These observations indicate that the molecular weight of PTC is high and the content of a low-molecular-weight material in PTC is little in comparison with the case of PC*. Thus, the results of measurements using GPC show that PTC is not simply a blend of polycarbosilane and titanium tetrabutoxide, but is a cross-linked polymer of increased molecular weight obtained by a bonding of the above two materials.

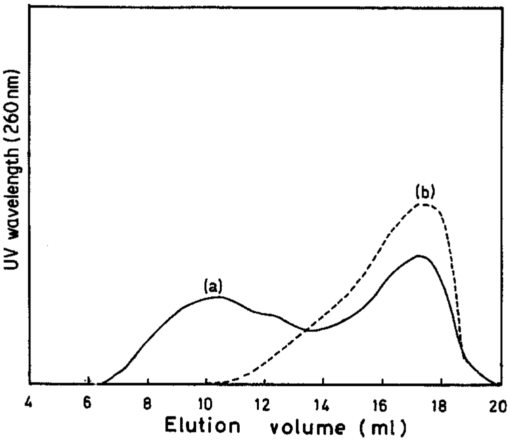
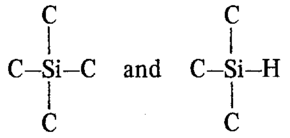


Figure 1 GPC of (a) PTC and (b) PC.

In the IR spectrum of PC, shown in Fig. 2b, absorptions at 1400, 2900 and 2950 cm^{-1} (C–H), 600 to 920 cm^{-1} and 1250 cm^{-1} (Si–Me), 1020 and 1355 cm^{-1} (Si–CH_2–Si) and 2100 cm^{-1} (Si–H) [8–10] are observed. The atomic group bonded to silicon atoms in PC was also investigated using ^{29}Si-NMR spectrum measurements (^{1}H decoupling) in order to learn more of the chemical structure of PC, and the results of these measurements are shown in Fig. 3. The NMR spectrum shows two peaks at − 0.22 and − 17.04 ppm which are corresponding to



$$\text{C}-\overset{\displaystyle\text{C}}{\underset{\displaystyle\text{C}}{\text{Si}}}-\text{C} \quad \text{and} \quad \text{C}-\overset{\displaystyle\text{C}}{\underset{\displaystyle\text{C}}{\text{Si}}}-\text{H}$$

respectively, in a ratio of about 1 : 1.

The results of both the IR and ^{29}Si-NMR spectra analyses of PC reveals that PC is the polycarbosilane consisting mainly of structural units

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* In GPC, the lower the figure of a peak on the abscissa (elution volume), the higher the corresponding molecular weight.

