Journal of the European Ceramic Society **15** (1995) 591–597
© 1995 Elsevier Science Limited
Printed in Great Britain. All rights reserved
0955-2219/95/$9.50

0955-2219(95)00012-7

Manufacture of Monolithic Ceramic Bodies from Polysilazane Precursor

M. F. Gonon,[a] G. Fantozzi,[b] M. Murat[b] & J. P. Disson[c]

[a]Ceramic Research Unit, University of Limerick, National Technological Park, Limerick, Ireland
[b]Institut National des Sciences Appliquées de Lyon, Groupe d'Etude de Métallurgie Physique et de Physique des Matériaux - URA CNRS 341, 20 avenue Albert Einstein, 69621 Villeurbanne cedex, France
[c]Elf Atochem, Centre de Recherche Rhône-Alpes, rue Henri Moissan, 69310 Pierre-Bénite, France

(Received 16 May 1994; revised version received and accepted 10 November 1994)

Abstract

A low temperature process for the manufacture of non-oxide monolithic ceramic bodies is presented. This process is based on the pyrolysis at temperatures between 1000 and 1400°C of the polysilazane precursor.

The different steps of the process are precisely described. The physical (porosity, density, crystalline phases) and mechanical properties (flexural strength, Young's modulus, toughness and hardness) of the bodies obtained are studied versus the maximum temperature of the pyrolysis. The high temperature oxidation resistance in air is also presented.

1 Introduction

Non-oxide monolithic ceramic bodies, (e.g. SiC, Si_3N_4...) generally result from powders sintering. Materials obtained by this process show interesting mechanical characteristics (e.g. 600–700 MPa for sintered Si_3N_4). However, the very high temperatures (1700°C–2500°C) required to densify ceramic bodies imply expensive energy costs. The homogenisation of the initial slurry (powder + additives) presents difficulties on what effects on the flaw distribution in the final ceramic.

Another way to obtain non-oxide ceramics is the use of organometallic precursors. Indeed, polycarbosilane and polysilazane which lead to SiC or Si_3N_4 derived ceramics, respectively, are frequently used for the manufacture of non-oxide matrix composites. However, only a few experiments have been performed on the elaboration of monolithic bodies from these products.

Such processes may present some interests. The temperatures relative to the precursor's pyrolysis are significantly lower (1000–1400°C) than those required for powder sintering (1700–2500°C). Moreover, powder sintering imposes the use of organic additives which have to be eliminated by heat treatment before sintering. In the present process, no additives are used, therefore very few impurities are present in the final ceramic.

ELF ATOCHEM[†] has recently developed the synthesis of the polysilazanes PYROFINE PV[‡] and PYROFINE PM.[1,2] Research performed on the manufacture of ceramic matrix composites from PYROFINE PV,[3,4] required the optimisation of the ceramic characteristics versus the pyrolysis parameters.[5] The study of mechanical properties needing dense samples, the following process has been developed.

2 The Polysilazane

The following information is more detailed in Refs. 1 and 2.

At room temperature the polysilazane is a highly viscous liquid. Its density is about 1 and its typical elemental composition is given in Table 1 (oxygen originates from the hydrazine used for the synthesis).

Its viscosity decreases with an increase in temperature up to 200°C (Table 2).

The structure of this polymer is cyclic and is shown in Fig. 1.

Upon heating up to 300°C under nitrogen, the opening of the vinyl groups allows the precursor cross-linking. The product obtained is solid, unmeltable and insoluble.

Above 300°C mineralization starts and changes the precursor into an amorphous ceramic. The typical elemental composition of the ceramic obtained after

---

[†] ELF ATOCHEM — Centre de Recherche Rhône-Alpes, rue Henri Moissan, 69310 Pierre-Bénite, France
[‡] PYROFINE PV registered trade mark of ELF ATOCHEM.

