Ceramics International **24** (1998) 411–414

PII: S0272-8842(97)00010-02
0272-8842/98 $19.00+.00

The Pyrolytic Conversion of Perhydropolysilazane into Silicon Nitride

Stuart T. Schwab, Renee C. Graef & Cheryl R. Blanchard*
Materials & Structures Division, Southwest Research Institute, 6220 Culebra Road, San Antonio, TX 78228-0510, USA

Steven F. Dec & Gary G. Maciel
Department of Chemistry, Colorado State University, Boulder, CO 80523, USA

(Received 20 January 1996; accepted 9 April 1996)

Abstract: Polymeric precursors to ceramics have the potential to enable production of ceramic articles in novel forms, with novel microstructures, and improved properties. The polymer-to-ceramic conversion process is not sufficiently understood for this approach to be widely utilised. Perhydropolysilazane converts to high purity silicon nitride (Si_3N_4), and has been shown to be a useful coating and matrix precursor. The conversion of PHPS to Si_3N_4 is being examined by Solid State, Magic Angle Spinning (MAS) NMR spectroscopy and other techniques. This paper summarises the results to date of this investigation. © 1998 Elsevier Science Limited and Techna S.r.l. All rights reserved

1 BACKGROUND

Excellent high-temperature strength retention and resistance to oxidation gives ceramics the potential to replace metals in many structural applications, including airframes and engines.[1] The high strength-to-density ratio of ceramic components helps to decrease a system's total weight, and thus to increase its operating efficiency.[1] Difficulties inherent to the traditional, powder-based techniques for manufacturing complex structures of advanced ceramics prompted the development of chemical approaches to ceramic processing, including the polymeric precursor to ceramic ('preceramic polymer') technique.[2] Preceramic polymers are composed of a chain or backbone of main-group inorganic elements with organic-appendages. When heated to sufficient temperatures under the proper conditions, these organic appendages are shed through a process generally referred to as 'pyrolysis' to yield an amorphous, covalent ceramic.[3] Subsequent heat treatment-transforms this amorphous material into a crystalline ceramic. Polymeric precursors in general, and those to Si_3N_4 and SiC have been reviewed.[2,4,5]

A particularly useful family of polymeric precursors to Si_3N_4 has been developed at the Southwest Research Institute (SwRI). These polymers, known as perhydropolysilazanes (PHPS), contain only the elements silicon, nitrogen, and hydrogen, and so convert to carbon-free ceramics when fired. These polymers are isolated as waxes or low-viscosity thermosetting liquids that exhibit ceramic yields of 80% by weight or greater. Although originally developed as binders for Si_3N_4 powder pressing,[6] these polysilazanes have also demonstrated their ability in the repair of damaged oxidation protection coatings on carbon–carbon composities,[7] and have been shown to be effective matrix precursors for the processing of fibre-reinforced Si_3N_4 composites.[8] Nonetheless, little is known about the conversion of PHPS to Si_3N_4. It is believed that understanding of the polymer-to-ceramic conversion process will enable development of improved preceramics, or preceramics which convert to a predetermined microstructure.

2 EXPERIMENTAL

Unless otherwise noted, all manipulations of uncured polysilazanes were carried out under

*To whom correspondence should be addressed.

anhydrous and anaerobic conditions using common synthetic techniques.[9] The polymer is prepared by ammonolysis of a mixture of dichloro- and trichlorosilane in ether; details are provided elsewhere.[10] Thermogravimetric Analyses (TGA) were performed on a Perkin-Elmer Thermal Analyzer System 7/4 with a PC 286 Data Collection System using a TGS-2 Thermogravimetric Analyzer and a DSC-4 Differential Scanning Calorimeter. Differential Thermal Analysis (DTA) was performed at Harrop Industries (Columbus, OH). TGA experiments were performed on the as-isolated PHPS, while DTA experiments were performed on char materials obtained by firing PHPS to 800°C under flowing nitrogen. Density measurements were obtained with a helium pycnometer. All nuclear magnetic resonance (NMR) experiments were conducted at the National Center for NMR Applications at Colorado State University. NMR samples were handled under strictly anhydrous and anaerobic conditions. ^{29}Si and ^{1}H chemical shifts are reported relative to tetramethylsilane (TMS).

