Journal of the European Ceramic Society **8** (1991) 29–34

Synthesis and Characterization of Si–Zr–C–O Ceramics from Polymer Precursors

Florence Babonneau

Chimie de la Matière Condensée, Université Pierre et Marie Curie, 4 place Jussieu, 75005 Paris, France

&

Gian Domenico Sorarù

Dipartimento di Ingegneria dei Materiali, Università di Trento, 38050 Mesiano-Trento, Italy

(Received 17 December 1990; Revised version received 6 February 1991; accepted 25 February 1991)

Abstract

Polyzirconocarbosilane has been prepared from polycarbosilane and zirconium alkoxide. The structure of this Zr-modified polymer as well as its conversion process into SiC/ZrC crystalline material has been investigated, using mainly MAS–NMR and XRD techniques. This work is part of a more comprehensive study on the pyrolysis process of polycarbosilanes modified with metallic alkoxide $M(OR)_n$ *(M = Ti, Zr, Al). The crystallization behavior has been compared with results already found for Si–Ti–C–O and Si–Al–C–O systems and will be discussed.*

Aus Polycarbosilan und Zirkoniumalkoxid wurde Polyzirkoncarbosilan hergestellt. Die Struktur dieses durch Zirkonium veränderten Polymers und die Umwandlung in kristallines SiC/ZrC-Material wurde hauptsächlich mit MAS–NMR und XRD untersucht. Die hier vorgestellten Ergebnisse stellen nur einen Teil einer umfassenderen Studie über das Pyrolyseverhalten von mit metallischen Alkoxiden $M(OR)_n$ *(M = Ti, Zr, Al) veränderten Polycarbosilanen dar. Das Kristallisationsverhalten wird diskutiert und mit dem der bereits bekannten Si–Ti–C–O und Si–Al–C–O Systeme verglichen.*

Le polyzirconocarbosilane a été préparé à partir de polycarbosilane et d'un alcoxyde de zirconium. La structure de ce polymère modifié par la présence de zirconium ainsi que sa transformation en un matériau cristallisé SiC/ZrC ont été étudiées principalement par RMN–MAS et diffraction des rayons X. Ce travail fait partie d'une étude plus générale sur la pyrolyse de divers polycarbosilanes modifiés par un alcoxyde métallique $M(OR)_n$ *(M = Ti, Zr, Al): le processus de cristallisation a donc été comparé avec les résultats précédemment trouvés pour les systèmes Si–Ti–C–O et Si–Al–C–O et ceci fera l'objet d'une discussion.*

1 Introduction

Among the new methods for processing non-oxide ceramics with improved properties, pyrolysis of metal–organic polymers is playing an increasing role.[1,2] This method offers several advantages like lower processing temperatures and possibilities for fabricating ceramic fibers or coatings. Indeed, in 1975, the pioneering work of Yajima demonstrated the feasibility of obtaining high-strength silicon carbide fibers by the pyrolysis of a polycarbosilane.[3] Since then, many other metal–organic precursors have been studied with the aim of extending this process to different ceramic systems such as Si_3N_4,[4] BN,[5,6] AlN[7] and B_4C.[8]

One of the most attractive and challenging features of this process is the possibility of controlling the microstructure and the properties of the final ceramic material by modifying the polymer composition and/or its structure. By reacting, in solution, a polycarbosilane (PC) precursor for Nicalon (Nippon Carbon Co., Tokyo, Japan) SiC fibers with a titanium alkoxide, a new polymer called polytitanocarbosilane (PTC) is obtained that gives, after pyrolysis, ceramic materials of the Si–Ti–C–O system.[9] Commercially available Tyranno (Ube Industries Ltd, Tokyo, Japan) fibers produced from

Journal of the European Ceramic Society 0955-2219/91/$3.50

this precursor display superior tensile strength compared with SiC Nicalon (Nippon Carbon Co., Tokyo, Japan) fibers.[10]

The same reaction used to produce PTC can give the opportunity to modify the polycarbosilane with different elements just by changing the nature of the metal alkoxide. Therefore, by using this strategy, it could be possible to prepare a large variety of new metal–organic polymers, precursors for Si–M–C–O systems. The authors' attention was first focused on the Si–Ti–C–O system, and then on two new systems, Si–Al–C–O and Si–Zr–C–O.

