
Polysilazane Precursors to Advanced Ceramics

Polysilazanes offer a convenient route to the preparation of fibers, coatings and 3-D continuous-fiber-reinforced ceramic-matrix composites that often cannot be prepared using traditional ceramic-processing methods

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Polysilazanes are polymers that consist of silicon, nitrogen, hydrogen and, in certain cases, carbon. Such polymers can be considered either “inorganic” (perhydropolysilazanes) or “organic” (organopolysilazanes or polycarbosilazanes) in nature. However, all polysilazanes contain silicon and nitrogen atoms in their backbone. Although inorganic polysilazanes contain no carbon, organopolysilazanes typically have carbon-containing groups, such as methyl or vinyl appended to silicon or nitrogen atoms within the polymer chain.

Principally because of their high pyrolytic mass yields of silicon-based ceramic material (often >80 wt%), polysilazanes have been extensively used as precursors to SiO_2 ,¹ Si_3N_4 and SiC ceramics.²⁻⁸ They offer a convenient route for preparing silicon-based ceramic materials, such as fibers, coatings or 3-D continuous-fiber-reinforced ceramic-matrix composites (CMCs), which often cannot be made through traditional ceramic-processing methods.³

However, the use of polysilazanes in many markets has been hindered by lack of availability and price. These impediments to large-scale use derive mainly from lack of a suitable manufacturing technique. Traditionally, polysilazanes have been prepared using an ammonolysis reaction of various dichlorosilanes and trichlorosilanes in organic solvent using gaseous ammonia. The resulting NH_4Cl byproduct always has been difficult to separate from the polysilazane product. Once the salt has been removed, the polysilazane has to be isolated by solvent stripping.

It is only recently that large volumes of reasonably priced polysilazanes have become available. KiON Corp. uses a liquid-ammonia process and is now able to supply multi-55-gallon drum quantities of a variety of silazane polymers to interested customers. As a result, the commercial use of polysilazanes has now expanded considerably over what it was several years ago and into many surprising markets. A variety of these applications are described herein

Inorganic and Organic Polysilazanes

Inorganic polysilazanes are currently used extensively in the electronics industry as precursors in the manufacture of dense or porous surface coatings of pure SiO_2 . Such coatings can be deposited from relatively dilute solutions of perhydropolysilazanes in organic solvent (20 wt%). Conversion to SiO_2 is achieved by either

allowing the deposited polysilazane coating to slowly crosslink in moist air at ambient temperature or by heating it in a water-vapor-containing atmosphere at temperatures $\leq 250^\circ\text{C}$. Alternatively, radiation curing (e.g., ultraviolet) can be used.

When such techniques are used, pure SiO_2 coatings that have dry film thicknesses of 50 nm to 5 μm can be obtained. Various applications for such polysilazane-derived SiO_2 coatings include thin, flexible, gas-barrier films; anticorrosion coatings for aluminum metal; and antitamish coatings for silver and photocatalytic coatings that contain embedded anatase TiO_2 for the protection of ultraviolet-sensitive substrates. Studies have shown, for instance, that the deposition of 500 nm thick polysilazane-derived SiO_2 films on the surface of PET films decreases oxygen transmission rates through these films from 45–50 $\text{cm}^3\cdot\text{m}^{-2}\cdot\text{d}^{-1}\cdot\text{bar}^{-1}$ at 0% relative humidity to values that approach 0.2 $\text{cm}^3\cdot\text{m}^{-2}\cdot\text{d}^{-1}\cdot\text{bar}^{-1}$.

Such films also provide corrosion protection to bright, reflective aluminum surfaces at coating thicknesses of 9–10 μm , which pass aggressive, copper-accelerated salt-spray testing at exposure times >240 h (internal data, Clariant Corp.). In the manufacture of semiconductor devices, such SiO_2 coatings are routinely produced on the surface of silicon wafers by coating the silicon surface with a polysilazane-containing coating solution and then converting the coating layer of polysilazane into a SiO_2 -based coating film.⁹ Typically, such surfaces are prepared by spin-coating and then substantially converting the polysilazane layer to a silicon-oxide-containing ceramic, such as SiO_2 . The coatings are referred to by the generic term spin-on-glass (SOG).