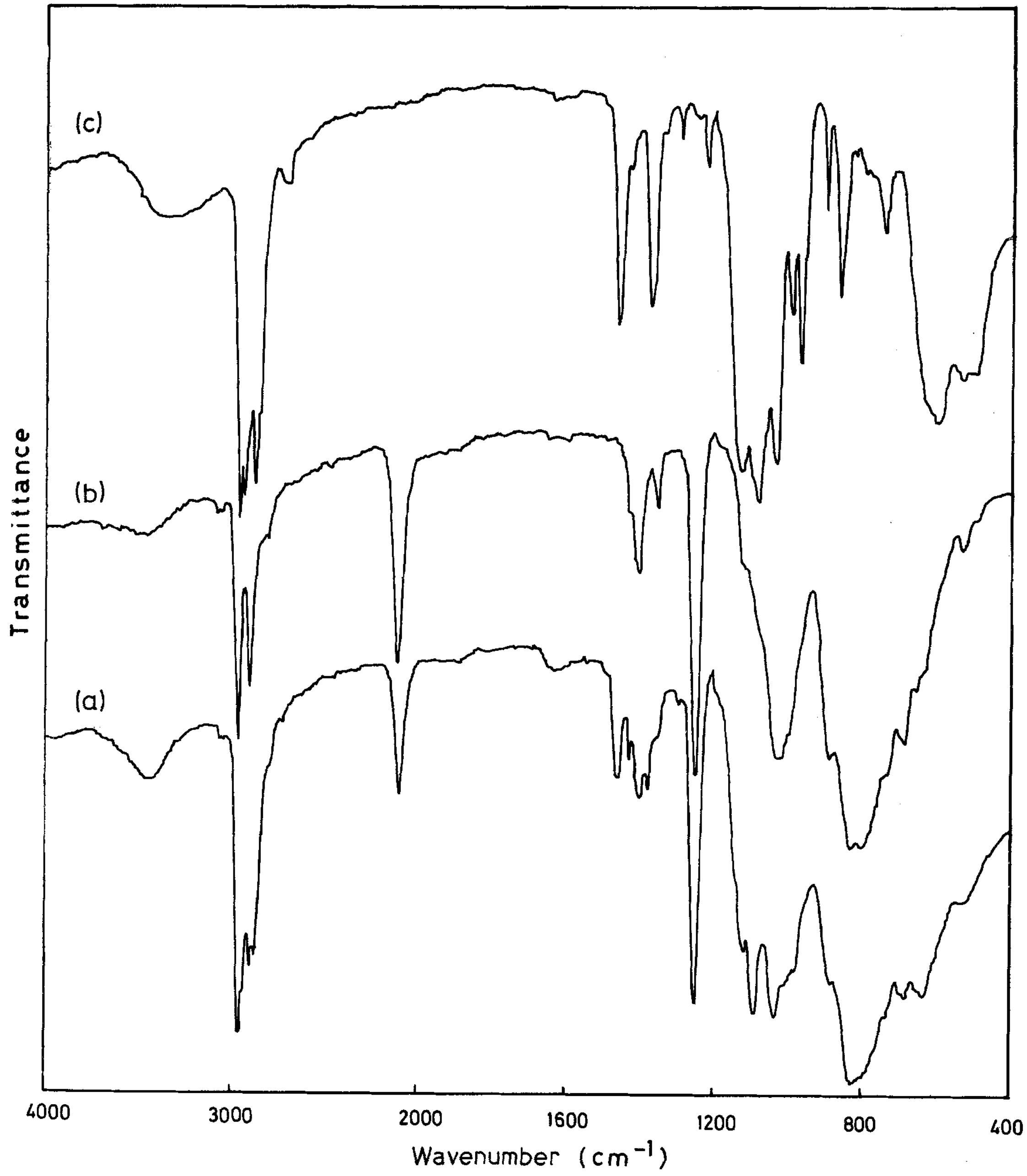
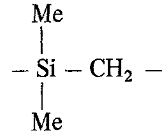


Figure 2 IR spectra of (a) PTC, (b) PC and (c) titanium tetrabutoxide.

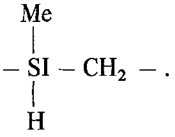
A and *B*, see below, in an *A* : *B* ratio of about 1 : 1

(*A*)



$$-\overset{\displaystyle Me}{\underset{\displaystyle Me}{Si}}-CH_2-$$

(*B*)



$$-\overset{\displaystyle Me}{\underset{\displaystyle H}{SI}}-CH_2-. \qquad (1)$$

From a comparison of the IR spectrum of PTC shown in Fig. 2a with those of PC and titanium tetrabutoxide shown in Fig. 2b and c, respectively, it is seen that PTC consists of polycarbosilane and titanium tetrabutoxide. The ratio of the intensity of an absorption at 2100 cm^{-1}, ascribable to Si–H bond absorption, to that of an absorption at 1250 cm^{-1}, ascribable to Si–CH_3 bond absorption, in the IR spectrum given in Fig. 2b is 0.642; the equivalent ratio for the IR spectrum given in Fig. 2a is 0.380. This shows that, as a result of the reaction of polycarbosilane with titanium tetrabutoxide, some of the Si–H linkages in the polycarbosilane disappear and a cross-linked polymer is obtained. The ratio of cross-linkage of PTC calculated on the basis of the above