Table 1. Elemental composition of polysilazane

	Si	*C*	*N*	*O*	*H*
wt.%	31·5	37·2	20·3	3·2	7·8
at.%	8·2	22·7	10·5	1·4	57·2

Table 2. Variation of the viscosity versus temperature

Temperature	(°C)	50	100	150
Viscosity	(mPa.s)	1000	100	20

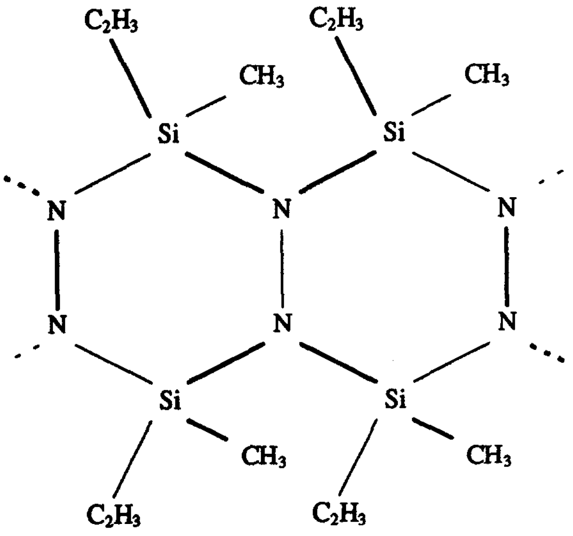

Fig. 1. Structure of the polysilazane.

Table 3. Elemental composition of the ceramic issued from presursor pyrolysis at 1000°C

	Si	*C*	*N*	*O*
at.%	30·0	34·7	27·1	8·2
wt.%	47·5	23·6	21·5	7·4

pyrolysis at 1000°C is given in Table 3. Its absolute density is 2·13 g/cm^3 (measured by He picnometry).

At 1000°C, the ceramic yield is 60–65 wt.%, depending on the heating-up rate used during the cross-linking.[2] The volumetric yield of the transformation is about 30%.

3 Manufacture of Monolithic Ceramic Samples

Due to the foaming of the precursor during pyrolysis,[2] conventional pyrolysis leads in the best case to a ceramic having about 1 g/cm^3 apparent density corresponding to more than 50% porosity.

Such samples cannot be used for the physical and mechanical characterisation of the ceramic, and a specific process has been developed to obtain relatively dense ceramic samples.

3.1 Principle

The basic idea of this process is first to manufacture a mixture of powder and precursor, press it and then pyrolyse it (Fig. 2).

The powder is obtained by heat treatment and milling of the precursor.

To reduce the viscosity of the precursor and to obtain a good homogeneity, toluene is added to the mixture following the ratio a volume toluene per volume precursor. The solvent is then evaporated at 60°C under 500 Pa for 2 h.

Finally the mixture is pressed in a die with a pressure of 150 MPa before proceeding to the pyrolysis.

3.2 Use of ceramic powder

For the first attempts the powder used was obtained by milling the ceramic residue issued from the precursor pyrolysis at 1000°C. The absolute density of this powder is 2·13 g/cm^3 (determined by He picnometry).

The powder alone, pressed under 150 MPa forms a green body having 60% of the absolute density. Therefore the mixture is manufacture in order to obtain a precursor/powder ratio of 40/60 in volume (12/88 wt.%) after toluene evaporation.

The green body obtained after moulding is pyrolysed following the temperature schedule given in Table 4.

The samples obtained have about 30% porosity (apparent density 1·5 g/cm^3) corresponding to the theoretical calculation (28%) based on the volume

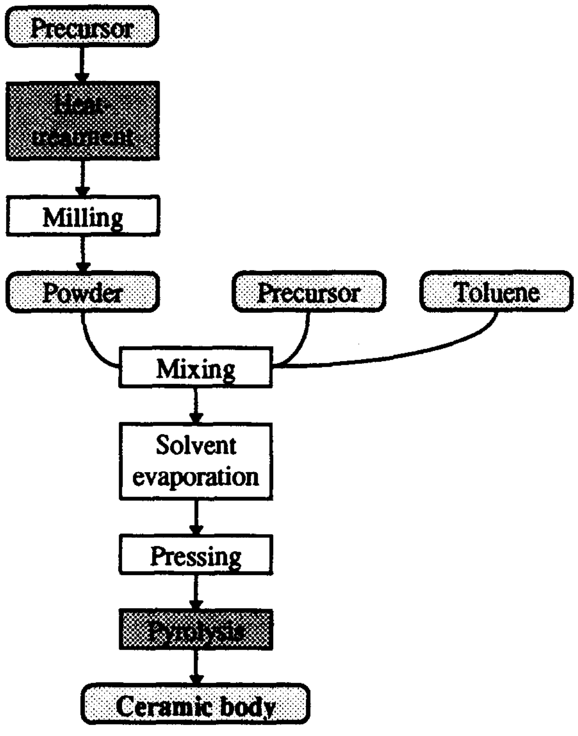

Fig. 2. Elaboration of monolithic ceramic bodies (first process).