Recently, a body of work has focused on the ability of various organic polysilazanes to form amorphous, nonglassy silicon carbonitride (SiCN) ceramics. These ceramics are resistant to chemical degradation,¹⁰ creep,^{11–13} oxidation,¹⁴ thermal shock, decomposition and softening.¹⁵ Thus, they are attractive for a variety of structural ceramic and electronic applications.¹⁶

Electronic Ceramics

In the electronics industry, a viable new technique to fabricate ceramic devices for microelectromechanical systems (MEMS) by microcasting ultraviolet-curable organopolysilazanes has been developed recently.^{17–21} This technique has been successfully used, for example, in the fabrication of a SiCN microactuator.²¹ The utility of SiCN ceramics in this area derives broadly from the need for MEMS devices that can operate at temperatures $>1000^\circ\text{C}$. The microactuator development effort targeted the creation of a microactuator that can operate in such extreme thermal environments and can be used to measure Young's modulus of the material from which it is constructed.

A microfabrication technique for constructing 3-D photonic crystals by deep X-ray lithography using organopolysilazanes also has been demonstrated.²² In this process, X-ray lithography is used to make a mold that is filled with a curable liquid polysilazane that can be transformed into SiCN ceramic using pyrolysis. The technique yields 3-D photonic crystals with a lattice constant of 85 μm and rod diameter of 22 μm . The transmission spectrum shows a 3-D photonic bandgap centered at 125 μm (2.4 THz). This result is in good agreement with theoretical calculations.

A polysilazane-derived SiCN composite that has magnetic properties also has been prepared using a technique whereby Fe_3O_4 powder is batched with polysilazane and pyrolyzed. At pyrolysis temperatures of 700–1000 $^\circ\text{C}$, reduction of the Fe_3O_4 phase to $\alpha\text{-Fe}$ is observed via the reducing action of CH_4 and H_2 that are present in the pyrolysis off-gas of the polysilazane. Magnetization curves for the composite indicate that $\alpha\text{-Fe}$ is the predominant magnetic phase. Such composites are envisioned for use as high-temperature stable materials for use in harsh-environment applications.

Structural Ceramics

In the structural ceramics industry, monolithic and composite ceramic structures have been fabricated using organopolysilazane ceramic precursors. Two methods have been developed to prepare crack-free monolithic ceramics from polysilazanes. The first method involves a warm-pressing technique, in which the polymer is first crosslinked to an infusible state, compacted by cold isostatic pressing or warm-pressing and then pyrolyzed at a slow heating rate.^{23,24} The second method involves prepyrolysis of the polymer to a ceramic powder. The powder is subsequently compounded with additional polysilazane, and the composition is cured during a pressing step.^{25–27} The first method results in ceramics that have a high fraction of open porosity, whereas the second method results in much less gas generation and volume shrinkage in the resulting ceramic.

Porous monolithic ceramic bodies also can be fabricated using organopolysilazanes. Representative of this work is the preparation of high-surface-area catalyst supports made of macroporous SiCN produced using a capillary micromolding technique.²⁸ When this method is used, SiCN and SiC ceramic monoliths that consist of highly interconnected inverted beaded networks of uniform pores with diameters of 50 nm to 10 μm are obtained. These crack-free, porous monoliths demonstrate important material characteristics for use as catalyst supports for hydrocarbon reforming: high surface area per unit volume; compatibility with temperatures $>800^\circ\text{C}$; and low pressure drop while maintaining a high surface area by having an inverted beaded bed structure to form the network of interconnected pores with a porosity $>70\%$.

