

Influence of Microstructural Changes on the Oxidation Resistance of Silicon Carbonitrides Derived from a Polyvinylsilazane

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Abstract

The behaviour of silicon carbonitrides derived from a polyvinylsilazane (ViSiHNNH)_n and obtained under different conditions of pyrolysis is investigated in oxidizing atmospheres. Various experimental techniques (TGA, MS, microprobe and XRD) were used to study the degradation of this ceramic product. The microstructural changes and the formation of porosity at high temperature are thought to modify the oxidation mechanisms. In the same way, higher temperature and longer duration of pyrolysis allow the organization of carbon crystallites which are readily oxidized. The combustion of the carbon (CO/CO₂ departure) is followed by the oxidation of the silicon carbonitride (CO, CO₂, N₂ and NO_x departure).

Es wurde das Verhalten von Silizium-Karbonitriden, die unter verschiedenen Pyrolyse-Bedingungen aus Polyvinylsilazanen (ViSiHNNH)_n hergestellt wurden, in oxidierenden Atmosphären untersucht. Um den Zerfall dieser keramischen Produkte zu untersuchen, wurden verschiedene experimentelle Methoden angewendet (TGA, MS, Mikrosonde, Röntgenbeugung). Es wird angenommen, daß die Gefüge- und die Porositätsentwicklung bei hohen Temperaturen die Oxidationsmechanismen verändern. Ebenso führen hohe Temperaturen und lange Pyrolysezeiten zu einer bevorzugten Koaleszenz von Kohlenstoffkristallen, die leichter oxidieren. Auf die Verbrennung des Kohlenstoffs (CO/CO₂-Entwicklung) folgt die Oxidation des Silizium Karbonitrids (Entwicklung von CO, CO₂, N₂ und NO_x).

Le comportement de carbonitrides de silicium obtenus par pyrolyse du polyvinylsilazane (ViSiHNNH)_n est étudié en atmosphères oxydantes. La dégradation de ces produits céramique a été suivie à l'aide de diverses techniques expérimentales (ATG, SM, microsonde,

DRX). Les évolutions microstructurales et la formation de porosité à haute température sont susceptibles de modifier les mécanismes d'oxydation. De même, les températures élevées et les longues durées de traitement favorisent la coalescence des cristallites de carbone dont l'oxydation est plus facile. La combustion de ce carbone (départ de CO/CO₂) est suivie de l'oxydation du carbonitride de silicium (départ de CO/CO₂/N₂/NO_x).

1 Introduction

The impregnation of a fibrous texture with a liquid precursor converted into a ceramic by pyrolysis is a promising process for the fabrication of composites. During the last few years, several studies have been devoted to the synthesis of precursors and their transformation at high temperature into ceramic residues.^{1–18} These works have been developed mainly in order to produce high performance fibers.

The conversion of an organometallic precursor into a ceramic depends on different parameters such as the molecular structure of the precursor or the pyrolysis conditions (temperature, duration, atmosphere). It leads to a poorly organized material whose microtexture evolves with the temperature.^{12,16,19,20} In order to inhibit the structural reorganization and to preserve an amorphous state until the temperature reaches 1400–1500°C, Si/C,¹⁵ Si/C/N,^{12,21} Si/N,⁶ Si/C/N/O,^{22–25} Si/Ti/C/O^{26,27} systems have been investigated. Thus, the incorporation of carbon in the system Si/N allows the modification of the kinetics of crystallization in Si₃N₄. In return, if the composition is not controlled, the presence of free carbon influences the oxidation behaviour of the ceramic product.^{10,28} This work is devoted to the study of the degradation mechanisms in oxidizing atmospheres of silicon carbonitrides obtained from the pyrolysis of a polyvinylsilazane.

2 Material and Experimental Procedure

The synthesis and the structural analysis of the polyvinylsilazane used are detailed elsewhere.^{3,4} This precursor was prepared by ammonolysis of dichlorovinylsilane in toluene. The cross-linking of the polyvinylsilazane is achieved by heating in toluene at 110°C. After evaporation of the solvent, the precursor obtained is a viscous liquid. The polymer is then heated to 1200–1400°C in flowing nitrogen (2 litres/h, quality N48). During the pyrolysis H₂ and hydrocarbons (CH₄, C₂H₄) were released. Elemental analysis gives the following composition: SiN_{0.98}C_{1.47}O_{0.06}H_{0.06}. The determined percentage of carbon content, in a 'free' carbon phase, is near 24.5 wt%, based on the assumption that oxygen, nitrogen and carbon are bonded to silicon as binary SiO₂, Si₃N₄ and SiC species and that the remaining carbon is a 'free' carbon phase. Currently, the hydrogen atoms are usually neglected.