Table 4. Pyrolysis temperature schedule

Heating rate	*Temperature*	*Holding time*
(°C/h)	(°C)	(h)
100	20–130	0
5	130–300	0
50	300–1000	4

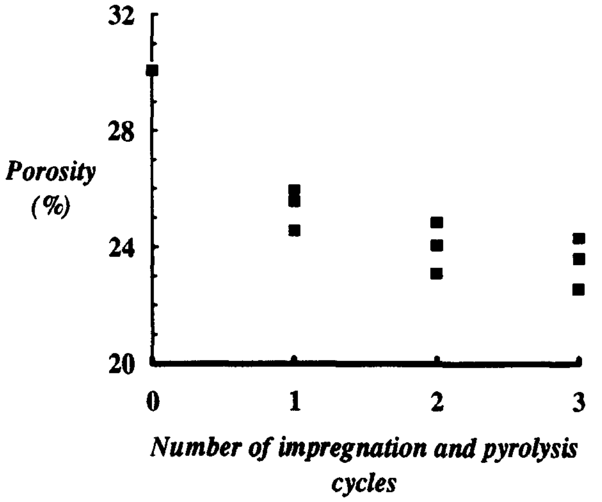

Fig. 3. Variation of porosity of the monoliths versus the number of impregnation and pyrolysis cycles.

ratio of the components, and the volume yield of the precursor to ceramic transformation (about 30 vol.%).

The porosity can be reduced by successive impregnation and pyrolysis cycles with the precursor. However, the larger part of the porosity is closed and a porosity lower than 20–25% cannot be achieved (Fig. 3).

On the other hand numerous cracks are present on the sample surface due to the difference of shrinkage between the precursor (about 70 vol.%) and the ceramic powder (no shrinkage).

To avoid these phenomena and to achieve a lower porosity, new experiments have been completed using a cross-linked precursor powder in place of the ceramic powder.

3.3 Use of cross-linked precursor powder

3.3.1 Theory

A cross-linked precursor powder results from heat treatment under nitrogen at 300°C of the polysilazane. After milling (mortar) the size of the powder grains is about 100–1400 μm in diameter (Fig. 4).

The absolute density of this powder is approx. 1·13 g/cm^3. After pyrolysis at 1000°C its ceramic yield is 72 wt.% corresponding to 38 vol.%.

The powder alone, pressed under 150 MPa, forms a green body having 70% of the absolute density. Assuming an apparent sample shrinkage during the pyrolysis equal to that of the precursor powder (about 62 vol.%), the porosity of the ceramic samples would be only 7–8%.

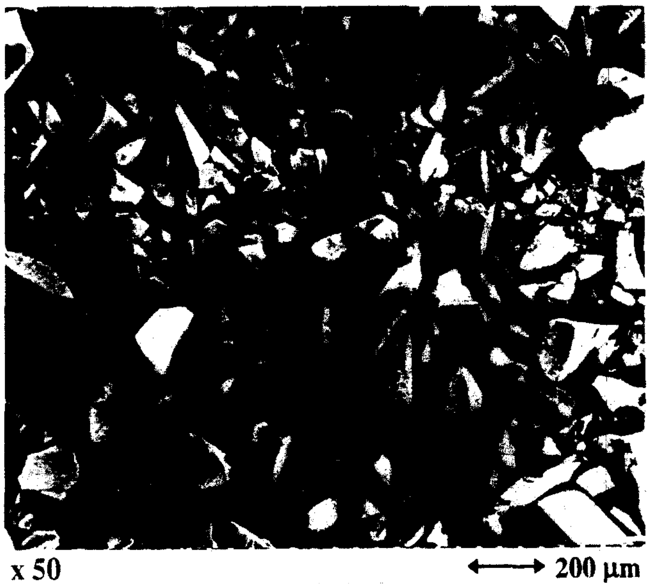

Fig. 4. SEM observation of the cross-linked precursor powder.