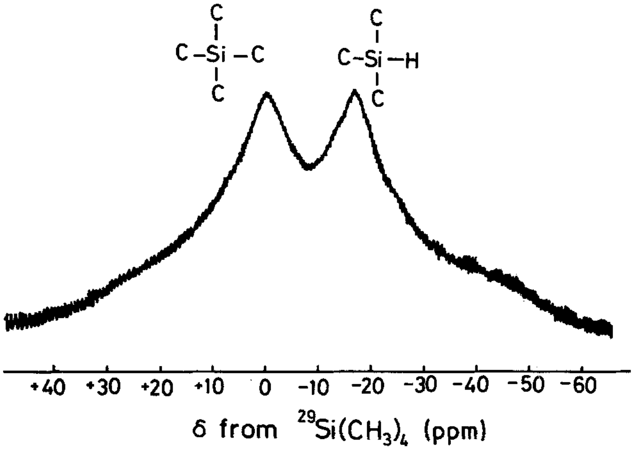
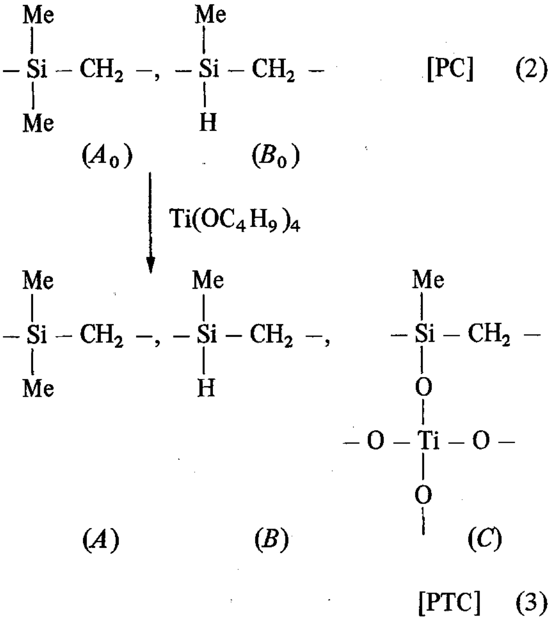


Figure 3 ^{29}Si-NMR spectrum (^{1}H decoupling) of PC.

IR absorption data, is 40.8% [= (0.642 − 0.380) 100/0.642], supposing that the cross-linkage occurs only by the disappearance of the Si–H linkage which can be considered to be more reactive than the Si–CH$_3$ linkage. Thus, the formation of PTC from the results of a GPC analysis, ^{29}Si-NMR analysis and IR spectra analysis is presumably represented by structural units as follows:



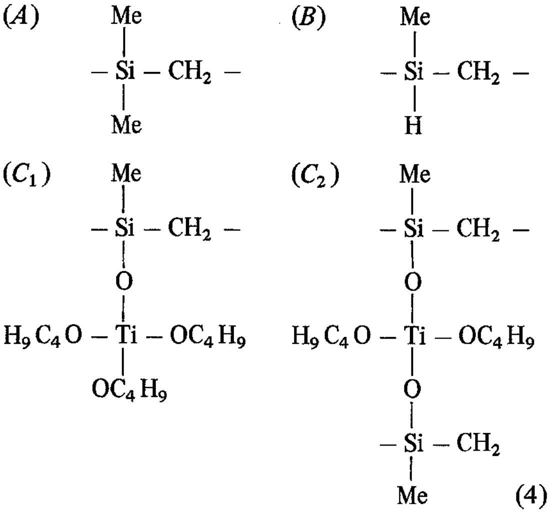
$$\underset{(A_0)}{-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{CH}_2-}, \quad \underset{(B_0)}{-\underset{\text{H}}{\overset{\text{Me}}{\text{Si}}}-\text{CH}_2-} \qquad [\text{PC}] \quad (2)$$

$$\Big\downarrow \text{Ti(OC}_4\text{H}_9)_4$$

$$\underset{(A)}{-\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{CH}_2-}, \quad \underset{(B)}{-\underset{\text{H}}{\overset{\text{Me}}{\text{Si}}}-\text{CH}_2-}, \quad \underset{(C)}{\begin{array}{c}\text{Me}\\ |\\ -\text{Si}-\text{CH}_2-\\ |\\ \text{O}\\ |\\ -\text{O}-\text{Ti}-\text{O}-\\ |\\ \text{O}\\ |\end{array}}$$