NMR studies²⁹ of the amorphous silicon carbonitride obtained at 1400°C revealed that the environments of silicon atoms are mixed tetrahedra SiN_xC_{4-x} (x = 0 to 4). Excess carbon is present as graphite (free carbon). The crystallization of the pyrolysate in Si₃N₄ and SiC was slow. The residues obtained after pyrolysis with a low heating rate (150°C/h) were compact and microcracked. Oxidation experiments were performed on either powdered samples ($\phi < 40 \mu\text{m}$) or cubic compacts (4 × 4 × 4 mm³) by means of thermogravimetry analysis (B60 Setaram, Ugine-Eyraud System) and mass spectrometry (Quadrex 200, Leybold Heraeus) (70 eV, electron impact) in flowing 2% O₂/He mixture. The oxidized products were examined and analysed by microprobe (Camebax, Microbeam) and XRD (CuK_α) (PW 1130, Philips).

3 Oxidation Kinetics

3.1 Linear temperature-programmed oxidation

The oxidation in air of the pyrolysates at the heating rate of 12°C/min starts in the 550–600°C temperature range, and proceeds with several stages (Fig. 1). At first, a weight loss is observed between 550 and 1000°C, which is more important as the temperature of the initial pyrolysis treatment increases.

During the second stage, a weight gain appears, more pronounced when the pyrolysates are treated at 1400°C. In the third domain, the oxidation rate diminishes and finally tends to stabilize.

The products obtained at 1400°C with varying thermal cycles exhibit a similar oxidation behaviour. A strong affinity of silicon carbonitride residues for oxygen is observed for long initial thermal cycle (low

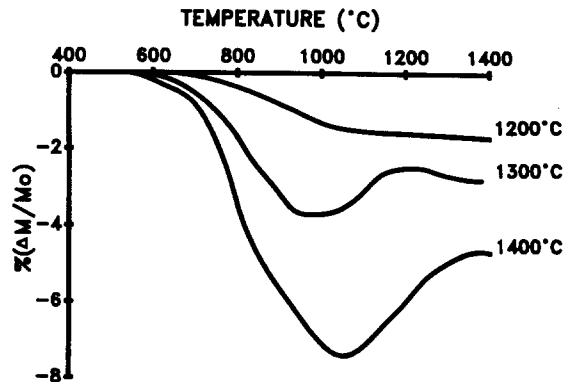


Fig. 1. TGA profiles in air, of powdered samples pyrolysed under N₂ at various temperatures.

heating rate, holding time—see Fig. 2). The same observations have already been mentioned for pyrolysates obtained from the octamethylcyclotetrasilazane (OMCTS).²⁸

3.2 Isothermal oxidation

Two silicon carbonitrides were particularly studied (1200°C, 1 h and 1400°C, 24 h) as either monolithic or powdered samples in order to develop the oxidation stages.

3.2.1 Powdered silicon carbonitride (1200°C, 1 h)

Whatever the oxidation temperature (Fig. 3), the reaction rate decreases versus time. The weight loss increases with the oxidation temperature until

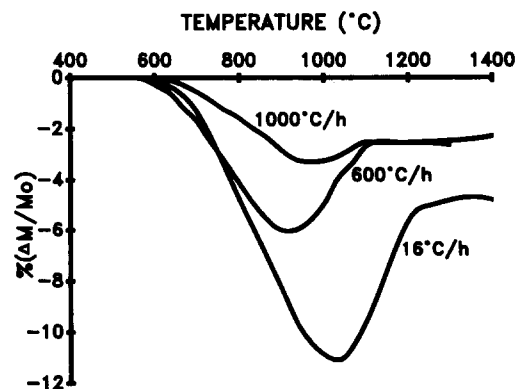


Fig. 2. Influence of the heating rate during pyrolysis on the variation of the relative mass $\Delta m/m_0$ in air.