3.3.2 Experiment

(a) Manufacture of the initial mixture

The mixture is obtained following the same process as when using the ceramic powder (see 3.2).

The relative density of the powder in the sample (powder volume/apparent volume of the sample) depends on the precursor amount added (Fig. 5).

As this one remains below 22 wt.%, the relative density of the powder in the sample is equal to the green density of the powder (about 70 vol.%). The precursor fills the spaces separating the powder grains without disturbing their arrangement.

Above 22 wt.% the powder cannot be compacted properly and the relative density of the powder in the sample significantly decreases.

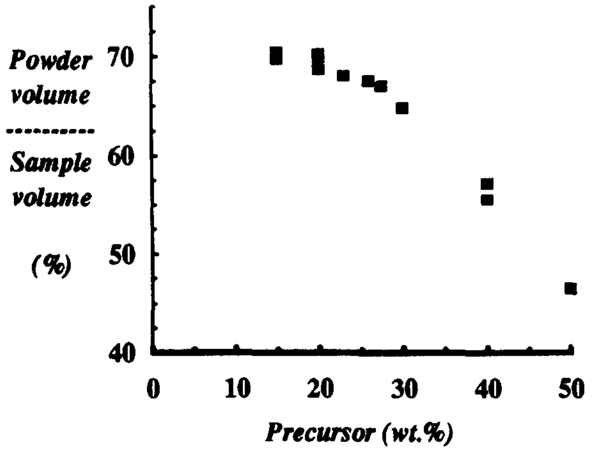

Fig. 5. Variation of the ratio powder volume/sample apparent volume versus the precursor amount added.

Table 5. Cross-linking temperature schedule

Heating rate	*Temperature*	*Holding time*
(°C/h)	(°C)	(h)
100	20–130	0
5	130–300	1

(b) Cross-linking

Using the optimal precursor/powder ratio previously determined, (22/78 wt.%), samples were pressed and cross-linked following the temperature schedule given in Table 5.

After heat treatment, an increase in the apparent volume of the samples is ascertained. This may be due to the precursor 'foaming'.[2] This phenomenon occurs as the precursor amount is higher than 15 wt.%. This value is significantly lower than that corresponding to a complete filling of the intergranular spaces (precursor/powder ratio = 27·5/72·5 wt.%, 30/70 vol.%).

(c) Pyrolysis

Using mixtures having various precursor/powder ratios, samples were pressed, cross-linked and then pyrolysed following the temperature schedule given in Table 4.

The shrinkage of the apparent volume of the sample after cross-linking and after pyrolysis is approximately 60 – 62%, as expected.

The lowest porosity measured is about 24% and corresponds to an initial precursor/powder ratio: 15/85 wt.% (Fig. 6).

This result is not as low as expected due to the apparent volume increase during the cross-linking as the precursor/powder ratio of the initial mixture is high. To avoid this problem and to obtain lower porosity a new step has been added to the process (Fig. 7).

A cross-linked precursor preform is manufactured by moulding and cross-linking the precursor + cross-linked precursor powder mixture. The precursor/powder ratio used is 5/95 wt.% in order to avoid the apparent volume increase of the samples during the cross-linking (see 3.3.2 (b)) and to favour open porosity.

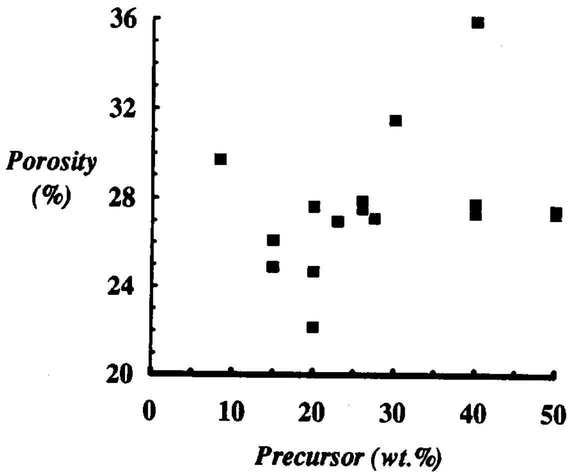

Fig. 6. Porosity of the ceramic monolith versus the initial precursor content.