The main goals of these studies were the following: (i) a structural characterization of the polycarbosilane-modified precursor to understand how the metallic alkoxide reacts with the polycarbosilane, and (ii) a study of the structural evolution of the material during the pyrolysis to see the influence of the extra metallic atoms on the crystallization process. The Si–Ti–C–O system that leads to SiC/TiC polycrystalline materials has been investigated in detail using solid state MAS–NMR,[11] XPS[12] and X-ray absorption.[13] Results concerning the aluminum-containing material will be reported in a separate communication.[14] In this paper, experimental results concerning the structure of the Zr-modified polymer (PZC) and its conversion into the final Si–Zr–C–O ceramics will be reported. The study has mainly been carried out by using multinuclear MAS–NMR spectroscopy and XRD analysis.

2 Experimental

The modified polymer was prepared by mixing 10 g of polycarbosilane (Dow Corning X9-6348, Dow Corning Corporation, Midland, USA) with 17·7 g of zirconium n-butoxide, $Zr(OBu^n)_4 . Bu^nOH$ (Fluka, Fluka Chemika-Biochemika, Buchs, Switzerland) in 150 ml of toluene. The molar ratio Zr/Si is 25%. The solution was refluxed for 1 h under argon and then the solvent was distilled. A cross-linked polymer was obtained by a further heat-treatment up to 300°C, when the polymer became no longer fusible. This experimental procedure is close to the one used by Yajima to prepare the Ti-modified PC.[9] The chemical analysis performed on the final polymer (Service Central d'analyse du CNRS, Vernaison, France) gave $SiZr_{0.20}C_{3.91}O_{1.22}H_{9.20}$.

The polymer (polyzirconocarbosilane; PZC) was characterized by infrared (Nicolet FT–IR 5DXC, Vicenza, Italy) and MAS–NMR (Bruker MSL 400, Bruker, Wissenbourg, France). MAS–NMR spectra have been recorded on powders packed into zirconia rotors and spun at 4 kHz. For the CP–MAS experiments, contact times of 2 ms and 1 ms were used for ^{29}Si and ^{13}C, respectively, with relaxation delays of 6 s. For the ^{29}Si MAS–NMR experiments, 2·5 μs pulses were applied with delays between pulses of 60 s.

DTA and TGA were performed using a Netzsch STA 409 equipment (Netzsch, Verona, Italy). The polymer was then pyrolyzed under argon at various temperatures up to 1500°C (Astro furnace, Thermal Technology Inc., Verona, Italy). The pyrolyzed products were characterized by XRD analysis (Philips, Mahwah, NJ, USA) and ^{29}Si MAS–NMR.

3 Results

3.1 Characterization of the polymer

A comparison between the ^{29}Si CP–MAS NMR spectra of PC and PZC is presented in Fig. 1. The spectrum of PZC exhibits three peaks, the usual two peaks characteristic of pure polycarbosilane at 0 ppm (SiC_4 units) and at −17 ppm (SiC_3H units) and a new peak at 10 ppm characteristic of SiC_3O units. (A $SiC_{4-n}X_n$ unit corresponds to a silicon atom surrounded by $(4-n)$ C atoms and n X atoms.) A comparison between the spectra of PC and PZC clearly shows that Si–O bonds are formed with a decrease in the Si–H bonds.