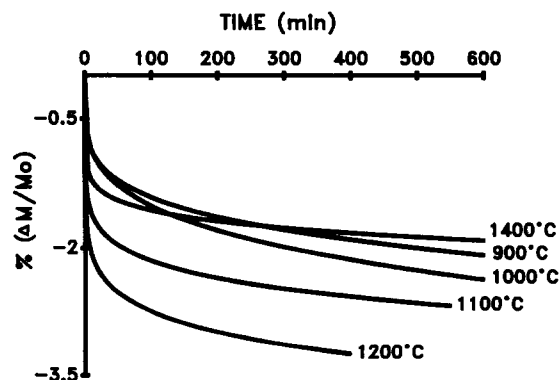


Fig. 3. Isothermal oxidation in air between 900°C and 1400°C of powdered product (1200°C, 1 h, N₂).

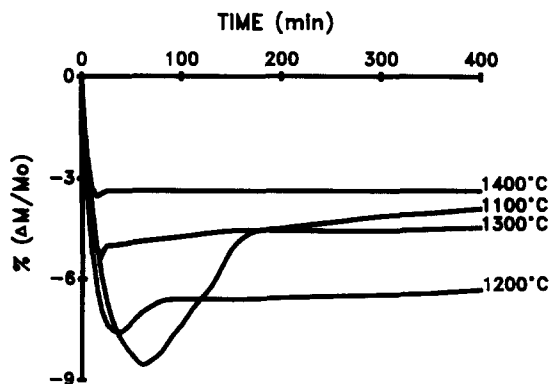


Fig. 4. Isothermal oxidation in air of powdered product (1400°C, 24 h, N₂).

1200°C. In contrast, at 1400°C, the lowest weight loss is registered. It is worth noting that at any time the weight change is negative.

3.2.2 Powdered silicon carbonitride 1400°C, 24 h

Isothermal curves (Fig. 4) consist of three stages whose respective extents change with the oxidation temperature. During the first step, the weight loss is increased when the temperature is low ($T_{ox} = 1200^\circ\text{C}$).

A similar observation can be noted for the weight gain in the second stage. The last stage is characterized by the inhibition of the reaction which occurs earlier as the temperature rises.

3.2.3 Monolithic silicon carbonitrides

The monolithic pyrolysates are hardly oxidizable above 1100°C and the weight loss is very low. For the oxidation temperature of 700°C, the behaviour in oxygen (Fig. 5(a)–(c)) strongly depends on the pyrolysis conditions.

A 1200°C, 1 h treatment leads to a ceramic residue which is poorly reactive. The same behaviour is also observed for the 1400°C, 1 h treatment. In contrast, for a longer treatment (1400°C, 24 h) the pyrolysate reacts with oxygen. As will be described hereafter, this behaviour is due to the combustion of free carbon, followed by the oxidation of the silicon carbonitride which occurs in both different temperature ranges and kinetics.

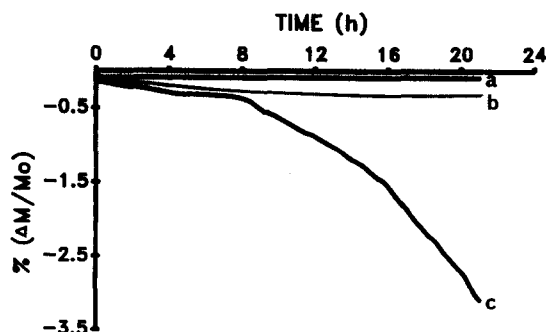


Fig. 5. Isothermal oxidation in air at 700°C of monolithic products pyrolysed at a, 1200°C, 1 h, N₂; b, 1400°C, 1 h, N₂; c, 1400°C, 24 h, N₂.

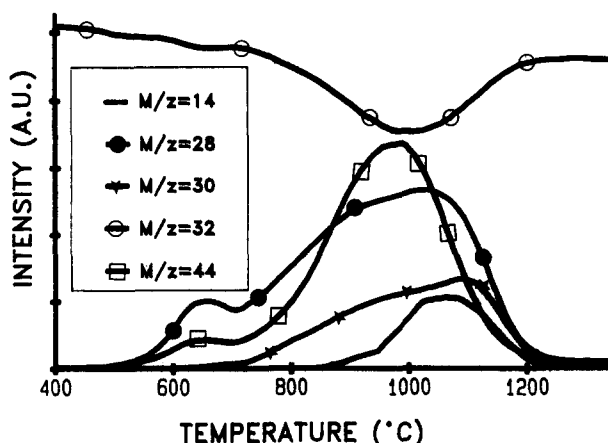


Fig. 6. Gas analysis by mass spectrometry of the pyrolysis residue oxidized in 20% O₂/He mixture.