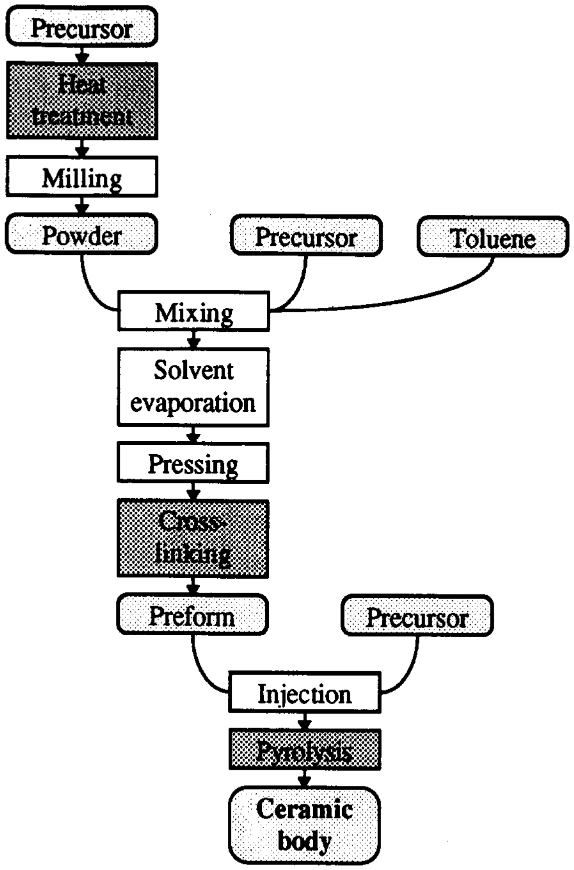

Fig. 7. Elaboration of monolithic ceramic bodies (second process).

The preform obtained after cross-linking is solid. The high porosity of this preform (about 27%) is filled by precursor impregnation. The preform is charged into a reactor (Fig. 8) and degassed under dynamic vacuum (500 Pa) at 150°C for 2 h.

The precursor, preheated at 150°C to reduce its viscosity, is then injected into the preform by means of the pressure gradient between the outside

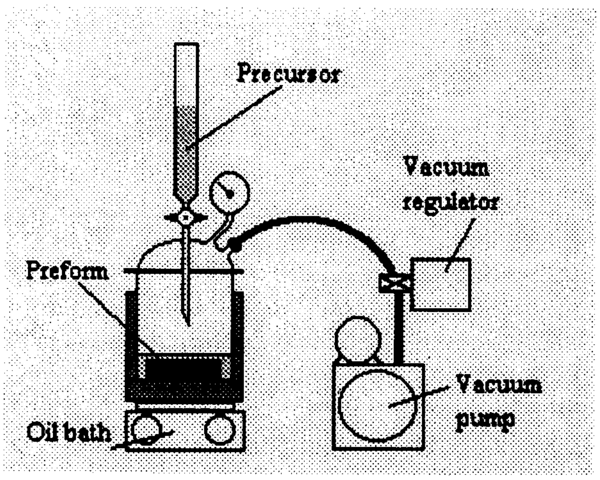

Fig. 8. Diagram of the device used for the precursor injection.

(Nitrogen atmospheric pressure) and the inside of the reactor. After injection the preform is soaked in the precursor for 2 h at 150°C under nitrogen before being removed and placed in the pyrolysis furnace.

The weighing of the performs after the precursor injection and before the pyrolysis indicates that 3–4% of the porosity is not filled. Therefore, the porosity of the monolith obtained after pyrolysis is about 12% instead of 8% as expected from the theoretical calculation.

4 Characterisation of the Monolith Bodies

Seven samples (45 × 40 × 10 mm^3 after pyrolysis) were manufactured using pyrolysis temperatures from 1000°C to 1600°C.

The large size of these samples imposed a very slow heating rate (10°C/h) above 300°C to avoid the crack formation during pyrolysis.

4.1 Porosity

After pyrolysis, the porosity of the monoliths was determined from the ratio between the apparent and absolute density (The absolute density was determined by He picnometry on samples after milling).