$$[\text{PTC}] \quad (3)$$

where the component ratio of $A_0:B_0$ is about 5:5, and of $A:B:C$ is about 5:3:2. Henceforth, from the chemical analysis of PTC shown in Table I with its pyrolysed products at 1000, 1400 and 1700° C in N$_2$, in which the correct chemical analysis of C and O in PTC was unmeasurable, it may be finally assumed that PTC is a cross-linked polymer, having a number average molecular weight of 1674, consisting mainly of structural units of A, B, C_1 and C_2, see below, where the component ratio of $A:B:C_1:C_2$ is about 5:3:1:0.5:



$$(A)\ -\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}-\text{CH}_2- \qquad (B)\ -\underset{\text{H}}{\overset{\text{Me}}{\text{Si}}}-\text{CH}_2-$$

$$(C_1)\ \begin{array}{c}\text{Me}\\ |\\ -\text{Si}-\text{CH}_2-\\ |\\ \text{O}\\ |\\ \text{H}_9\text{C}_4\text{O}-\text{Ti}-\text{OC}_4\text{H}_9\\ |\\ \text{OC}_4\text{H}_9\end{array} \qquad (C_2)\ \begin{array}{c}\text{Me}\\ |\\ -\text{Si}-\text{CH}_2-\\ |\\ \text{O}\\ |\\ \text{H}_9\text{C}_4\text{O}-\text{Ti}-\text{OC}_4\text{H}_9\\ |\\ \text{O}\\ |\\ -\text{Si}-\text{CH}_2\\ |\\ \text{Me}\end{array} \quad (4)$$

TABLE I Compositions of unpyrolysed PTC, and PTC pyrolysed at 1000, 1400 and 1700° C

Sample	Si (wt%)	Ti (wt%)	C (wt%)	O (wt%)	H (wt%)	N (wt%)
PTC: experimental value	28.8	7.1	–	–	8.1	–
theoretical value*	28.2	7.2	49.4	6.4	8.8	–
PTC pyrolysed at 1000° C	44.7	10.2	27.3	11.7	1.2	4.7
PTC pyrolysed at 1400° C	44.2	11.0	24.5	12.3	0.6	3.4
PTC pyrolysed at 1700° C	53.2	13.2	18.3	5.1	0.1	5.8

* The theoretical value is calculated on the basis of the aforesaid structure.

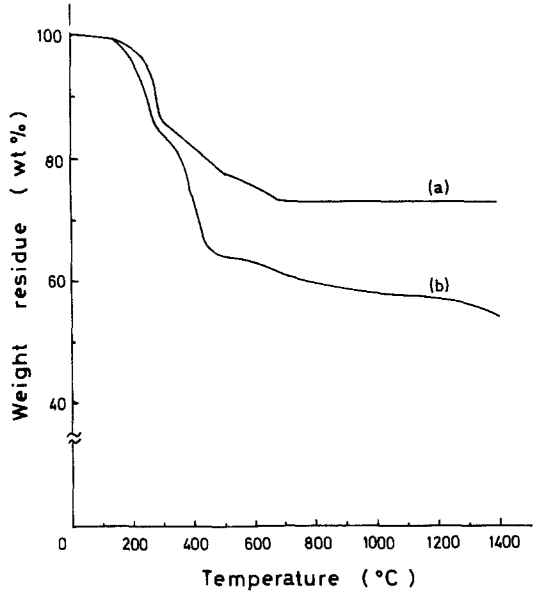


Figure 4 TG curves of (a) PTC and (b) PC.

3.2. Conversion of PTC into inorganic compounds

As seen from Fig. 4, TG analysis indicates that the weight residue is constant at temperatures above 700° C and the organic group in PTC is decomposed below this temperature. TG analysis, raising the temperature under N_2 gas to 1400° C, shows the weight residue in PTC is 72.3 wt% which is significantly larger than the 54.5 wt% found with PC.