Organopolysilazanes also are useful for producing either fibers or matrices in the fabrication of CMCs. Fibers, for example, can be produced by the melt-spinning and pyrolysis of pure polysilazanes²⁹⁻³¹ or through the modification of polysilazanes with, for example, metal alkoxides (such as titanium or zirconium alkoxides) followed by spinning and a subsequent pyrolysis step.^{32,33} In the former case, SiCN fibers are produced, whereas, in the latter case, various oxycarbonitride compositions are obtained. SiCN-ZrO₂ fibers can be prepared, for example, from liquid polysilazane precursors by reacting a vinyl-substituted polysilazane with a solution of 70 vol% tetrapropyl zirconate in isopropanol.³³

It is proposed that such chemical modification makes the polymer amenable to fiber drawing by producing linear chains in the polysilazane, which results in such suitable rheological behavior. Although such work has been reported using zirconium alkoxide, the idea of modifying SiCN polysilazane precursors with other metal alkoxides also has been proposed. Titanium, hafnium, silicon and aluminum alkoxides are proposed as alternatives to zirconium alkoxides in such a process.

Highly corrosion-resistant monolithic ceramics also have been prepared recently using the technique of metal alkoxide modification by the reaction of organopolysilazanes with aluminum isopropoxide.^{34,35} Although fibers have not been drawn from such compositions, it has been demonstrated that polysilazane-derived SiAlCN ceramics possess much better oxidation resistance than simple SiCN ceramics. Oxidation rates an order of magnitude lower than those for pure SiCN have been measured. It also has been subsequently shown that such SiAlCN ceramics exhibit excellent water-vapor corrosion resistance at 1100°C .³⁵

CMC matrices also can be generated from polysilazanes. Variations of the polymer infiltration pyrolysis (PIP) technique have been demonstrated.³⁶⁻³⁸ PIP and resin-transfer-molding (RTM) techniques into fibrous preforms with suitable organopolysilazane precursors (e.g., low viscosity, solvent-free), followed by thermally induced crosslinking and pyrolysis at temperatures of $\geq 1300^\circ\text{C}$ or higher, have been used. These techniques result in dense CMC materials when an iterative process of reinfiltration and pyrolysis is followed.

Using such techniques, Nicalon® and Hi-Nicalon® fiber-reinforced composites were fabricated using a liquid, vinyl-appended polysilazane precursor.³⁷ Nicalon® fiber-reinforced plates fabricated by infusion of C/SiC preforms and densified seven times at 1300, 1400, 1500 and 1600°C demonstrated flexural strengths of 263–447 MPa, fracture toughness of 24–30 MPa·m^{1/2} and composite densities of 2.57–2.87 g/cm³. The maximum room-temperature four-point flexural strength, 575 MPa, was demonstrated when the composite was pyrolyzed at 1300°C . The strength of the composites decreased with increased pyrolysis temperature, presumably because of the degradation of the Hi-Nicalon fibers at temperatures $>1300^\circ\text{C}$.

Continuous C-fiber/SiC composites also have been produced using a low-cost manufacturing method. The porosity in a 2-D carbon-fiber preform is filled with a SiC powder using a pressure-infiltration method to produce a high-particle-packing density in the fiber preform.³⁹ The preform then is heat-treated at 400°C to form a porous framework that then is infiltrated with a liquid polysilazane precursor. Subsequently, the infiltrated polysilazane is pyrolyzed in argon at 1300°C . The developed C-fiber/SiC/SiCN composites are considered as promising candidates for low- and high-temperature applications, such as brake disks, seals, components of chemical reactors and gas turbines.

CMCs also have been prepared using a directed-metal oxidation process into a preform fabricated by a low-pressure pressing technique using a polysilazane binder.⁴⁰ In this process, a SiC powder preform is prepared using a liquid poly(urea)silazane binder to shape-stabilize the preform for processing at high temperatures. The ceramic matrix then is introduced into the SiC powder preform through a ceramic matrix “growth” process. The process involves the infiltration and simultaneous oxidation of molten aluminum metal into the porosity of the SiC powder preform in an air atmosphere at 900°C . Such a process has been used to produce a SiC-powder/Al₂O₃ CMC valve seat.