A minimum in porosity, about 10–11%, is observed for pyrolysis at 1400°C (Fig. 9).

4.2 Mechanical properties

Ten test bars (40 × 3·5 × 8 mm^3) were cut in each sample. Room temperature flexural strengths were measured in three-point bending on a Schenk RM-T 25 kN using a support span of 50 mm and a crosshead speed of 0·5 mm/min.

Young's modulus was determined from the load/displacement curves. The toughness was determined by the single edge notched beam technique (S.E.N.B.) with $a/w = 0{\cdot}5$ (a = initial crack length; w = thickness of the test bar).

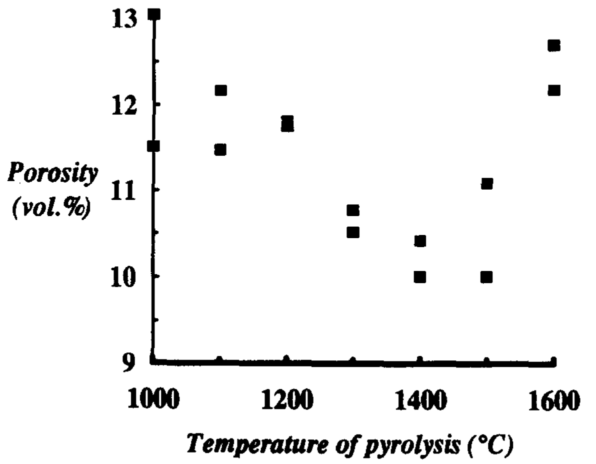

Fig. 9. Porosity of the monoliths versus the highest temperature of the pyrolysis.

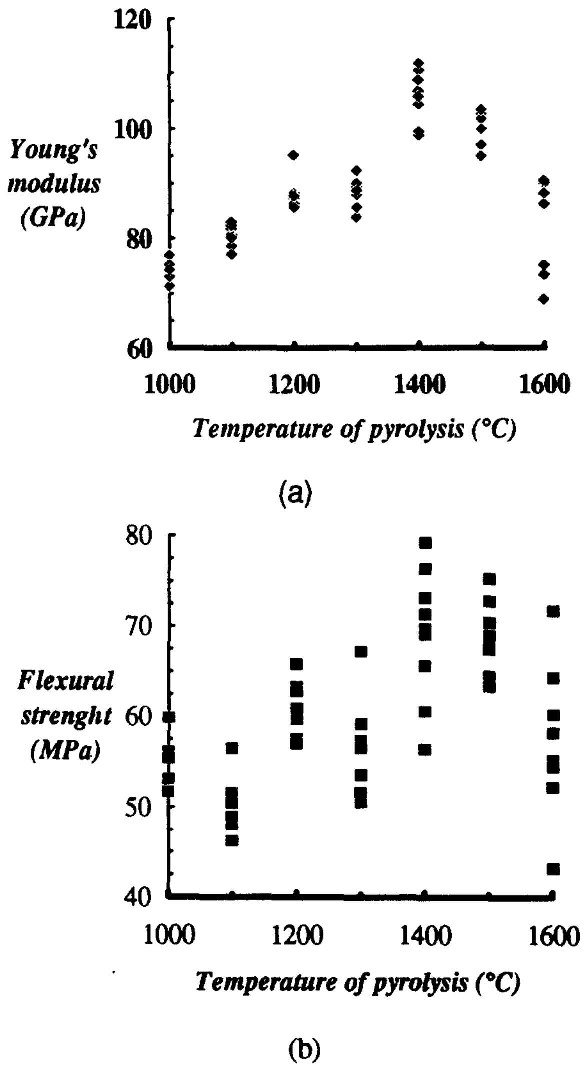

Fig. 10. Evolution of the flexural strength (a) and of the Young's modulus (b) versus the maximum of the pyrolysis.

Highest flexural strength and Young's modulus are observed after pyrolysis at 1400°C corresponding to the minimum in porosity (Figs. 10(a) and (b) and Table 6).

4.3 X-ray diffraction

After milling, the samples were characterised by X-ray diffraction.

Only weak diffractions of SiO_2 are detected on the monoliths pyrolysed at temperatures lower than 1400°C. This SiO_2 is probably polution originating from the milling process and does not belong to the ceramic itself.