The results of the chemical analysis of PTC and its pyrolysis products are shown in Table I. The empirical atomic ratios of PTC and its pyrolysis products at 1000, 1400 and 1700° C in N_2 were found to be $SiTi_{0.15}C_{4.11}H_{8.80}O_{0.40}$ *, $SiTi_{0.13}C_{1.43}H_{0.75}O_{0.46}$, $SiTi_{0.15}C_{1.30}H_{0.38}O_{0.49}$ and $SiTi_{0.15}C_{0.80}H_{0.05}O_{0.17}$, respectively. As can be seen from these results the Si and Ti atomic ratio is almost the same in the polymer as it is in its pyrolysis products at each temperature. The content of carbon and hydrogen in the pyrolysis product at 1000° C is markedly decreased in comparison with that seen in the polymer. These phenomena support the result of TG analysis that the organic group in the polymer is decomposed below 700° C. The carbon content slightly changes by pyrolysis between 1000 and 1400° C and decreases by pyrolysis at 1700° C. The hydrogen content gradually reduces as the pyrolysis temperature is raised from 1000 to 1700° C, and only a trace amount of hydrogen is contained in the pyrolysis product at 1700° C. Much oxygen is included in the polymer and its pyrolysis products below 1400° C, but the oxygen content in the pyrolysis product at 1700° C has decreased remarkably.

Fig. 5 shows X-ray powder diffraction patterns of PTC and its pyrolysed products at temperatures from 1000 to 1700° C in N_2 gas atmosphere. Very broad diffraction lines are seen for the pyrolysis product at 1000° C, as is shown in Fig. 5b. From this, and the results of the chemical analysis shown in Table I, the product obtained by pyrolysis of PTC at this temperature is considered to be an amorphous phase consisting of Si, Ti, C, H and O. As the pyrolysis temperature is raised from 1200 to 1700° C, sharp, high-intensity diffraction lines of the SiC-type and TiC-type phases begin to appear in Fig. 5c, d and e. The diffraction pattern of the pyrolysis product at 1400° C is considered to indicate the microcrystalline state of silicon carbide and titanium carbide. In the X-ray powder diffraction pattern of the pyrolysis product at 1700° C (Fig. 5e) the following diffraction peaks are observed: the diffraction line (1 1 1) of β-SiC-type phases appearing at $2\theta = 35.8°$, (2 2 0) appearing at $2\theta = 60.2°$ and (3 1 1) appearing at $2\theta = 72.1°$ and the diffraction on line (1 1 1) of TiC-type phase appearing at $2\theta = 36.4°$, (2 0 0) appearing at $2\theta = 42.4°$, (2 2 0) appearing at $2\theta = 61.4°$, (1 1 3) appearing at $2\theta = 73.5°$ and (2 2 2) appearing at $2\theta = 77.4°$. In addition to these X-ray powder diffraction lines, weak-intensity diffraction lines, presumably based on α-SiC, appear at $2\theta = 34°$ and $2\theta = 38.3°$. A small amount of α-SiC phase is considered to be contained in the pyrolysed PTC at 1700° C.

From the results of X-ray diffraction measurements, it became clear that SiO_2 and TiO_2 were not contained in the pyrolysis products formed in N_2 gas, in spite of the presence of oxygen atoms in the pyrolysed PTC.

Because of the heat treatment in N_2, nitrogen atoms are included in the pyrolysed PTC, as shown in Table I, but no nitrides are observed in the X-ray powder diffraction patterns of the pyrolysed PTC obtained at any of the temperatures. The chemical bonding state of nitrogen atoms in the pyrolysis products is now ambiguous.

In the diffraction patterns of the pyrolysis product at 1700° C, the Bragg angle, θ, of β-SiC was

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* The empirical atomic ratio of PTC was calculated from the theoretical value given in Table I.