Organopolysilazanes also are used in the production of metal-matrix composites (MMCs), where they can serve as extreme high-temperature binders for preforms into which molten silicon or aluminum metals are introduced.^{40,41} The fabrication of Al_2O_3 -particulate-reinforced aluminum-metal-matrix composite brake rotors and disks with maximum operating temperatures of 482°C (900°F) using polysilazane preform binders has been demonstrated.⁴⁰ The manufacturing technique for such $\text{Al}_2\text{O}_3/\text{Al}$ MMCs uses pressed Al_2O_3 particulate preforms, which include 2.83 wt% polysilazane binder. The aluminum-metal matrix is introduced using a pressureless metal infiltration process in a nitrogen atmosphere.

Ceramic Coatings and Joining

Organopolysilazanes also have found utility in the joining of ceramics and as the continuous phase in formulated, high-temperature coatings. Coatings and joints from filled organopolysilazanes have been demonstrated for Si_3N_4 -matrix composites,⁴² microwave joining of SiC,⁴³ seals for solid oxide fuel cells⁴⁴ and as electronic adhesives for bonding integrated circuit chips to carriers or circuit boards.⁴⁵ In this last application, a layer of a paste prepared from methylhydridopolysilazane, Al_2O_3 , microballoons and glycidoxypropyltrimethoxysilane is applied between an electronic component and the substrate to which it is to be adhered. The component can be a silicon-based device, gallium arsenide-based device, focal play array, optoelectronic device, photovoltaic cell or optical device.

The assemblage then is heated to 400°C for 4 h to convert the polysilazane to a ceramic. Strong joins are obtained. Polysilazanes also have been used for preform joining in the fabrication of CMCs and MMCs.⁴⁰

Several coatings companies are currently selling formulated ceramic coatings based on organopolysilazanes for under-the-hood automotive and truck applications (e.g., exhaust systems and pistons). Organopolysilazane-based coatings for firearms and high-temperature applications requiring substantial heat insulating characteristics also are being developed. Organopolysilazanes also have been used effectively as antioxidation layers on carbon structures,⁴⁶ C/SiC composites,⁴⁷ carbon fiber or SiC fiber⁴¹ and in the strength enhancement of carbon foams.⁴⁸

Graphite plates were coated with a polysilazane and then pyrolyzed in air to 1000°C. An adherent, SiO_2 -containing coating was obtained.⁴⁶ When the coated sample was further heated to $\geq 1400^\circ\text{C}$, a β -SiC coating was obtained. When subjected to five coating and heat-treatment cycles, a 9.4 μm thick ceramic coating resulted. A ratio of weight loss of only 1.3% was realized in an oxidation test in which the coated carbon sample was heated for 20 h at 800° C.

Nanoscale Applications

Recent investigations also have shown that selective pyrolysis of organopolysilazanes under controlled atmospheres or in the presence of various organic polymers can result in ceramics with well-defined nanoscale structural features, including such novel structures as Si_3N_4 nanobelts.⁴⁹

Controlled pyrolysis of organopolysilazanes also has resulted in the generation of ceramic nanocomposite structures with 30 nm grains.⁵⁰ The major crystalline phases are nanocrystalline SiC, Si_3N_4 , a small amount of $\text{Si}_2\text{N}_2\text{O}$ and free carbon. Heterogeneous and homogeneous crystallization is observed. The grain boundaries are free of oxide-nitride glassy phases, which indicate the possibility of high creep resistance for these nanocomposites.