3 DISCUSSION

3.1 Thermal analysis

PHPS is obtained as a low viscosity, thermosetting liquid. TGA of the as-isolated material (Fig. 1) shows a ceramic yield of 80% by weight when the material is heated at a constant rate of 10°C min^{-1}. The ceramic yield can be raised to over 90% by weight by holding the material at a temperature of *ca.* 110°C for 30–60 min. The density of the char material is also plotted against firing temperature in Fig. 1.

The increase in density from room temperature to *ca.* 100°C may be attributed to cross-linking, as virtually no weight loss was observed. The cross-linked perhydropolysilazane appears to be rather stable as neither mass loss nor density change is observed between 100–200°C. From 200°C to 500°C, the increase in density is accompanied by mass loss. It is likely that volatile species such as silanes, aminosilanes, and hydrogen are evolved in this interval. Although minimal mass loss is observed above 500°C, the density of the material continues to increase up to 700°C, at which point it may be described as an amorphous covalent ceramic. Little change in density is observed between 700–1260°C, at which point the amorphous Si_3N_4 crystallises.

A DTA study was conducted to characterise the behaviour of the amorphous Si_3N_4 at higher temperatures. The PHPS was fired at 800°C under N_2, and this amorphous material was analysed under N_2. As seen in Fig. 2, exotherms are observed at *ca.* 900°C, 1260°C, and 1490°C, and an endotherm is observed at 1400°C. Previously, analysis of the PHPS-derived ceramic by X-ray diffraction (XRD),[11] has revealed the presence of crystalline silicon in chars obtained at *ca.* 1000°C. The weak endotherm observed at 900°C is consistent with the crystallisation of this phase. The exotherm at 1260°C corresponds to the crystallisation of Si_3N_4.[11] The PHPS-derived ceramic obtained at 1270°C is observed to be largely crystalline (Fig. 3) with a phase composition of approximately 60% α-Si_3N_4, and 20% β-Si_3N_4, and 20% elemental silicon.[11] This crystallisation temperature is well below that typically observed for polymer-derived ceramics. The endotherm observed at *ca.* 1400°C is consistent with the melting of elemental silicon (MP = 1410°C), and we assign the exotherm at 1490°C to nitridation of the molten silicon to form additional Si_3N_4.

3.2 NMR analysis.

The ^{1}H NMR spectrum of the as-isolated PHPS consists of three rather broad multiplets: δ 3.0–1.6,

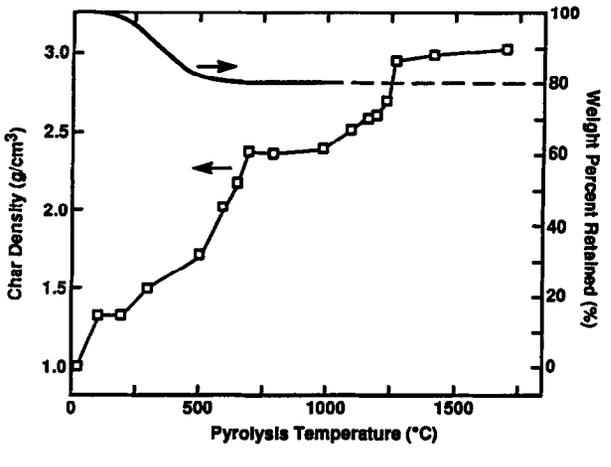

Fig. 1. Thermogravimetric analysis and density versus pyrolysis temperature for perhydropolysilazane.