The ^{13}C CP–MAS spectra of PC and PZC are also presented in Fig. 1. The spectrum of PZC presents a broad peak at 4 ppm due to the C atoms of the PC chains. In addition, sharp peaks can be seen at 14·1, 19·3, 26·8, 35·1 and 61·9 ppm. The zirconium butoxide, $Zr(OBu^n)_4 . Bu^nOH$, presents peaks at 14·2 (C^4), 19·4 (C^3), 36·4 (C^2), 67·4 and 69·8 (C^1) ppm

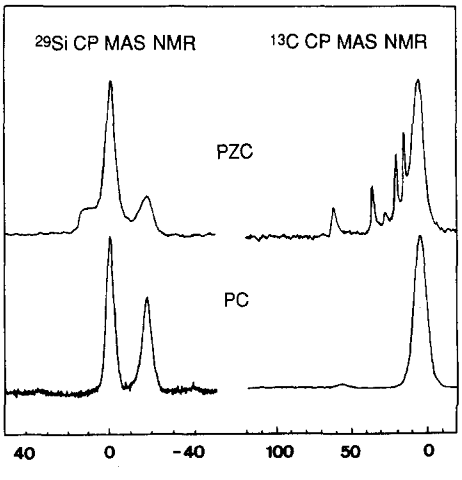

Fig. 1. ^{29}Si and ^{13}C CP–MAS NMR spectra of PC and PZC.

corresponding to the C atoms of the butoxy chains $O{-}C^1H_2{-}C^2H_2{-}C^3H_2{-}C^4H_3$. The presence of two peaks for the C^1 atoms is related to terminal and bridging groups in the zirconium alkoxide that is known to be an oligomeric species.[15] The peaks at 14·1, 19·3 and 35·1 ppm PZC are thus due to butoxy groups. However, the chemical shift due to the C^1 atom does not correspond to the one found in zirconium butoxide, but is close to the value found in silicon butoxide (6·30 ppm) or in n-butanol (61·4 ppm). However, the presence of only free n-butanol in this polymer already heated at 300°C is unlikely. Thus, it seems that the butoxy groups are no longer bonded to Zr atoms, but now to Si atoms. As for the remaining weak peak at 26·8 ppm, it could be assigned to the C^2 atom of n-propoxy chains, $-O{-}C^1H_2{-}C^2H_2{-}C^3H_3$. These propoxy groups could be formed from the cleavage of the butoxy groups.

The infrared spectra of PC, PZC and the two alkoxides are shown in Fig. 2. The spectrum of PZC presents the typical bands due to PC chains at 2900 and 2960 cm^{-1} (νC–H), 2100 cm^{-1} (νSi–H), 1410 cm^{-1} (δCH_3), 1355 cm^{-1} (δCH_2), 1250 cm^{-1} (ν $Si{-}CH_3$), 1025 cm^{-1} (ν $Si{-}CH_2{-}Si$) and 830 cm^{-1} (δ $Si{-}CH_3$).[16] Additional bands are present at 2940 and 2880 cm^{-1}, 1460 and 1380 cm^{-1}, 1150, 1120 and 1095 cm^{-1}, 500 cm^{-1}. The bands around 2900 cm^{-1} and 1400 cm^{-1} are due to the stretching and angular deformation of the CH_2 and CH_3 groups of the alkoxy groups. The three bands around 1100 cm^{-1} are due to the C–O stretching vibration of the alkoxy groups and should be sensitive to the atom bonded to this group. In fact, a comparison between the position of these bands and those found in silicon and zirconium butoxides for this vibration mode shows that the alkoxy groups are bonded to Si still in agreement with the NMR data. As for the broad band around 500 cm^{-1}, it can be assigned to the stretching vibration ν Zr–O.

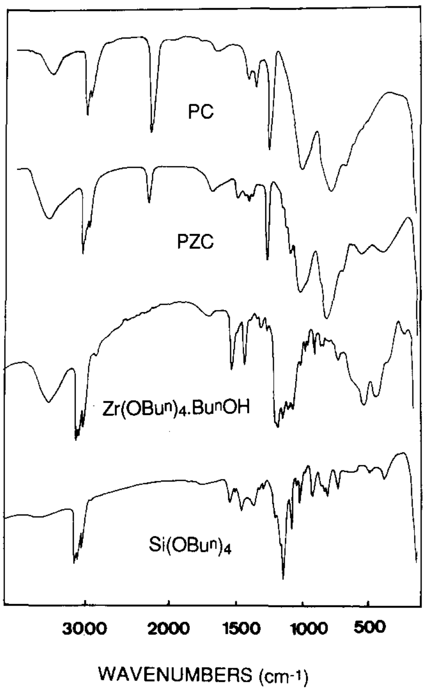

Fig. 2. Infrared spectra of PC, PZC, zirconium butoxide ($Zr(OBu^n)_4 \cdot Bu^nOH$) and silicon butoxide ($Si(OBu^n)_4$).