3.2.4 Gas analysis by mass spectrometry

Gaseous products evolved during the oxidation were analysed by mass spectrometry.

As shown in Fig. 6, two peaks, for CO ($M/z = 28$) and for CO₂ ($M/z = 44$), appear as the temperature increases. In parallel, the intensity of the signal $M/z = 32$ decreases, accounting for an oxygen consumption.

The first peak begins as soon as 500°C is reached and corresponds to the combustion of free carbon. The second one, starting from 700°C, is accompanied by a release of CO₂ ($M/z = 44$), CO and N₂ ($M/z = 28$). The departure of nitrogen being confirmed by the signal at $M/z = 14$ assigned to N₂⁺. As well, a signal at $M/z = 30$ appears and is attributed to NO. Similar observations have been already reported.²⁸

XRD patterns of pyrolysates being oxidized above 1100°C show the presence of silica (α -cristobalite) on the surface of the samples.

For further information, the monolithic samples obtained after oxidation at 700°C were analysed using a microprobe and their morphology examined by SEM. On the micrographs (Fig. 7), the surface of the polished samples exhibits some heterogeneities. Nodules appear, in particular when the pyrolysis treatment is long. These nodules have a composition near Si₃N₄.

The back-scattered electrons technique allows the changes in the composition induced during the oxidation to be revealed. The two kinds of samples (1200°C, 1 h; 1400°C, 24 h) differ considerably in their oxidation behaviour.

On Fig. 8(a) and (b) some bright areas of irregular extent can be seen. These surfaces correspond to oxidized domains, as confirmed by the elemental distribution of oxygen (Fig. 8(c)). These observations indicate that the oxidation reaction front does not always start from the sample surface, but moves in depth along a preferential direction and sometimes

