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^{29}Si MAS-NMR investigation of the conversion process of a polytitanocarbosilane into SiC–TiC ceramics

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A polytitanocarbosilane has been prepared from polycarbosilane and titanium n-butoxide. ^{29}Si MAS-NMR was used to characterize the various steps of the conversion process of the polymer into the final ceramic. The reaction of titanium butoxide with polycarbosilane introduces oxygen into the polymer that seems to play an important role in the pyrolysis process. In the first stage up to 1000° C, the study reveals the cleavage of Si–C bonds and the formation of $SiC_{4-x}O_x$ units. In the second stage, above 1000° C, the number of Si–O bonds decreases, probably due to a carbothermal reduction process. At 1500° C, the product can be described as a mixture of crystalline SiC and TiC with no excess carbon.

1. Introduction

In 1975, Yajima *et al.* [1] first demonstrated the possibility of obtaining non oxide ceramics from a polymeric precursor. The precursor was a polycarbosilane which could be converted to SiC with high yield [2–4]. That process has now been successfully applied to the production of BN from aminoborazine [5], Si_3N_4 from polysilazane [6] and B_4C from carborane [7].

The major advantage of that process was the preparation of covalent ceramic fibres. Commercial silicon carbide fibres used in advanced composite materials are now produced by the Nippon Carbon company based on the pioneering work of Yajima. These fibres have high tensile strength and high Young's modulus [8]. However, their mechanical properties deteriorate at temperatures above 1200° C, when grain growth occurs [9].

Improvement of the mechanical properties at higher temperatures has been partially achieved by the use of a new precursor, a polytitanocarbosilane (PTC), which can be converted to Si–Ti–C fibres after pyrolysis [10, 11]. The crystallization process of this type of fibres is delayed, compared to the fibres prepared from polycarbosilane, and their mechanical properties have maximum values around 1400° C. The mechanical strength of the fibres seem to be closely related to the crystallization process. The retention of the amorphous state at higher temperatures appears to enhance the mechanical properties.

A better understanding of the structural evolution of these materials during the pyrolysis process is obviously quite important in order to improve their properties. This paper presents a structural investigation of the pyrolysis process of a polytitanocarbosilane as followed by ^{29}Si MAS–NMR.

2. Experimental section

Following published procedures [10], commercial polycarbosilane (Dow Corning X9-6348) was dissolved in xylene with titanium n-butoxide in a given ratio (Ti/Si = 25 mol %) in order to get an homogeneous solution. This solution was then refluxed under argon for 1 h. After distillation of the solvent, a polymer was obtained, being the precursor of the Si–Ti–C–O system. During the reflux procedure, the transparent solution turned blue and after distillation, the polymer was still blue. However, as soon as it was put in contact with air, the blue colour started to disappear and finally a yellow polymer was obtained. The change in colour will be discussed later.

^{29}Si liquid NMR spectra were recorded on a AM 360 Bruker spectrometer. A pulse width of 10 μsec was applied with a relaxation delay of 6 sec. TMS (tetramethylsilane) was used as a reference. ^{29}Si MAS-NMR spectra were obtained on a MSL 300 Bruker spectrometer, with a pulse width of 2.5 μsec and a relaxation delay of 60 sec. Infrared spectra were recorded on a Perkin Elmer 1330 spectrometer in the 4000–200 cm^{-1} range. Thermogravimetric analysis was performed using a Perkin Elmer TGS-2 thermogravimetric analyser connected to a system 7/4 thermal analysis controller. XRD diffractograms were recorded on a Phillips diffractometer.

3. Results

3.1. Characterization of the precursor

The chemical analysis of the precursor PTC is shown

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TABLE I Chemical composition (wt %) of PTC and PTC pyrolysed at 1500° C

Sample	Si	C	H	Ti
PTC	32.58	41.30	8.27	8.05
PTC pyrolysed at 1500° C	56.94	27.11	0.16	15.36

in Table I and reveals a Ti/Si ratio of 14.5%. Oxygen was not analysed. The O/Si ratio can be estimated to be 0.53 by difference. This ratio can also be evaluated, assuming that the introduction of one titanium atom should bring four oxygen atoms; it is thus, found to be 0.58. The chemical formula of PTC appears to be: $SiC_{2.96}Ti_{0.15}H_{7.07}O_x 0.5 < x < 0.6$.