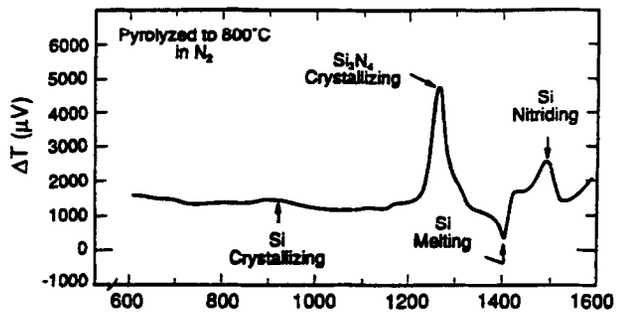

Fig. 2. DTA analysis of PHPS-derived amorphous ceramic prepyrolysed to 800°C under N_2. Analysis was carried out under N_2

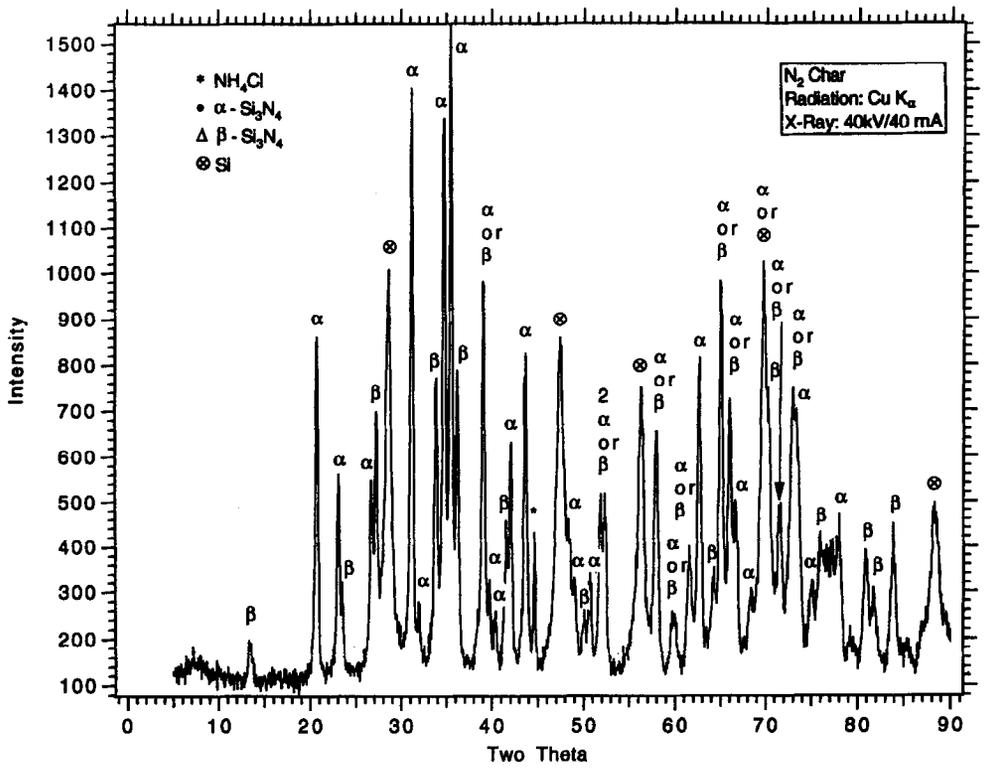

Fig. 3. X-ray diffraction pattern obtained from PHPS-derived ceramic at 1270°C under N_2.

δ 4.3–4.6, and δ 4.6–5.3. These resonances are consistent with the presence of HN, SiH, and SiH_2 functions. The ^{29}Si NMR spectrum of the as-isolated PHPS consists of two broad multiplets: δ−27 to −45 and δ −46 to −55. These resonances indicate the presence of quaternary (SiN_4) functions in addition to the SiH and SiH_2 functions revealed by the ^1H NMR. Based on this and other data, we propose a linked ring structure of PHPS, in which the rings vary in size from four to perhaps ten members and are connected by very short (SiH_2-NH) linkages.