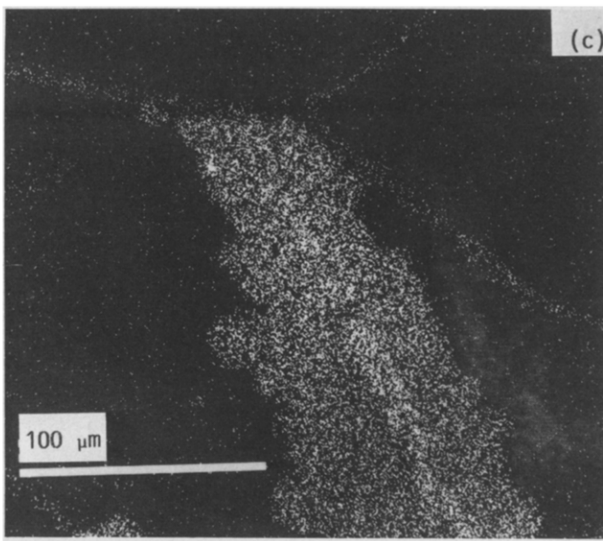
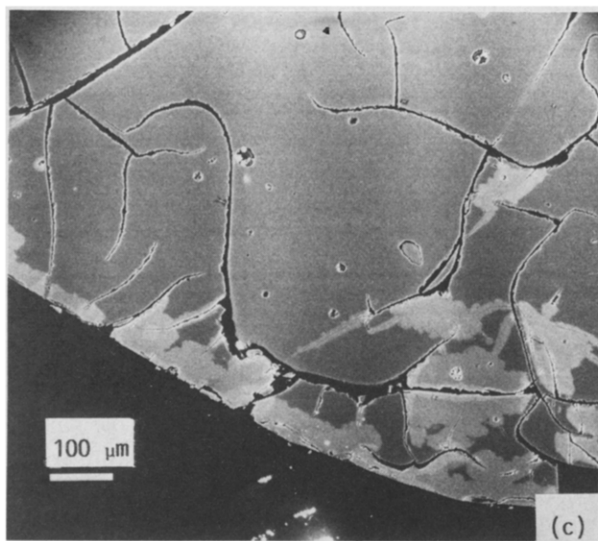
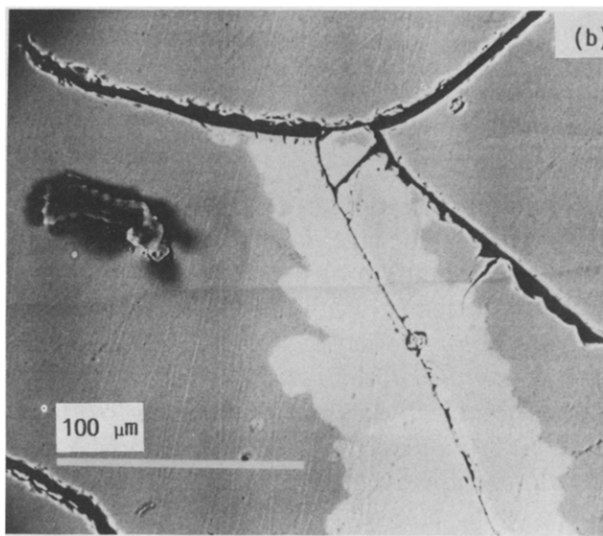
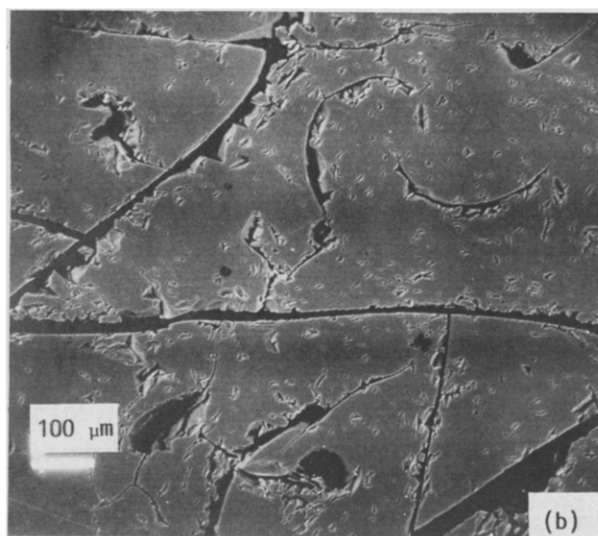
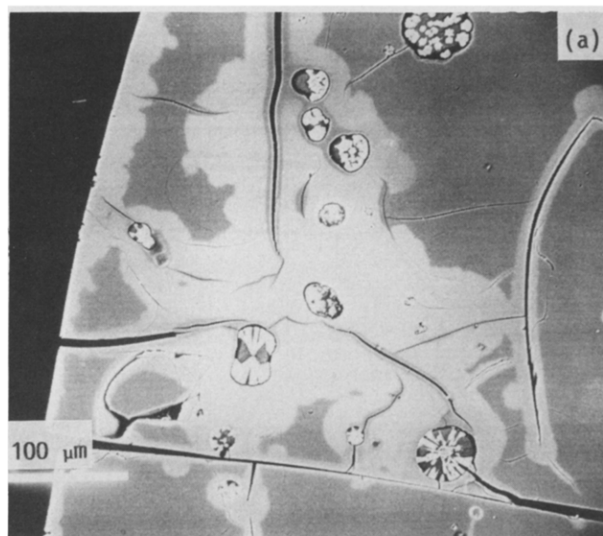
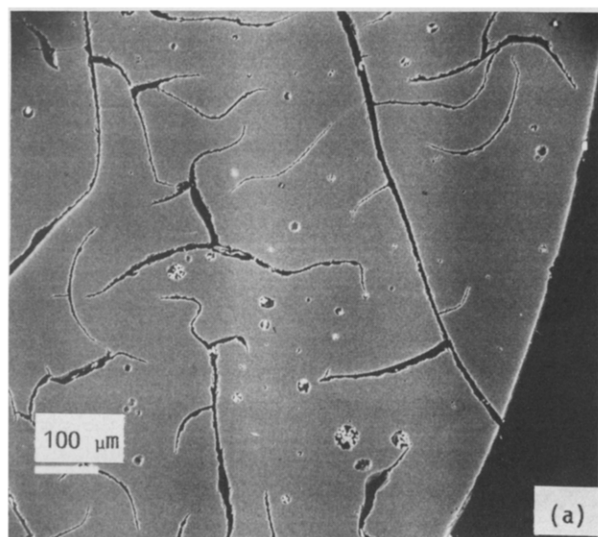


Fig. 7. Back-scattered electron image of the surface of silicon carbonitride samples: (a) Non-oxidized; (b) 1200°C, 1 h, N₂, oxidized at 700°C in air; (c) 1400°C, 24 h, N₂, oxidized at 700°C in air.