Mesoporous ceramic materials also have been produced based on the use of an organic diblock copolymer structuring agent in combination with an organopolysilazane.⁵¹ The diblock copolymer is an amphiphilic poly(isopreneblock-ethylene oxide) and is used as a method of directing structure in a polysilazane during pyrolysis. The mesoporous ceramic prepared using this technique is stable to 1500°C, and it has a lamellar nanostructure that consists of hexagonally packed cylinders with an average pore diameter of ~13 nm. ■

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References

- ¹H. Matsuo, M. Kokubo, T. Ohbayashi, Y. Tashiro, T. Suzuki, M. Kizaki, H. Hashimoto, Y. Shimizu, T. Sakurai and H. Aoki, "Method and Composition for Forming Ceramics and Article Coated with the Ceramics," U.S. Pat. No. 5 747 623, 1998.
- ²M. Pauckert, T. Vaahs and M. Brueck, *Adv. Mater.*, **2** [9] 398–404 (1990).
- ³K.J. Wynne and R.W. Rice, *Ann. Rev. Mater. Sci.*, **14**, 297–334 (1984).
- ⁴R.M. Laine, Y.D. Blum, D. Tse and R. Glaser; pp. 124–42 in *Inorganic and Organometallic Polymers*, ACS Symposium Series 360. Edited by M. Zeldin, K.J. Wynne and H.R. Allcock. American Chemical Society, Washington, D.C., 1988.
- ⁵D. Seyferth, G.H. Wiseman, J.M. Schwark, Y.-F. Yu and C.A. Poutasse; see Ref. 4, pp. 143–55.
- ⁶G. Pouskouleli, *Ceram. Int.*, **15**, 213–29 (1989).
- ⁷W.H. Atwell; pp. 593–606 in *Silicon Based Polymer Science*, Advances in Chemistry Series 224. Edited by J.M. Zeigler and F.W.G. Fearon. American Chemical Society, Washington, D.C., 1990.
- ⁸J. Wan, M.J. Gasch and A.K. Mukherjee, "Effect of Ammonia Treatment on the Crystallization of Amorphous Silicon-Carbon-Nitrogen Ceramics Derived from Polymer Precursor Pyrolysis," *J. Am. Ceram. Soc.*, **85** [3] 554–64 (2002).
- ⁹J.-H. Lee, J.-H. Cho, J.-S. Choi and D.-J. Lee, "Spin-On Glass Composition and Method of Forming Silicon Oxide Layer in Semiconductor Manufacturing Process using the Same," U.S. Pat. Appl. No. US2004/0224537 A1.
- ¹⁰R. Riedel, "Advanced Ceramics from Inorganic Polymers"; pp. 1–50 in *Materials Science and Technology*, Vol. 17B. Edited by R.W. Cahn, P. Hassen and E.J. Kramer. Wiley-VCH Verlag, Weinheim, Germany, 1996.
- ¹¹G. Thurn and F. Aldinger, "Compression Creep Behavior of Precursor-Derived Ceramics"; pp. 237–45 in *Precursor-Derived Ceramics*. Edited by J. Bill, F. Wakai and F. Aldinger. Wiley-VCH Verlag, Weinheim, Germany, 1999.
- ¹²R. Riedel, L.M. Ruswisch, L. An and R. Raj, "Amorphous Silicoboron Carbonitride Ceramic with Very High Viscosity at Temperatures above 1500°C," *J. Am. Ceram. Soc.*, **81** [12] 3341–44 (1998).