The ratio between the intensities of the ν Si–H and the ν $Si{-}CH_3$ bands is 0·7 in PZC and 1 in PC. It shows the consumption of Si–H bonds during the preparation procedure in perfect agreement with the NMR data.

The NMR and IR results found for PZC are similar to those found for Ti-modified PC (PTC):[17] Si–O bonds are formed with consumption of the Si–H bonds. They seem to be due to Si–OR groups and not to Si–O–Zr bonds. A reaction mechanism between the alkoxide and the polycarbosilane is quite difficult to propose. For the PTC system, it has been shown that Ti–OBu bonds are cleaved during the reaction with a reduction of the titanium ions to Ti^{3+}. The OBu groups could thus react with the Si–H bonds to form Si–OBu groups[17] according to :

$$2Si{-}H + 2Ti^{4+}{-}OBu^n \rightarrow 2Ti^{3+} + 2Si{-}OBu^n + H_2$$

For the PZC system, such a mechanism can also be proposed, even if there is no evidence of any reduction of the zirconium ions. However, the Zr^{3+} ions are known to be quite unstable and such species could only be intermediates in the reaction.

The formation of $Si{-}OBu^n$ bonds can also be due to the reaction of the Si–H bonds of the PC with the butanol introduced with the Zr precursor. In this case, the Zr butoxide can act as a catalyst for this reaction. However, it has to be noted that the same reaction done with zirconium *n*-propoxide, $Zr(OPr^n)_4$, that is not solvated by any alcohol molecules, gave the same results with the formation of $Si{-}OPr^n$ bonds. This mechanism is thus less unlikely. The absence of any Zr–OBu bonds could also be due to hydrolysis of these groups by ambient moisture, which would lead to the formation of Zr–O–Zr bridges.

Since no evidence for the presence of Si–O–Zr bonds was found in PZC, it could thus be described as a polymer containing small zirconium-oxide-based particles trapped inside the PC chains.

3.2 Pyrolysis process

TGA analysis performed in flowing Ar (Fig. 3) shows two regions of weight loss: below 800°C, the weight losses correspond to the conversion of the polymer into an inorganic network, while above 1500°C, the weight loss corresponds to a solid-state reaction occurring with the evolution of volatile species. The first domain can be divided into three steps: from room temperature to 380°C ($\simeq 2\%$), from 380 to 600°C ($\simeq 6\%$) and from 600 to 750°C ($\simeq 7\%$). The last two losses have already been found in the TGA analysis of pure PC. They correspond to condensation reactions between the chains with evolution of volatile species such as CH_4 and H_2.[18] They lead to the formation of an amorphous silicon carbide network. The first weight loss should be due to the presence of the alkoxy groups inside the PZC polymer, which should decompose at relatively low temperatures.

The DTA pattern (Fig. 3) presents two main endotherms up to 800°C, in the temperature ranges of the first and third weight losses. The final weight loss above 1500°C seems also associated with an endothermic effect.

The conversion of the polymer into an inorganic network was followed by ^{29}Si, ^{13}C CP–MAS NMR (Fig. 4) and infrared. The evolution of the ^{13}C NMR spectra clearly shows the decrease of the peaks due to the alkoxy groups, which completely disappear at 600°C. The infrared data are also in agreement with these results, showing a decrease in the bands assigned to the alkoxy groups, especially the three bands around 1100 cm^{-1}. The ^{29}Si NMR spectrum of the sample heated at 400°C does not show any evolution in the peaks due to SiC_4 and SiC_3H units. This confirms the stability of the PC chains up to 400°C. The main change comes from a broadening and a slight shift of the peak due to SiC_3O units. It could be due to a change in the O atom environment: the removal of the OBu groups shown by ^{13}C NMR and IR could lead to the formation of some bridging O atoms between the PC chains. At 600°C, all the peaks are broadening showing a disordering of the various Si sites. A new peak appears around −50 ppm and is assigned to the presence of some $SiCO_3$ units. The broad peak around −20 ppm should be due to SiC_2O_2 units and no longer to SiC_3H units, since at this temperature, most of the Si–H bonds have already been consumed, as revealed by the IR spectrum. The formation of these $SiC_{4-x}O_x$ units has already been found during the pyrolysis of the Ti-modified PC.[11]