^{29}Si MAS-NMR and ^{29}Si CP MAS-NMR spectra have been recorded on PC and PTC. The MAS-NMR spectra were obtained after about 1000 scans with a relaxation delay of 60 sec, while the CP MAS-NMR spectra were recorded in about 200 scans with a relaxation delay of 6 sec. The spectra are represented in Fig. 1 and clearly illustrate the advantages of cross polarization techniques, a faster rate for data accumulation and an enhancement of the observed signal.

^{29}Si NMR spectra of PC have already been described and reveal two peaks at -0.8 and -18.1 p.p.m. respectively assigned to silicon atoms surrounded by four carbon atoms (SiC_4 units) and silicon atoms surrounded by three carbon atoms and one proton (SiC_3H units). These units have been more precisely described [2–4] as $(CH_3)_2Si(CH_2)_2$ and (CH_3)-$HSi(CH_2)_2$ units although some bridging CH groups between polycarbosilane chains can exist in the starting PC. In the PTC sample, these two peaks are always present, but a new one appears at 10 p.p.m. that is assigned to the presence of SiC_3O units in which silicon atoms are now surrounded by three carbon atoms and one oxygen atom. A comparison between the CP MAS-NMR spectra of PC and PTC clearly shows that the formation of Si–O bonds occurs with a decrease in the number of Si–H bonds.

PTC is slightly soluble in solvents such as xylene and chloroform. Liquid ^{29}Si and ^{1}H NMR have thus been performed. Fig. 2 represents the NMR spectra of PTC as well as those of PC as reference.

^{29}Si NMR spectrum of PC reveals the two peaks at -0.8 and -17.6 p.p.m. due to SiC_4 and SiC_3H units in a ratio of 1 : 0.75. In the spectrum of PTC, three peaks due to SiC_4, SiC_3H and SiC_3O units are present in a ratio 1 : 0.60 : 0.20.

^{1}H NMR spectrum of PC shows a peak at 0.18 p.p.m. with two shoulders at -0.20 and -0.65 p.p.m. assigned to protons bound to carbon atoms, while protons bound to silica atoms give rise to peaks at 4.1, 4.3 and 4.6 p.p.m. The ratio between $\underline{H}$-(C) and $\underline{H}$-(Si) atoms is 11 : 1.

^{1}H NMR spectrum of PTC still exhibits the peaks around 0 p.p.m. assigned to $\underline{H}$-(C). New peaks appear at 0.93, 1.39, 1.54, 3.57 and 3.68 p.p.m. due to protons of the butoxy groups. The broadness of the peaks can be due to the polymeric nature of the sample.

The two peaks at 3.57 and 3.68 p.p.m. correspond to two kinds of CH_2 groups bound to oxygen atoms. A chemical shift of 3.57 p.p.m. corresponds to $-O{-}C\underline{H}_2-$ groups in butanol. It seems that some free butanol is present in the solution of PTC. It could be present in the PTC polymer, but the polymer was obtained after distillation of the xylene around 200°C. It could also have been produced during the dissolution into $CDCl_3$. Some water could have been present in the solvent, and thus could have hydrolysed some butoxy groups. The chemical shift of 3.68 p.p.m. does not correspond to $-O{-}CH_2-$ groups in $Ti(OBu^n)_4$. However, the shift compared to butanol shows that these groups are bound to silicon or titanium.