- ¹³B. Baufeld, H. Gu, J. Bill, F. Wakai and F. Aldinger, "High-Temperature Deformation of Precursor-Derived Amorphous Si-B-C-N Ceramics," *J. Eur. Ceram. Soc.*, **19**, 2797–814 (1999).
- ¹⁴R. Raj, L. An, S.R. Shah, R. Riedel, C. Fasel and H.-J. Kleebe, "Oxidation Kinetics of an Amorphous Silicon Carbonitride," *J. Am. Ceram. Soc.*, **84** [8] 1803–10 (2001).
- ¹⁵S.R. Shah and R. Raj, "Nanoscale Densification Creep in Polymer-Derived Silicon Carbonitrides at 1350°C," *J. Am. Ceram. Soc.*, **84** [10] 2208–12 (2001).
- ¹⁶P.A. Ramakrishnan, Y.T. Wang, D. Balzar, L. An, C. Haluschka, R. Riedel and A.M. Hermann, "Silicoboron-Carbonitride Ceramics: A Class of High-Temperature, Dopable Electronic Materials," *Appl. Phys. Lett.*, **78** [20] 3076–78 (2001).
- ¹⁷L.-A. Liew, W. Zhang, L. An, S. Shah, R. Luo, Y. Liu, T. Cross, M.L. Dunn, V. Bright, J.W. Daily and R. Raj, "Ceramic MEMS, New Materials, Innovative Processing and Future Applications," *Am. Ceram. Soc. Bull.*, **80** [5] 25–30 (2001).
- ¹⁸L.-A. Liew, W. Zhang, V.M. Bright, L. An, M.L. Dunn and R. Raj, "Fabrication of SiCN Ceramic MEMS Using Injectable Polymer-Precursor Technique," *Sens. Actuators A*, **89**, 64–70 (2001).
- ¹⁹L.-A. Liew, T. Cross, V.M. Bright and R. Raj, "Fabrication of Novel Polysilazane MEMS Structures by Microcasting"; pp. 1–8 in *Proceedings of 2001 ASME International Mechanical Engineering Congress and Exposition* (Nov. 11–16, 2001, New York).
- ²⁰L.-A. Liew, Y. Liu, R. Luo, T. Cross, L. An, V.M. Bright, M.L. Dunn, J.W. Daily and R. Raj, *Sens. Actuators A*, **95**, 120–34 (2002).
- ²¹R.A. Saravanan, L.-A. Liew, V.M. Bright and R. Raj, "Integration of Ceramics Research with the Development of a Microsystem," *J. Am. Ceram. Soc.*, **86** [7] 1217–19 (2003).
- ²²G. Feiertag, W. Ehrfeld, H. Freimuth, H. Kolle, H. Lehr, M. Schmidt, M.M. Sigalas, C.M. Soukoulis, G. Kiriakidis, T. Pedersen, J. Kuhl and W. Koenig, "Fabrication of Photonic Crystals by Deep X-ray Lithography," *Appl. Phys. Lett.*, **71** [11] 1441–43 (1997).
- ²³E. Kroke, Y.-L. Li, C. Konetschny, E. Lecomte, C. Fasel and R. Riedel, "Silazane-Derived Ceramics and Related Materials," *Mater. Sci. Eng.*, **26**, 97–199 (2000).
- ²⁴J. Seitz and J. Bill, "Production of Compact Polysilazane-Derived Si-C-N Ceramics by Plastic Forming," *J. Mater. Sci. Lett.*, **15**, 391–93 (1996).
- ²⁵J. Wan, M.J. Gasch and A.K. Mukherjee, "Silicon Carbonitride Ceramics Produced by Pyrolysis of Polymer Ceramic Precursor," *J. Mater. Res.*, **15** [8] 1657–60 (2000).