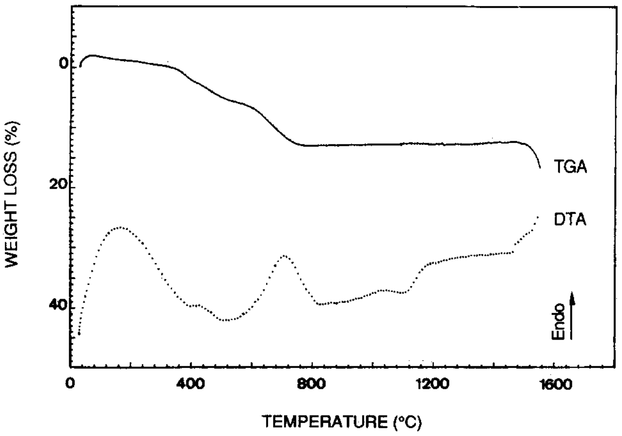

Fig. 3. TGA (—) and DTA (····) of the PZC sample (argon flow: 100 cm^3/min; heating rate: 10 K/min).

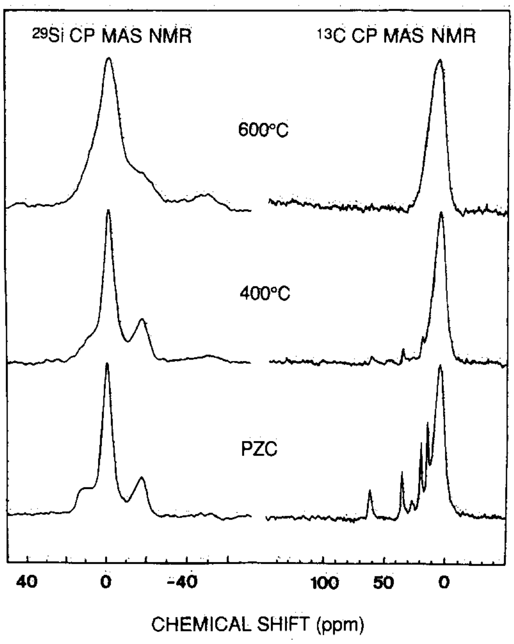

Fig. 4. ^{29}Si and ^{13}C CP–MAS NMR spectra of PZC samples fired at 400°C and 600°C.

The PZC polymer was pyrolyzed under argon at various temperatures up to 1500°C and the samples were characterized by X-ray diffraction and ^{29}Si MAS–NMR. Figure 5 represents the X-ray diffraction patterns of PZC fired at 1000, 1400 and 1500°C for 1 h. At 1000°C, the sample is poorly crystalline; the main phase is tetragonal ZrO_2. The broad peak around $2\theta = 35$ degrees indicates that the crystallization of the SiC matrix is just starting. At 1400°C, the peaks due to ZrO_2 are sharpening as well as those due to the SiC phase that can be identified as the cubic polytype SiC 3C. New sharp peaks present are due to crystalline ZrC phase. At 1500°C for 1 h, the only crystalline phases are ZrC and SiC 3C. The chemical analysis gave $SiZr_{0.39}C_{1.81}O_{0.04}H_{0.10}$ for this sample. The large increase in the Zr/Si ratio compared to the initial one in PZC clearly shows a loss of Si atoms. The observed weight loss in the TGA curve can thus be related to the evolution of some SiO. This species can be formed by the reaction of ZrO_2 with SiC phase, leading to the formation of ZrC. This is in agreement with the consumption of the crystalline ZrO_2 phase and the rapid increase of