Fig. 8. Back-scattered electron image of the surface: (a) and (b) 1400°C, 24 h, N₂, oxidized at 700°C in air; (c) X-ray map of oxygen on sample in (b).

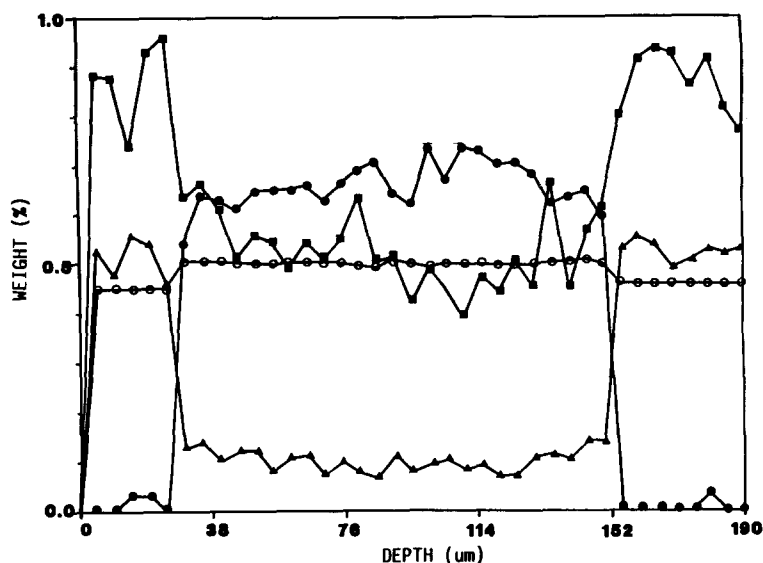


Fig. 9. Concentration profiles of elements (C, O, N, Si) in product shown in Fig. 8(b). Full scale units: ▲, C, 50%; ●, O, 50%; ■, N, 20%; ○, Si, 100%.

reaches the middle of the specimen for the material previously treated at 1400°C, 24 h.

Dark surfaces, which have the same composition as the nonoxidized product are widely predominant. Concentration profiles have been registered and several regions analysed. From typical results (Fig. 9), it can be noted that the oxygen content increases sharply from dark to bright areas. In parallel, the carbon content decreases more rapidly than the nitrogen content. However, the changes in composition are low for oxidized regions.

4 Discussion

For pyrolysis products derived from polyvinylsilazanes, NMR studies by Gerardin *et al.*²⁹ give some information about silicon environments. Mixed sites $\text{SiC}_x\text{N}_{4-x}$ ($x=1$ to 4) form the carbonitride phase.

During oxidation, oxygen substitutes for carbon and nitrogen. Taking account of their respective valencies and atomic weight, oxygen fixation is accompanied by a weight gain. Only the combustion of free carbon induces a weight loss with the departure of CO and CO₂ gases. The selective combustion of the total free carbon content corresponds to a 24.5% weight loss, whereas the complete oxidation of the product would lead to 0.6% weight loss. This result shows that for a fixed temperature, a weight loss means that the carbon is accessible to oxygen and that the organization state of the microstructure is developed. At first, the carbon combustion is the major process, then NO evolution indicates that the mixed tetrahedra $\text{SiC}_x\text{N}_{4-x}$ are oxidized. Temperature-programmed oxidation and isothermal kinetics show that the weight gain increases with the advance of the

reaction in the first domain. This phenomenon can be explained by the creation of porosity which enhances the oxidation of the carbonitride. A high-temperature treatment may facilitate the separation of larger graphitic crystallites between the other phases (SiC, Si₃N₄, SiCN). Furthermore, the long heat treatment induces microstructural changes and the opening of carbon chains as confirmed by TEM.²⁴ These phenomena explain the formation of microcracks and porosity. It is worth noting that the oxidation of silicon carbonitride products depends on the evolution of their microstructure after pyrolysis treatment. Moreover, experimental results on monolithic samples indicate that during pyrolysis, gas evolution induces stresses and heterogeneities. This behaviour is related to the quantity and the nature of the initial precursor.