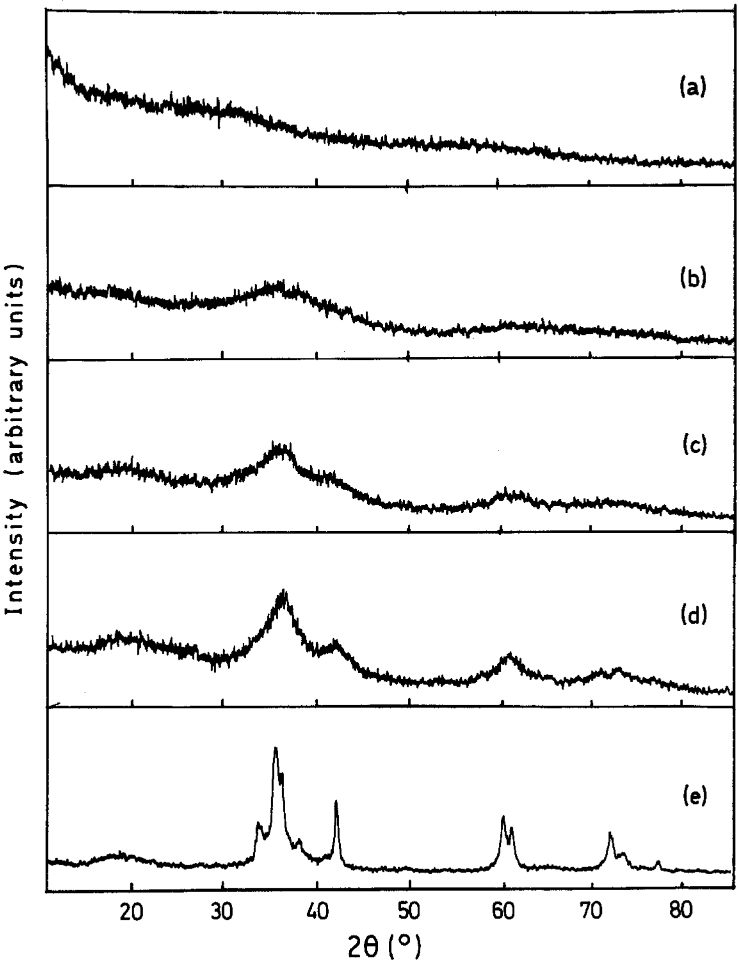

Figure 5 X-ray diffraction patterns (CuKα) of PTC and the pyrolysed PTC products at different temperatures: (a) unpyrolysed PTC, (b) PTC pyrolysed at 1000° C, (c) PTC pyrolysed at 1200° C, (d) PTC pyrolysed at 1400° C and (e) PTC pyrolysed at 1700° C. Full-scale intensity of the pattern at (e) is twice that of patterns at (a), (b), (c) and (d).

found to be the same as that given in the published data [11], and the diffraction-peak values of TiC-type phase in this pyrolysis product were shifted to the higher angles than those given in the published data for TiC [12]: (1 1 1) of TiC appearing at $2\theta = 35.8°$, (2 0 0) appearing at $2\theta = 41.4°$, (2 2 0) appearing at $2\theta = 60.3°$, (1 1 3) appearing at $2\theta = 72.1°$ and (2 2 2) appearing at $2\theta = 75.8°$. The lattice constant of the TiC-type phase was found to be 0.4271 nm, which differs from the value of 0.4329 nm found for TiC; the lattice constant of this TiC-type phase has shrunk in comparison with that of the TiC. For TiC_{1-x}, the lattice constant becomes smaller than that of TiC, as x increases [13]. The TiC-type phase obtained by pyrolysis at 1700° C is considered to be a carbon-less non-stoichiometric compound of TiC_{1-x}. The carbon atom which corresponds to a lattice constant of 0.4721 nm is about $x = 0.5$. It is an interesting phenomenon that SiC and $TiC_{0.5}$ are obtained by the heat treatment of PTC.

4. Conclusions

The new polytitanocarbosilane (PTC) consisting of Si, Ti, C, O and H was obtained by the cross-linking of polycarbosilane (PC) with titanium tetrabutoxide. This polymer was converted by pyrolysis at 1700° C in either an inert gaseous atmosphere or a non-oxidizing atmosphere into carbides consisting mainly of β-SiC-type and TiC-type phases. PTC, in which the weight residue by heat treatment is larger than that in PC, can be more advantageous for obtaining inorganic materials producing higher yields than PC. This new PTC is considered to be useful as the precursor of inorganic materials, as well as of PC and polyborodiphenylsiloxane.

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Received 15 October and accepted 14 November 1980.