On samples pyrolysed at 1500 and 1600°C the X-ray diffraction spectra exhibit signals corresponding to α SiC and α Si_3N_4.

The SEM observation shows the formation of whiskers in the porous volume and of a layer, looking like a skin, on the pore surface (Fig. 11).

This crystallisation may cause the decrease in mechanical properties observed for pyrolysis temperatures higher than 1400°C.

Table 6. Mechanical properties of the composites

Highest temp. *(°C)*	*Apparent density* *(g/cm³)*	*Absolute density* *(g/cm³)*	*Porosity* *(%)*	*Young's modulus* *(GPa)*	*3-point flexural strength* *(MPa)*	*Vickers hardness* *(MPa)*	*Toughness* K_{IC} *(MPa.√m)*
1000	1·87 ± 2	2·13	12	74 ± 3	56 ± 4	888 ± 37	3·33
1100	1·92 ± 3	2·18	12	80 ± 3	51 ± 5	927 ± 31	3·92
1200	2·01 ± 1	2·27	12	90 ± 4	62 ± 4	998 ± 44	4·26
1300	2·05 ± 2	2·31	11	89 ± 4	59 ± 8	955 ± 30	—
1400	2·12 ± 2	2·35	10	106 ± 6	68 ± 11	996 ± 29	—
1500	2·13 ± 2	2·38	11	99 ± 4	69 ± 6	970 ± 28	4·10
1600	2·12 ± 6	2·48	12	69 ± 22	52 ± 20	965 ± 20	—

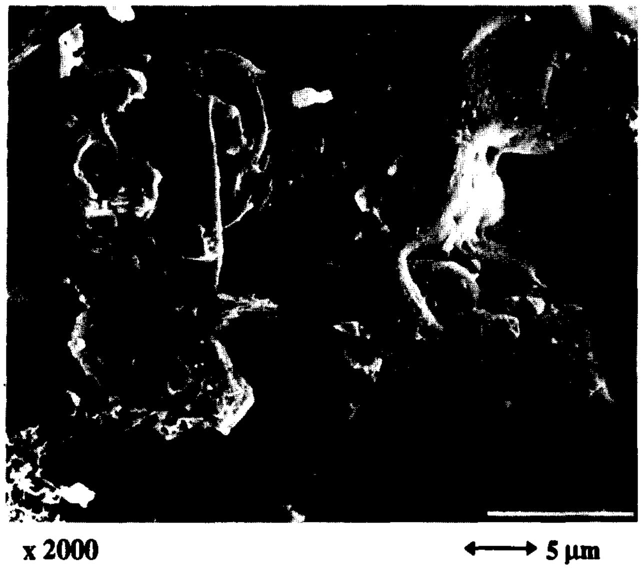

Fig. 11. SEM observation of the monoliths pyrolysed at 1600°C.

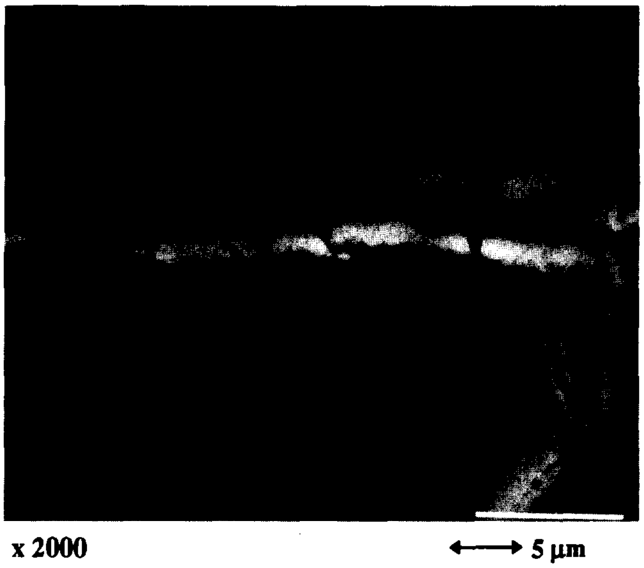

Fig. 13. SEM observation of the surface of the monoliths after 6 h in air at 1400°C.