The infrared spectrum of PTC is similar to that published by Yajima *et al.* [10]. Bands characteristic of PC are present at 2900 and 2960 cm^{-1} (C–H), at 2100 cm^{-1} (Si–H), at 1400 cm^{-1} (H–C–H), at 1355 and 1020 cm^{-1} (Si–CH_2–Si), at 1255 cm^{-1} and at 830 cm^{-1} (Si–CH_3). The ratio between the intensities of the band at 2100 cm^{-1} (Si–H) and of the band at 1255 cm^{-1} (Si–CH_3) is 0.93 in the starting PC. In PTC, this ratio is 0.65, showing the consumption of Si–H groups

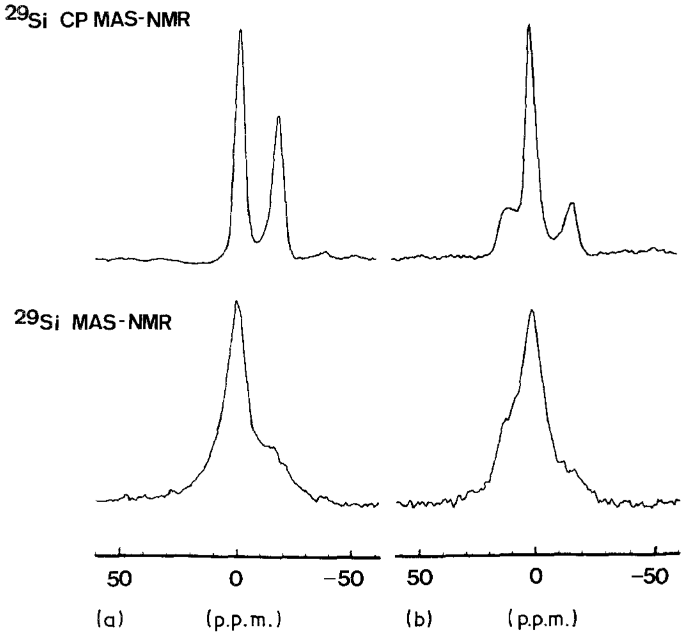

Figure 1 ^{29}Si MAS-NMR and ^{29}Si CP MAS-NMR of (a) PC and (b) PTC polymers.

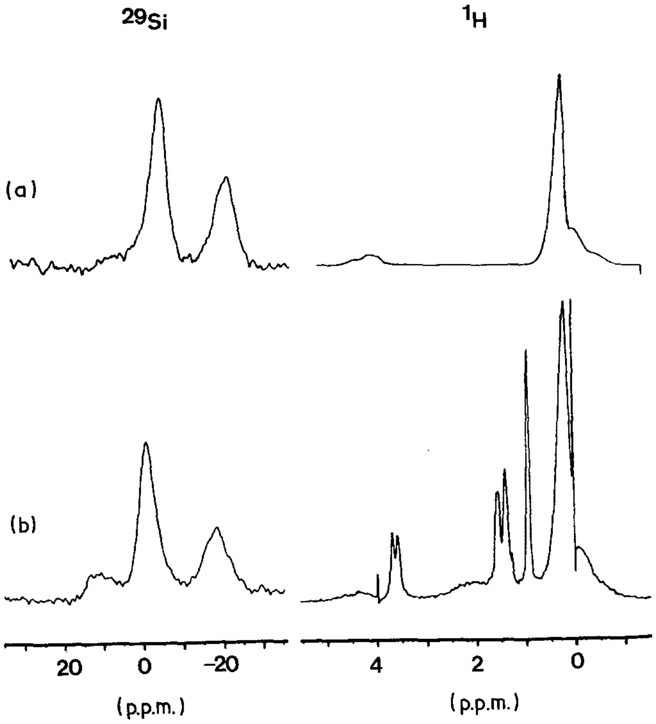

Figure 2 ^{29}Si and ^{1}H NMR spectra of a solution of (a) PC and (b) PTC in $CDCl_3$.

during the reaction of PC with titanium butoxide. The decrease of 20% in the intensity of the Si–H band is of the same order of magnitude as the decrease in the intensity of the NMR peak due to SiC_3H units.