The conversion of PHPS to amorphous ceramic is further characterised in the montage of solid

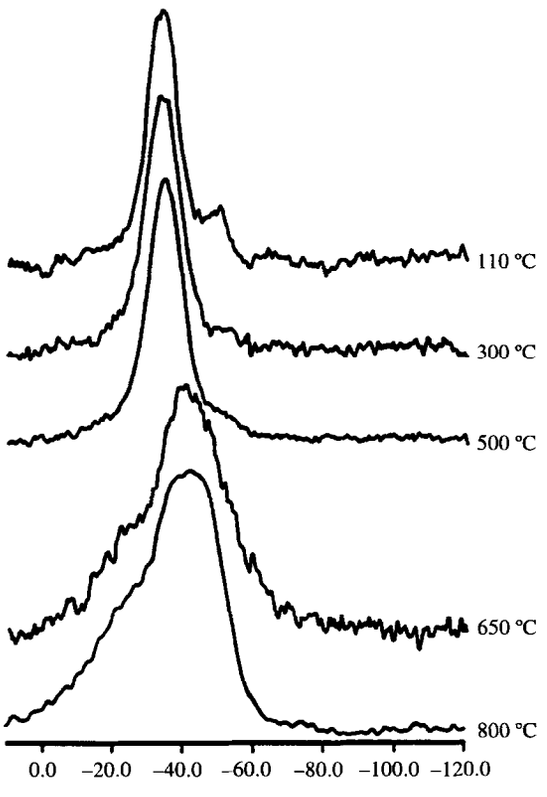

Fig. 4. Solid state ^{29}Si CPMAS analysis of the conversion of perhydropolysolizane to amorphous silicon nitride.

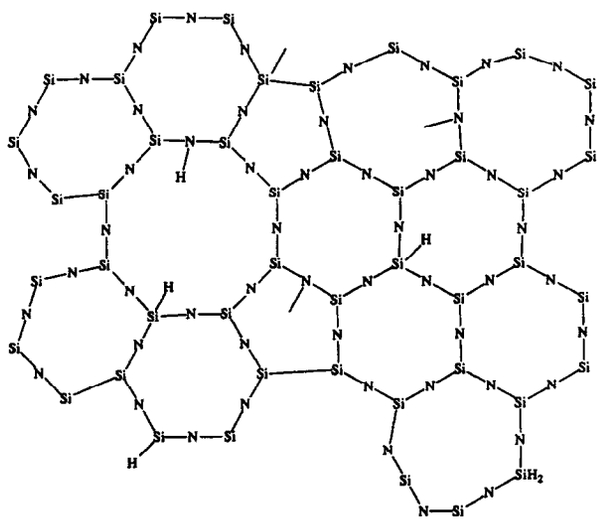

Fig. 5. Proposed structure for amorphous silicon nitride.

state ^{29}Si Cross-Polarised Magic Angle Spinning (CPMAS) spectra presented in Fig. 4. The spectrum of the cross-linked material obtained at 100°C presents two broad resonances, similar to the as-isolated polymer, centred at *ca.* δ −34 and δ −50. As the firing temperature is increased, these resonances coalesce, the chemical shift moves upfield to *ca.* δ − 44, and the peak width increases substantially. We believe the upfield migration of the chemical shift results from an increase in contribution of quaternary silicon functions with a concomitant decrease in protonated silicon functions. We have found that the char material is completely amorphous to X-ray diffraction when fired to temperatures below *ca.* 1000°C.[11] Using the results of solid state ^{29}Si and ^{1}H NMR studies,[12] we propose the structure outlined in Fig. 5 for the amorphous covalent ceramic obtained at *ca.* 800°C.

The pyrolysis products of PHPS exhibit electron spin resonance (ESR) spectra, and so contain 'free' electrons. We have included 'dangling bonds' in the proposed structure of the amorphous Si_3N_4 to reflect ESR activity. As indicated by the ^{29}Si CPMAS spectra, the majority of silicon environments in amorphous covalent ceramic are indistinguishable from that present in Si_3N_4. The similarity of the local silicon environment to Si_3N_4 appears to lessen the energy required for the system to crystallise. The observed crystallisation temperature of 1260°C is within the operating limits of some of the newer advanced fibres, such as 'High-T' Nicalon. The use of PHPS as a matrix precursor may enable the fabrication of fully crystalline fibre-reinforced Si_3N_4 through polymer infiltration/pyrolysis (PIP) techniques.[8]

4 CONCLUSION

Perhydropolysilazane (PHPS) is an inorganic polymer that converts to high yield to an amorphous covalent ceramic. This amorphous material converts to crystalline Si_3N_4 at relatively low temperatures. This preceramic may be useful in the preparation of crystalline articles, such as coatings or composites, in which the processing temperature is limited by one of the components.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the technical support of Messrs Stephen Salazar, Walter Machowski, Arthur Nicholls, Donald Weed and Ms Julie McCombs. This effort was supported by the US Air Force through contract F49620-91-C-0045.