4.4 Oxidation resistance

The study of the thermal oxidation behaviour by thermogravimetric analysis in air at 1000, 1200 and 1400°C (Fig. 12) shows the high resistance of the ceramic.

After 6 h, no weight deviation is observed at 1000°C and a very low and asymptotic increase is seen at 1200 and 1400°C (respectively + 0·17 wt.% and + 0·28 wt.%).

The SEM observation (Fig. 13) shows that the weight increase observed at 1200 and 1400°C corresponds to the formation of a coating, probably composed of SiO_2, on the sample surface. This coating slows down the oxidation reaction thereby explaining the asymptotic appearance of the TG curves.

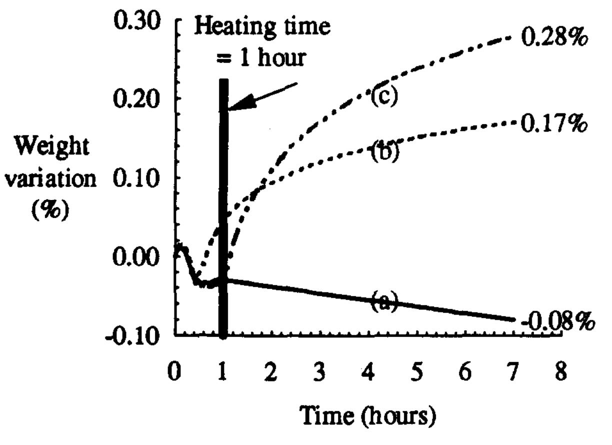

Fig. 12. TGA curves in air at 1000°C (a), 1200°C (b), 1400°C (c) on monoliths pyrolysed at 1000°C (a), 1400°C (b,c).

5 Conclusion

A new process route for ceramic bodies has been developed. Ceramic monoliths with less than 12% porosity can be obtained. As compared to ceramics obtained by sintering of powders, such values are high, but they are relatively good for a liquid precursor processing route. Moreover, the structure of the samples shows no apparent cracks.

The maximal flexural strengths measured in 3 point bending are approximately 70 MPa and Young's modulus 105 GPa. These results are low, but could possibly be improved by a decrease in the pore sizes. Such decrease could be obtained by the use of a cross-linked precursor powder having a lower grain size.

The maximum in mechanical properties is

obtained after pyrolysis at 1400°C, and correspond to the samples having the lowest porosity (about 10%). The decrease observed as the pyrolysis is operated as higher temperatures is probably due to the beginning of the α SiC and α Si_3N_4 crystallisation.

The TGA operated in air at temperatures between 1000–1400°C show the high oxidation resistance of such ceramics due to the formation of a coating (probably SiO_2) on the surface of the samples.

References

1. Colombier, C., *Study of new polysilazane precursors to Si–C–N–O ceramics*, Proceedings of the 1st European Ceramic Society Conference, 18–23 June 1989, Maastricht, The Netherlands. Ed. G. de With, R. Terpstra & R. Metselaar, Elsevier Science Publishers Ltd, Vol. 1, 1989 pp. 1·43–52.
2. Gonon, M. F., Fantozzi, G, Murat, M. & Disson, J. P., *Pyrofine PV: a polysilazane precursor for Si–C–N–O matrix composites. J. Eur. Ceram. Soc.*, in press.
3. Gonon, M. F., Fantozzi, G., Murat, M. & Disson, J. P., *Association of the C.V.I. process and of the use of polysilazane precursor for the elaboration of ceramic matrix composites reinforced with continuous fibres, J. Eur. Ceram. Soc.*, in press.
4. Gonon, M. F., Fantozzi, G., Murat, M. & Disson, J. P., *Densification of SiC–C–SiC composites preforms by successive impregnation and pyrolysis cycles with a polysilazane*, Proceedings of the 5th HT-CMC Congress, 20–24 September 1993, Bordeaux, France. Woodhead Publishing Ltd, 1993. pp. 450–5.
5. Gonon, M. F., *Elaboration et caractérisation de Composites à fibres longues et à matrice céramique obtenue par pyrolyse d'un précurseur organométallique de type Polysilazane*, Thêse de l'Insitut National des Sciences Appliquées de Lyon, France, 1993, p. 202.