New bands also appear in the PTC spectrum assigned to the presence of butoxy groups, at 2880 and 2940 cm^{-1} (ν(C–H)) and at 1380 and 1460 cm^{-1} (δ(H–C–H)). These bands do not allow us to determine whether butoxy groups belong to butanol or are bound to titanium or silicon. Sharp bands are also present at 1150, 1120 and 1095 cm^{-1}. None of these bands can be assigned to butanol. They can be due to ν(C–O) stretching vibrations of –Ti–O–CH_2– units (1130, 1085 and 1040 cm^{-1} in Ti(OBu^n)$_4$) or to ν(Si–O) stretching vibrations (1095 and 1110 cm^{-1} in Si(OEt)$_4$). A broad band around 600 cm^{-1} is also present in the spectrum of PTC, and is assigned to ν(Ti–O) vibrations.

As already mentioned in the experimental section, the polymer turns blue when refluxed under argon. This colour disappears when the polymer is exposed to air. This blue colour could be due to the presence of Ti^{3+} ions, that are oxidized to Ti^{4+} in air.

A solution of PTC in hexane has been irradiated with UV light in order to photoreduce Ti^{4+} ions and to create Ti^{3+} ions. Isopropanol was added to the solution as a reducing agent. After a few minutes, the solution turned blue. ESR spectra have been recorded at room temperature (Fig. 3). The spectrum exhibits two components at $g = 1.968$ and $g = 1.992$. These g values are characteristic of Ti^{3+} ions, and the spectrum should reflect the presence of at least two kinds of titanium sites in the polymer.

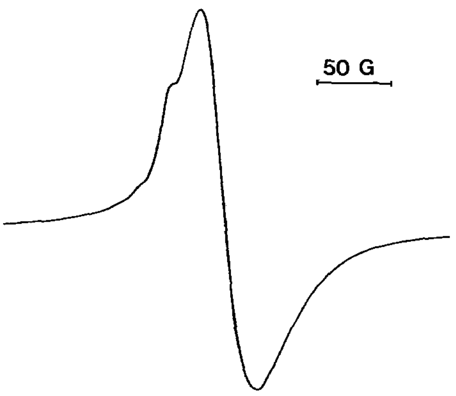

Figure 3 ESR spectrum recorded at room temperature of a solution in hexane of PTC irradiated with UV light.

3.2. Pyrolysis process

TGA on PTC has been performed in flowing argon. The total weight loss is 24% from room temperature to 780°C and can be divided into three stages: from

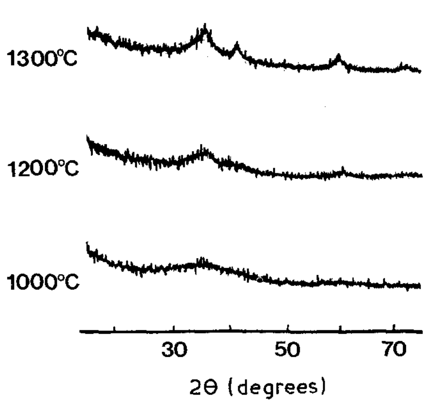

Figure 4 Evolution of the XRD patterns of PTC during the pyrolysis process.

room temperature to 380° C (12.5%), from 380 to 500° C (6.5%) and from 500 to 780° C (5%). The last two stages seem to correspond to the decomposition stages of PC that has already been described in the literature, while the first one is certainly due to the decomposition of the titanium alkoxide part.

PTC was pyrolysed under argon atmosphere and the crystallization process was followed by XRD (Fig. 4). The results are in agreement with data previously published [10]. At 1000° C, broad peaks are present roughly centered on *d* values corresponding to SiC phases. At 1200° C, the peaks sharpen and a new peak reveals the presence of crystalline TiC. At 1500° C, the system is rather well crystallized with peaks assigned to β-SiC and TiC. Some α-SiC also appears to be present. Compared to the crystallization process of PC, the product from PTC is less crystalline at 1200° C, but much more at 1500° C [11].