REFERENCES

1. WACHTMAN, Jr, J. B., *et al.*, Report of the research briefing panel on ceramics and ceramic composites. In *Research Briefings 1985*. National Academy, Washington, DC, 1985, pp. 67–71.
2. (a) WYNNE, K. J., *Transformation of Organometallics into Common and Exotic Materials: Design and Activation*, pp. 89–96; (b) WYNNE, K. J. & RICE, R. W., *Ann. Rev. Mater. Sci.*, **14** (1984) 297–334; (c) RICE, R. W., *Am. Ceram. Soc. Bull.*, **62** (1983) 889–892.
3. SORARU, G. D., BABONNEAU, F. & MACKENZIE, J. D., *J. Mater. Sci.*, **25** (1990) 3886–3893.
4. (a) PEUCKERT M., VAAHS, T. & BRÜCK, M., *Adv. Mater.*, **2** (1990) 398–411; (b) TOREKI, W. *Polymer News*, **16** (1991) 6–14; (c) POUSKOULELI, G., *Ceramics International*, **15** (1989) 213–229; (d) MUTSUDDY, B. C., *Ceramics International*, **13** (1987) 41–53.
5. ZIEGLER, J. M. & FEARON, F. W. G. (ed.), *Silicon Based Polymer Science*. Advances in Chemistry Series #224, American Chemical Society, Washington, DC, 1990.
6. (a) SCHWAB, S. T., GRAEF, R. C., DAVIDSON, D. L. & PAN, Y.-M., *Polymer Preprints*, **32** (1991) 556–558; (b) SCHWAB, S. T. & BLANCHARD-ARDID, C. R., *Mater. Res. Soc. Symp. Proc.*, **121** (1988) 581–587; (c) SCHWAB, S. T., BLANCHARD, C. R. & GRAEF, R. C., *J. Mater. Sci.*, **29** (1994) 6320–6328.
7. (a) SCHWAB, S. T. & GRAEF, R. C., NASA-CP 3133 (1991), Part 2, pp. 781–798; (b) SCHWAB, S. T., GRAEF, R. C., PAN, Y.-M., CURRY, D. M., PHAM, V. T., MILHOAN, J. D. & TILLIAN, D. J., *Proceedings of the 39th International SAMPE Symposium—Restricted Sessions*. Anaheim, CA, 4–14 April 1994, pp. 68–81.
8. SCHWAB, S. T., GRAEF, R. C., PAN, Y.-M. & DAVIDSON, D. L., NASA-CP 3175 (1992), Part 2, pp. 721–738. (b) SCHWAB, S. T., PAGE, R. A., DAVIDSON, D. L. & GRAEF, R. C., *Mater. Res. Soc. Symp. Proc.*, **365** (1995) 107–110.
9. (a) SHRIVER, D. F. & DREZDZON, M. A., *The Manipulation of Air-Sensitive Compounds*, 2nd edn. John Wiley, New York, 1986; (b) WAYDA, A. L. & DARENSBOURG, M. Y. *Experimental Organometallic Chemistry*, ACS Symposium Series 357, American Chemical Society, Washington, DC, 1987.
10. SCHWAB, S. T., Polysilazane precursors for silicon nitride and resultant products, US Patent 5,294, 425 15 Mar. 1994.
11. BLANCHARD, C. R. & SCHWAB, S. T., *J. Am. Ceram. Soc.*, 77 (1994) 1729–1739.
12. SCHWAB, S. T., DEC, S. F. & MACIEL, G. E., in preparation.