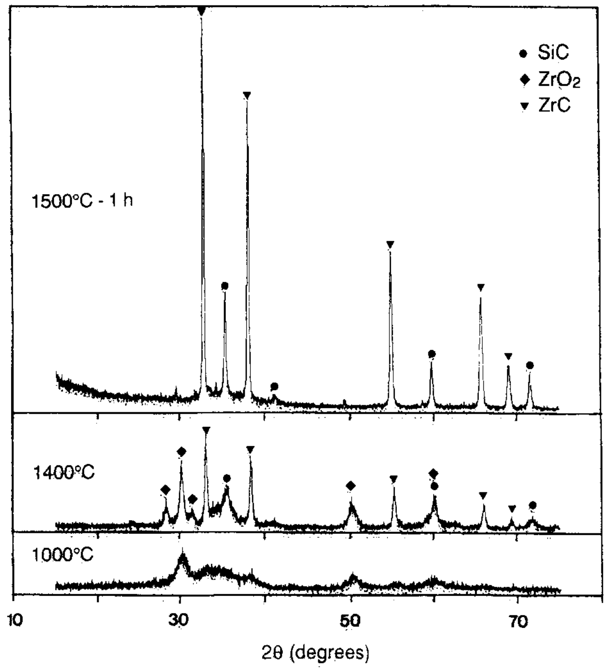

Fig. 5. X-Ray diffraction patterns of PZC samples fired at 1000, 1400 and 1500°C for 1 h under argon.

the ZrC peaks between 1400 and 1500°C. However, the formation of ZrC from ZrO_2 and free carbon with the evolution of CO can also occur. It has to be noticed that the onset for the crystallization of ZrO_2 particles seems dependent on the samples and can vary from 900 to 1200°C. It could be due to the sizes of the alkoxide-derived zirconia particles that are formed during the preparation of the polymer. However, the crystallization pathway to the final material SiC/ZrC is always the same for the various samples.

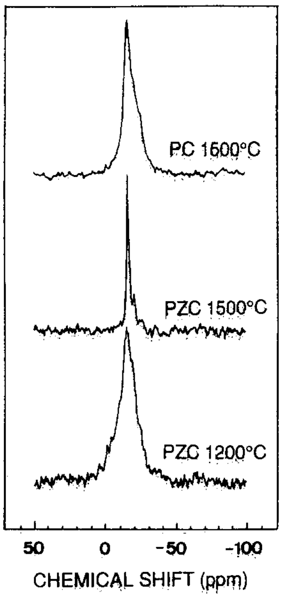

Fig. 6. ^{29}Si MAS–NMR spectra of PZC samples fired at 1200 and 1500°C for 1 h under argon. The spectrum of a PC sample fired at 1500°C for 1 h is also presented for comparison.

The ^{29}Si MAS–NMR spectra were recorded on the various fired samples and the results concerning the samples fired at 1200 and 1500°C for 1 h are represented in Fig. 6. At 1200°C, the spectrum shows a broad peak centred around −15 ppm, a typical value for SiC. The broadness reflects the poor crystallinity of the SiC phase in this sample. At 1500°C for 1 h the main evolution consists in a sharpening of the peak, which now presents at least two components, the main one at −16·1 ppm and a smaller one at −19·9 ppm. The sharpening effect shows that the local order around Si atoms is well defined in this sample. It is in agreement with the XRD pattern, characteristic of a well-crystallized material. The value of −16 ppm corresponds to the chemical shift found for a SiC 3C monocrystal.[19] The extra peak around −20 ppm could be related to the presence of some α-SiC polytypes.[19]

4 Discussion

This study has shown that the PZC polymer can be described as a two-phase system with zirconium-oxide-based particles dispersed inside a polycarbosilane matrix. The model has already been proposed for the Ti- and Al-modified polycarbosilanes.[13,14] During the pyrolysis process, the polymer leads first to the crystallization of ZrO_2 and SiC and is finally converted at 1500°C into a mixture of crystalline SiC 3C and ZrC phases. This behavior is quite different from what was found in the Si–Ti–C–O and Si–Al–C–O systems and thus it seemed very interesting in this discussion to compare the crystallization processes of the various systems.