Results of the chemical analysis of PTC pyrolysed at 1500° C are reported in Table I. Oxygen has not been analysed, but the total wt % (99.57%) seems to reveal a low oxygen content (O/Si < 2 mol %). The chemical formula thus appears to be $SiC_{1.11}Ti_{0.16}H_{0.08}$. Compared to PC, the amount of carbon is reduced in the pyrolysed PTC. Moreover, according to this chemical analysis, no excess carbon seems to be present, and if the hydrogen content is neglected, the chemical formula can be written SiC–0.15 TiC.

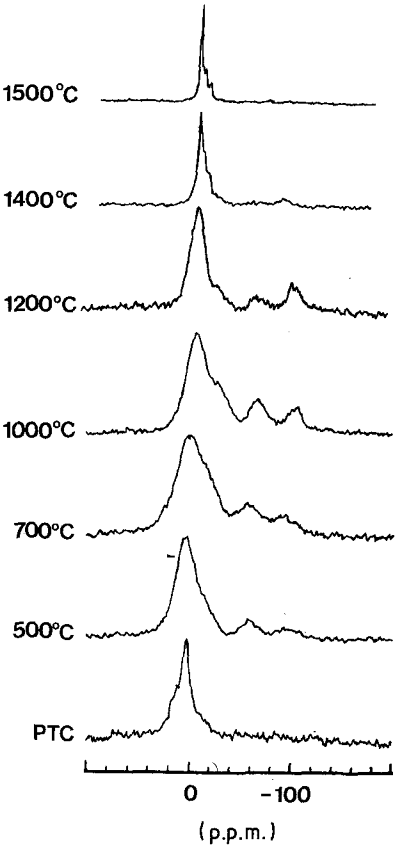

Figure 5 Evolution of the ^{29}Si MAS-NMR spectra of PTC during the pyrolysis process.

The pyrolysis process up to 1500° C, was followed by ^{29}Si MAS-NMR in order to follow the evolution of the local environment of the silicon atoms (Fig. 5). As soon as 500° C is reached, very interesting differences appear in the spectrum as compared to that of the precursor. The peak around 0 p.p.m. broadens and no longer shows any structure. More interestingly is the appearance of two broad peaks centred at −60 and −95 p.p.m. which are due to the presence of $SiC_{4-x}O_x$ units with $x = 3$ and $x = 4$ [13]. The spectrum at 700° C presents the same features with a broadening and shift of the main peak ($\delta = -5.2$ p.p.m.). At 1000° C, some differences have to be noted: (1) The main peak is continuously shifting ($\delta = -11.2$ p.p.m.), but is sharpening, so that another peak at −31 p.p.m. is now present that could be assigned to SiC_2O_2 units. (2) The two peaks assigned to $SiCO_3$ and SiO_4 units, have shifted upfield and are now centered at −75 and −110 p.p.m. At 1200° C, the peak due to SiC_4 is now centred at −14.0 p.p.m.. The two peaks corresponding to SiC_2O_2 and $SiCO_3$ units are decreasing. At 1400° C, almost all the peaks due to $SiC_{4-x}O_x$ ($x = 0$) have disappeared, except a small one around −110 p.p.m. due to SiO_4 units. Some structure appears in the main peak now centred at −16.0 p.p.m. At 1500° C, three peaks are clearly visible at −16.3,

TABLE II ^{29}Si MAS-NMR results after deconvolution of the spectra recorded after pyrolysis at various temperatures (δ, Δ and *I* represent, respectively, the chemical shift, the linewidth and the relative intensity of the peaks)