The different oxidation resistance of the two products may be explained by the presence of water vapour, even in low proportions, produced from residual hydrogen in the pyrolysate (1200°C, 1 h). Water vapour is known to enhance the oxidation of SiC, Si₃N₄ and probably SiCN phases.³⁰⁻³² The simultaneous oxidation of these phases with the combustion of poorly organized carbon aggregates embedded in the carbonitride phase could rapidly lead to silica. The diffusion through the silica could reduce the oxidant transport, and thus the reaction rate decreases. In contrast, by increasing the duration and temperature of the treatment (1400°C, 24 h), the reactivity of these ceramic products towards oxygen swiftly increases. Carbon combustion stage becomes clearly separated, giving evidence for a better reorganization of carbon in a structure called turbostratic.²⁴ At 700°C, the oxidation is not complete, as confirmed by microprobe analysis; 6 wt% carbon and 13 wt% nitrogen remain in the residues. Two possible explanations could be

proposed: (i) as the microstructural changes are not achieved, microdomains are not accessible to oxygen; (ii) Si_3N_4 and SiC crystallites are not oxidized at this temperature.

5 Conclusion

A polyvinylsilazane submitted to cross-linking treatment before pyrolysis leads to compact residues with a high carbon content. In an oxidizing environment the behaviour of the material depends more strongly on the reorganization of free carbon than its content. These structural changes are directly in relation to the pyrolysis conditions. Amorphous products (1200°C , 1400°C , 1 h, N_2) exhibit a high oxidation resistance. These results show that this precursor would be promising for a matrix or binder in ceramic composites.