The polycarbosilane is known to crystallize as the SiC 3C polytype above 1200°C, with some free carbon trapped inside the material.[18] The Ti-modified PC pyrolyzed at 1500°C gives a mixture of two crystalline phases SiC 3C and TiC, but in this case, no crystalline TiO_2 phase seems to be formed during the pyrolysis process. The mechanism for the formation of the TiC phase was investigated.[11–13] Small TiC particles are formed at low temperature (≅800°C) from the reaction between alkoxide-derived TiO_2 clusters and decomposition products of PC chains. This also leads to the formation of Si–O bonds. At high temperature, the growth of SiC 3C and TiC microcrystals is observed. No free carbon is present in the final material, due to the carbothermal reduction between the Si–O bonds and the carbon phase. The behavior of the Si–Al–C–O system is completely different:[14] the hexagonal polytype, SiC 2H polytype is formed at

1500°C, due certainly to the presence of isostructural aluminum oxycarbide, Al_2OC, which is known to form a solid solution with this particular polytype.

In the present study, it has been shown that ZrO_2 crystallites are intermediates during the crystallization process. The crystalline zirconium carbide phase is formed at high temperature above 1400°C. A possible mechanism is the reaction between the ZrO_2 and SiC phases with the formation of gaseous SiO. Another mechanism could be the carbothermal reduction of ZrO_2 with the carbon phase; however, free carbon is still present in the material fired at 1500°C. The silicon carbide polytype that is crystallizing is the cubic one (3C), as for the pure PC and the Ti-modified PC systems. The ^{29}Si MAS–NMR patterns for the three systems are quite similar, with a main peak around -16 ppm (Fig. 6). This value was found for SiC 3C monocrystals. However, a broader peak around -18 ppm has been reported for crystalline powdered samples.[19] This apparent discrepancy has recently been addressed in the literature.[20] It seems that the presence of a sharp peak at -16 ppm reflects a more ordered phase, while a broader peak around -18 ppm seems characteristic of the presence of defects in the sample such as stacking faults. This paper also shows that small amounts of α-polytypes are usually present together with the well-ordered 3C phase. Therefore, in these polycarbosilane-derived materials, the NMR spectra showing a sharp peak centered on -16 ppm and components due to some α-polytypes are in agreement with the presence of a well-ordered 3C phase. A comparison between the linewidth of the NMR peaks of the PC and PZC samples fired at 1500°C clearly shows a better order around the Si atoms in the PZC sample, in agreement also with sharper peaks in the XRD pattern. These features have already been pointed out for the SiC/TiC system.

Acknowledgements

The authors would like to greatly acknowledge Prof. J. D. Mackenzie (University of California, Los Angeles) who introduced them to the field of carbides prepared by the polymeric route. They would like also to thank NATO for financial support.