Temperature (° C)	Parameters	SiC_4	SiC_2O_2	$SiCO_3$	SiO_4
500	δ(p.p.m.)	−0.8	−15	−60	−95
	Δ(Hz)	1280	1350	860	1300
	I(%)	72.3	13.3	7.3	7.1
700	δ(p.p.m.)	−5.2	−23	−60	−95
	Δ(Hz)	1620	1510	1800	1250
	I(%)	54.2	20.8	17.9	7.1
1000	δ(p.p.m.)	−11.2	−31	−75	−110
−110					
	Δ(Hz)	1320	1780	1210	830
	I(%)	52.8	24.8	13.9	8.6
1200	δ(p.p.m.)	−14.0	−35	−78	−111
	Δ(Hz)	910	570	980	740
	I(%)	71.3	6.2	8.1	14.3
1400	δ(p.p.m.)	−16.3 −20.0 −24.5			−110
	Δ(Hz)	375 215 235			645
	I(%)	89.5			10.5

-20.0 and -24.5 p.p.m. No oxygen atoms now seem to be bonded to silicon.

The multiplicity of the sites appearing during the heat treatment show the complexity of the pyrolysis process. The reaction of PC with titanium alkoxide introduces oxygen in the product, and thus carbon and oxygen atoms compete to bond to silicon and titanium.

In order to get some quantitative data about the evolution of the local environment of silicon atoms, the spectra have been deconvoluted to extract the percentage of the various silicon units. The data are represented in Table II.

The peak around 0 p.p.m. was assigned only to SiC_4 units while these could have been a contribution from SiC_3O units ($\delta = 10$ p.p.m.). The position of this peak regularly shifts with the firing temperature towards a value corresponding to crystalline SiC phases. The linewidth of the peak reaches a maximum at 700° C and decreases by a large amount above 1000° C. Such an evolution has already been mentioned in the study of the pyrolysis process of pure PC [12]. The maximum could correspond to an amorphization of the pyrolysed polycarbosilane chains. The decrease in the linewidth is then due to an ordering of the SiC_4 units towards crystalline SiC phases.

The data concerning silicon sites with Si–O bonds are quite interesting. The variation of the chemical shifts of the SiC_3O and SiO_4 units between 700° C and 1000° C, a 15 p.p.m. shift upfield, reveals a modification of the environment of the silicon atoms in these units. In silica systems, a chemical shift of 95 p.p.m. for SiO_4 units is usually assigned to Q_3 units (silicon atom surrounded with three bridging oxygen atoms and one non bridging oxygen atom). In the present system, it could be also due to the presence of Si–O–Ti bonds. However, these bonds do not seem stable above 400° C [17]. Above 1000° C, the chemical shift of -110 p.p.m. correspond to Q_4 units similar to those found in SiO_2. The linewidth of these peaks also decrease for a firing temperature above 1000° C, showing an ordering in the units.

The formation of $SiC_{4-x}O_x$ units with $x > 1$ shows that the Si–C bonds of the polycarbosilane chains are not stable in the presence of oxygen. The number of oxygen atoms bonded to silicon per silicon atom, has been evaluated from the relative intensities of the various sites. This evolution with the firing temperature is represented in Fig. 6. The number of oxygen bonded to silicon atoms per silicon atom, first increases up to 700° C: this reveals a cleavage of Si–C bonds and formation of Si–O bonds. Then the curve presents a maximum around 0.60. According to the chemical analysis results ($0.5 < O/Si < 0.6$), it seems that all the oxygen atoms are bonded to silicon atoms between 700 and 1000° C. Above 1000° C, the number of Si–O bonds decreases regularly up to 1500° C. The oxygen is certainly consumed by reaction with carbon, that is present in excess in these materials.

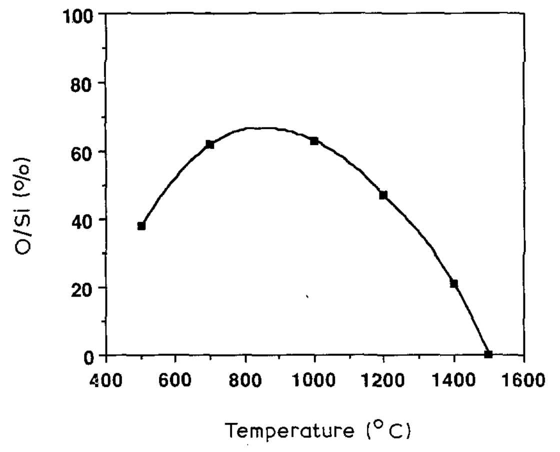

Figure 6 Evolution with the firing temperature of the number of oxygen atoms bonded to silicon, per silicon atom.