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References

- Bacque, E., Nouvelles approches dans le domaine des précurseurs organosiliciés de carbure et carbonitride de silicium: synthèses originales et études fondamentales. PhD Thesis, Université de Bordeaux I, France, 7 July 1987.
- Poupeau, J. J., Abbe, D. & Jamet, J., Gas analysis during the pyrolysis of carborosilane. *Mat. Sci. Res.*, **17** (1984) 287.
- Choong Kwet Yive, N. S., Corriu, R., Leclercq, D., Mutin, H. & Vioux, A., Polyvinylsilazane precursors to silicon carbonitride. *New J. Chem.*, **15** (1991) 85.
- Lavedrine, A., Bahloul, D., Goursat, P., Choong Kwet Yive, N. S., Corriu, R., Leclercq, D., Mutin, H. & Vioux, A., Pyrolysis of polyvinylsilazane precursors to silicon carbonitride. *J. Eur. Ceram. Soc.*, **8** (1991) 221.
- Verbeek, W., Production of shaped articles of homogeneous mixtures of silicon carbide and nitride. US patent 3853567, 1974.
- Seyferth, D., Wiseman, G. H. & Prud'Homme, C., A liquid silazane precursor to silicon nitride. *J. Am. Ceram. Soc.*, **66** (1983) C-13.
- Gaul, J. H., Silazane polymers from disilazanes and organochlorosilanes and their use. US patent 4312970, 1982.
- Cannady, J. P., Silicon nitride containing ceramics. US patent 4535007, 1985.
- Cannady, J. P., Silicon nitride containing ceramic materials prepared by pyrolysis of hydridosilazane polymer from $(\text{R}_3\text{Si})_2\text{NH}$ and HSiCl_3 . US patent 4543344, 1985.
- Burns, G. T., Angelotti, T. P., Hanneman, L. F., Chandra, G. & Moore, J. A., Alkyl- and arylsilsesquiazanes: effect of the R group on polymer degradation and ceramic char composition. *J. Mat. Sci.*, **22** (1987) 2609.
- Wills, R., Markle, R. A. & Mukherjee, S. P., Siloxanes, silanes and silazanes in the preparation of ceramics and glasses. *Am. Ceram. Soc. Bull.*, **62** (1983) 904.
- Legrow, G. E., Lim, T. F., Lipowitz, J. & Reaoch, R. S., Ceramics from hydridopolysilazanes. *Am. Ceram. Soc. Bull.*, **66** (1987) 363.
- Walker, B. E., Jr, Rice, R. W., Becher, P. F., Bender, B. A. & Coblenz, W. S., Preparation and properties of monolithic and composite ceramics produced by polymer pyrolysis. *Am. Ceram. Soc. Bull.*, **62** (1983) 916.
- Schilling, C. L., Jr, Wesson, J. P. & Williams, T. C., Polycarbosilane precursors for silicon carbide. *Am. Ceram. Soc. Bull.*, **62** (1983) 912.
- Yagima, S., Okamura, K., Khayashi, J. & Homori, M., Synthesis of continuous SiC fibers with high tensile strength. *J. Am. Ceram. Soc.*, **59** (1975) 324.
- Blum, Y. D., Schwartz, K. B. & Laine, R. M., Pre-ceramic polymer pyrolysis. *J. Mat. Sci.*, **24** (1989) 1707.
- Schmidt, W. R., Interrante, L. V., Doremus, R. H., Trout, T. K., Marchetti, P. S. & Maciel, G. E., Pyrolysis chemistry of an organometallic precursor to silicon carbide. *Chem. Mat.*, **3** (1991) 257.
- Du Zuodong, Chen Jianhua & Han Tangzen, Studies on the polysilane consisting cyclodisilazane units in the main chain. *Chinese J. Polym. Sci.*, **1** (1989) 31.
- Laffen, C., Flanck, A. M., Lagarde, P. & Bouillon, E., Study of the polymer to ceramic evolution induced by pyrolysis of organic precursor. *Physica*, **B158** (1989) 229.
- Toreki, W., Botich, C. D., Sacks, M. D. & Morrone, A. A., Synthesis and applications of a vinylsilazane pre-ceramic polymer. *Ceram. Eng. Sci. Proc.*, **11** (1990) 1371.
- Penn, B. G., Ledbetter, F. E., Clemons, J. M. & Daniels, J. C., Preparation of silicon carbide-silicon nitride fibers by the controlled pyrolysis of polycarbosilazane precursors. *J. Appl. Polym. Sci.*, **27** (1982) 3751.
- Bouillon, E., Pyrolyse de précurseurs organosiliciés en vue de l'élaboration des fibres céramiques base SiC. PhD Thesis, Université de Bordeaux I, France, 20 April 1989.
- Colombier, C., Study of new polysilazane precursors to Si-C-N-O ceramics. In *Euro-Ceramics*, Vol. 1, ed. G. Dewith & R. A. Terpstra. Elsevier Applied Science, London, 1989.
- Delverdiere, O., Evolution thermique de céramiques issues de polymères à base Si, C, N, O, H. PhD Thesis, Université de Pau, France, 14 June 1991.
- Lavedrine, A., Etude de la décomposition thermique de polyvinylsilazanes: comportement à l'oxydation du carbonitride de silicium obtenu. PhD Thesis, Université de Limoges, France, 26 November 1991.
- Okamura, K., Sato, M. & Hasegawa, Y., Silicon nitride fibers and silicon oxynitride fibers obtained by the nitridation of polycarbosilane. *Ceram. Int.*, **13** (1987) 55.
- 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. Mat. Sci.*, **23** (1988) 2589.
- Bahloul, D., Pereira, M. & Goursat, P., Silicon carbonitride derived from an organometallic precursor: influence of the microstructure on the oxidation behaviour. *Ceram. Int.*, **18** (1992) 1.
- Gerardin, C., Taulelle, F. & Livage, J., Pyrolysis of a polyvinylsilazane, polymeric precursor for silicon carbonitride: structural investigation by ^1H , ^{13}C , ^{29}Si , ^{15}N nuclear magnetic resonance. *J. Chim. Phys.*, **89** (1992) 461.
- Jorgensen, P. J., Wadsworth, M. E. & Cutler, I. B., Oxidation of silicon carbide. *J. Am. Ceram. Soc.*, **42** (1959) 613.
- Maeda, M., Nakamura, K. & Ohkubo, T., Oxidation of silicon carbide in a wet atmosphere. *J. Mat. Sci.*, **29** (1988) 3933.
- Schliching, T., Oxygen transport through silica surface layers on silicon-containing ceramic materials. *High Temp. High Press.*, **14** (1982) 717.