References

1. Wynne, K. J. & Rice, R. W., Ceramics via polymer pyrolysis. *Ann. Rev. Mater. Sci.*, **14** (1984) 297–334.
2. Pouskouleli, G., Metallorganic compounds as preceramic materials. I. Non-oxide ceramics. *Ceramics International*, **15** (1989) 213–29.
3. Yajima, S., Hayashi, J., Omori, M. & Okamura, K., Development of a silicon carbide fiber with high tensile strength. *Nature*, **261** (1976) 683–5.
4. Seyferth, D., Wiseman, G. & Prud'homme, C., A liquid silazane precursor to silicon nitride. *J. Amer. Ceram. Soc.*, **66** (1983) C-13–C-14.
5. Bender, B. A., Rice, R. W. & Span, G. R., Evaluation of potential BN polymer precursors. *Ceram. Eng. Sci. Proc.*, **6** (1985) 1171–83.
6. Narula, C. K., Paine, R. T. & Scaeffer, R., Precursors to boron–nitrogen macromolecules and ceramics. In *Better Ceramics Through Chemistry II, Mat. Res. Soc. Symp. Proc. 73*, ed. C. J. Brinker, D. E. Clark & D. R. Ulrich, Pittsburgh, PA, 1986, pp. 383–8.
7. Interrante, L. V., Carpenter II, L. E., Whitmarsh, C. & Lee, W., Studies of organometallic precursors to aluminum nitride. In *Better Ceramics Through Chemistry II, Mat. Res. Soc. Symp. Proc. 73*, ed. C. J. Brinker, D. E. Clark & D. R. Ulrich, Pittsburgh, PA, 1986, pp. 359–66.
8. Walker, B. E., Rice, R. W., Becher, B. A. & Coblenz, W. S., Preparation and properties of monolithic and composites ceramics produced by polymer pyrolysis. *Amer. Ceram. Soc. Bull.*, **62** (1983) 916–23.
9. Yajima, S., Iwai, T., Yamamura, T., Okamura, K. & Hasegawa, Y., Synthesis of polytitanocarbosilane and its conversion into inorganic compounds. *J. Mater. Sci.*, **16** (1981) 1349–55.
10. Yamamura, T., Ishikawa, T., Shibuya, M., Hisayuki, T. & Okamura, K., Development of a new continuous Si–Ti–C–O fibre using an organometallic polymer precursor. *J. Mater. Sci.*, **23** (1988) 2589–94.
11. Babonneau, F., Sorarù, G. D. & Mackenzie, J. D., ^{29}Si MAS–NMR investigation of the conversion process of a polytitanocarbosilane into SiC/TiC ceramics. *J. Mater. Sci.*, **25** (1990) 3664–70.
12. Sorarù, G. D., Glisenti, A., Granozzi, G., Babonneau, F. & Mackenzie, J. D., The pyrolysis process of a polytitanocarbosilane into SiC/TiC ceramics: an XPS study. *J. Mater. Res.*, **5** (1990) 1958–62.
13. Babonneau, F., Barré, P., Livage, J. & Verdaguer, M., Spectroscopic characterization of a pre-ceramic polymer for SiC/TiC system. In *Better Ceramics through Chemistry IV*, eds B. J. J. Zelinski, C. J. Brinker, D. E. Clark & D. R. Ulrich, *Mater. Res. Soc. Symp. Proc. 180*, Pittsburgh, PA, 1990, pp. 1035–40.
14. Babonneau, F., Sorarù, G. D., Thorne, K. & Mackenzie, J. D., Si–Al–C–O ceramic systems via polymeric route. *J. Am. Ceram. Soc.* (in press).
15. Bradley, D. C. & Carter, D. G., Metal oxide alkoxide polymers. Part 1, The hydrolysis of some primary alkoxides of zirconium. *Can. J. Chem.*, **39** (1961) 1434–43.
16. Yajima, S., Hasegawa, Y., Hayashi, J. & Iimura, M., Synthesis of continuous silicon carbide fibre with high tensile strength and high Young's modulus. Part 1: Synthesis of polycarbosilane as precursor. *J. Mater. Sci.*, **13** (1978) 2569–76.
17. Babonneau, F., Livage, J., Sorarù, G. D., Carturan, G. & Mackenzie, J. D., SiC/TiC ceramics via polymer route: A structural investigation. *New J. Chem.*, **14** (1990) 539–44.
18. Hasegawa, Y. & Okamura, K., Synthesis of continuous silicon carbide fibre. Part 3. Pyrolysis process of polycarbosilane and structure of the products. *J. Mater. Sci.*, **18** (1983) 3633–48.
19. Guth, J. R. & Petuskey, W. T., Silicon-29 magic angle sample spinning nuclear magnetic resonance characterization of SiC polytypes. *J. Phys. Chem.*, **91** (1987) 5361–4.
20. Carduner, K. R., Shinozaki, S. S., Rokosz, M. J., Peters, C. R. & Whalen, T. J., Characterization of β-silicon carbide by silicon-29 solid state NMR, transmission electron microscopy, and powder X-ray diffraction. *J. Am. Ceram. Soc.*, **73** (1990) 2281–6.