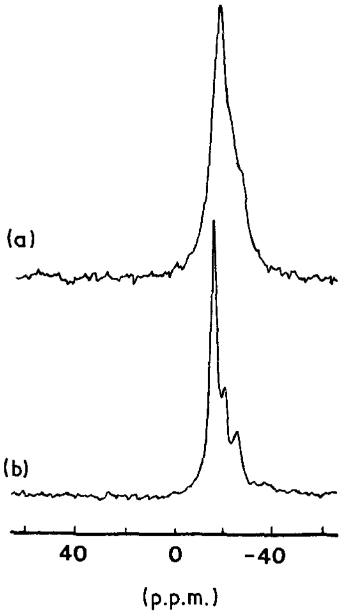

Figure 7 ^{29}Si MAS-NMR spectra of (a) PC and (b) PTC pyrolysed at 1500° C.

3.3. Crystallization process

Fig. 7 represents the ^{29}Si MAS-NMR spectrum of PTC pyrolysed at 1500° C compared to the spectrum of PC fired under the same conditions. The spectrum of PTC presents a main peak at -16.3 p.p.m. and two other peaks at -20.5 and -24.5 p.p.m. The presence of these three peaks has already been mentioned for the spectrum of PC fired at 1700° C [12]. The two peaks at -20.5 and -24.5 p.p.m. have been assigned to two of the three components due to α-SiC [15, 16]. The third peak should be at -14.3 p.p.m. and should be overlapped by the main peak. The position of this peak at -16.3 p.p.m. does not correspond to the chemical shift of crystalline β-SiC, -18.4 p.p.m. according to the literature [15] and -18.9 p.p.m. from a commercial sample. The X-ray diffractogram exhibits peaks corresponding to β-SiC; however, the identification of the phase is difficult due to the existence of many SiC polytypes. This apparent discrepancy between XRD and ^{29}Si MAS-NMR data has to be elucidated.

The comparison of the spectra of PTC and PC fired at 1500° C under the same conditions shows the presence of the same peaks, but much broader in the case of PC. The peaks at -20.5 and -25.0 p.p.m. appear only as shoulders in the spectrum of PC. The

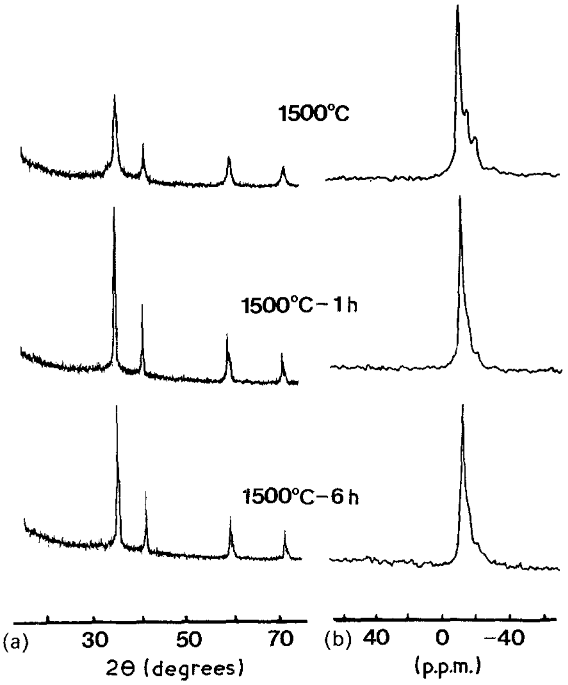

Figure 8 Influence of the firing time on (a) the XRD patterns and (b) the ^{29}Si MAS-NMR spectra of PTC pyrolysed at 1500° C.

difference in linewidth clearly shows a better crystallinity for PTC fired at 1500° C.

PTC has been fired at 1500° C with a heating rate of 10° C min^{-1}. One sample was just heated up and then cooled down. Two other samples were fired for 1 and 6 h, respectively, before being cooled down. The X-ray patterns and ^{29}Si MAS-NMR spectra are represented in Fig. 8. The influence of the firing time is clearly visible during the first hour at 1500° C. Data obtained after 1 or 6 h are quite similar. The X-ray patterns show an increase of the crystallinity of the sample with firing time: after 1 h, all the peaks present two components, one corresponding to SiC and one to TiC. In the NMR spectra, the main change is a decrease in the peaks at -20.5 and -24.5 p.p.m. which are assigned to α-SiC. This is in agreement with the decrease of the broad peak of the diffractogram at $2\theta = 34°$, corresponding to α-SiC.

4. Discussion and conclusion

A structure has already been proposed for polytitanocarbosilanes which is essentially based on infrared data [10, 17]. The present NMR study is in complete agreement with these results. During the refluxing procedure of the polycarbosilane with the titanium alkoxide, Si–H bonds are consumed and Si–O bonds are created leading to the formation of SiC_3O units. It seems that a chemical reaction occurs between the Si–H groups of the PC and OR groups of titanium alkoxide. The formation of Si–O–Ti bonds have been proposed according to infrared data [17]: in some polytitanocarbosilanes prepared from different routes, a band at 900 cm^{-1} assigned to the presence of Si–O–Ti bonds appears in the spectra. In the present study, such a band is not clearly visible. One reason could be the differences in the preparation procedure. The polymer is heated up to 220° C in the present study, and it seems that the Si–O–Ti bonds start to decompose at temperatures above 200° C.

The environment of titanium atoms cannot be precisely described. Comparing the chemical analysis of PC and PTC, and assuming that the excess carbon comes from the presence of butoxy groups, 1.3 OR groups per titanium seem to be present in the polymer. At least, two OR groups have reacted to form Si–O–Ti bonds or even Ti–OH bonds if some moisture was present in the atmosphere or in the solvent. As already proposed in the literature [10, 17], some of the titanium units can act as bridges between the polycarbosilane chains.

During the pyrolysis process, the presence of oxygen introduced via titanium alkoxides strongly modifies the local environment of silicon atoms. An infrared study has already mentioned that in the pyrolysis process of the Si–O–Ti bonds, decomposition occurs in the Ti–O bond and leads to Si–O–Si bonds. The present study shows that Si–O bonds are also formed via a cleavage of Si–C bonds and thus lead to the formation of $SiC_{4-x}O_x$ units with $1 < x < 4$. This reaction occurs up to 700° C where all the oxygen atoms present in the starting polymer, seem to be bonded to silicon atoms.

Above 1000° C, Si–O bonds are lost because of reactions with carbon. However, the remaining Si–O bonds seem to be more stable in SiO_4 units than in SiC_2O_2 and $SiCO_3$ units. The presence of silica can be assumed even if no evidence is shown by XRD. Above 1200° C, the consumption of Si–O bonds increases. At 1500° C, the material can be described as two main crystalline phases, SiC and TiC. From XRD data, the SiC phases are usually assigned to β-SiC with the presence of some α phase. However, the present NMR study seems to show the presence of other SiC_4 units that do not correspond exactly to β-SiC.

The SiC phases are more crystalline at 1500° C than SiC prepared under the same pyrolysis conditions from pure PC. In fact, starting from PTC, the crystallization process is delayed to above 1300° C. This is certainly due to the presence of titanium and oxygen inside the samples. However, as soon as the crystallization occurs, the process is quicker than in the case of PC. Also the consumption of the carbon phase by the extra oxygen atoms may help the growth of the crystallites.

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