- ²⁶J. Wan, M.J. Gasch and A.K. Mukherjee, "Silicon Nitride/Silicon Carbide Nanocomposites Derived from Polymer Precursor Pyrolysis"; pp. 276–79 in *Proceedings of International Conference on Engineering and Technological Sciences 2000* (Beijing, China, 2000). Edited by J. Song and R. Yin. New World Press, Beijing, 2000.
- ²⁷H.-J. Kleebe, D. Suttor, H. Mueller and G. Ziegler, "Decomposition–Crystallization of Polymer-Derived Si-C-N Ceramics," *J. Am. Ceram. Soc.*, **81** [11] 2971–77 (1998).
- ²⁸I.-K. Sung, M.M. Christian, D.-P. Kim and P.J.A. Kenis, "Tailored Macroporous SiCN and SiC Structures for High-Temperature Fuel Reforming," *Adv. Funct. Mater.*, **15**, 1336–42 (2005).
- ²⁹W. Verbeek, "Production of Shaped Articles of Homogeneous Mixtures of Silicon Carbide and Nitride," U.S. Pat. No. 3 853 567, 1974.
- ³⁰G. Winter, W. Verbeek and M. Mansmann, "Production of Shaped Articles of Silicon Carbide and Silicon Nitride," U.S. Pat. No. 3 892 583, 1975.
- ³¹B.G. Penn, J.G. Daniels, F.E. Ledbetter III and J.M. Clemons, "Preparation of Silicon Carbide–Silicon Nitride Fibers by the Pyrolysis of Polycarbosilazane Precursors: A Review," *Polym. Eng. Sci.*, **26** [17] 1191–94 (1986).
- ³²A. Saha, S.R. Shah and R. Raj, "Amorphous Silicon Carbonitride Fibers Drawn from Alkoxide Modified Ceraset™," *J. Am. Ceram. Soc.*, **86** [8] 1443–45 (2003).
- ³³A. Saha, S.R. Shah and R. Raj, "Oxidation Behavior of SiCN–ZrO₂ Fiber Prepared from Alkoxide-Modified Silazane," *J. Am. Ceram. Soc.*, **87** [8] 1556–58 (2004).
- ³⁴A. Dhamme, W. Xu, B.G. Fookes, Y. Fan, L. Zhang, S. Burton, J. Hu, J. Ford and L. An, "Polymer–Ceramic Conversion of Liquid Polyaluminasilazanes for SiAlCN Ceramics," *J. Am. Ceram. Soc.*, **88** [9] 2415–9 (2005).
- ³⁵Y. Wang, W. Fei and L. An, "Oxidation/Corrosion of Polymer-Derived SiAlCN Ceramics in Water Vapor," *J. Am. Ceram. Soc.*, **89** [3] 1079–82 (2006).
- ³⁶D.V. Miller, D.L. Pommell and G.H. Schiroky, "Fabrication and Properties of SiC/SiC Composites Derived from Ceraset™ SN Pre-ceramic Polymer," *Ceram. Eng. Sci. Proc.*, **18** (1997).
- ³⁷Z.S. Rak, "A Process for Cf/SiC Composites Using Liquid Polymer Infiltration," *J. Am. Ceram. Soc.*, **84** [10] 2235–39 (2001).
- ³⁸Z.S. Rak, "Novel CMC Material Based on a Si₃N₄ Matrix," *Adv. Eng. Mater.*, **2** [8] 503–507 (2000).
- ³⁹Z.S. Rak, "Cf/SiC Composites by a Novel Manufacturing Method," ECN-RX-00-040 (Project No. 7.6266, as part of EU Grant under Contract No 32.0176, and ECN TS&C funding in collaboration with the Institute for Advanced Materials (JRC) in Petten).
- ⁴⁰M.K. Aghajanian, J.W. Hinton, A. Lukacs III, J.A. Jensen, M.S. Nawkirod and R.K. Dwivedi, "Methods for Fabricating Shapes by use of Organometallic, Ceramic Precursor Binders," U.S. Pat. No. 5 641 817, 1997.
- ⁴¹D.J. Landini and R.L.K. Matsumoto, "Method for Processing Silicon Carbide Preforms Having a High-Temperature Boron Nitride Coating," U.S. Pat. Appl. No. US2004/0115348 (June 17, 2004).
- ⁴²M. Stackpoole and R. Bordia, "Processing and Properties of Si₃N₄ Matrix Composites, Coatings and Joints from Filled Pre-Ceramic Polymer Systems," Environmental Barrier Coatings Workshop, Nashville, Tenn., 2002.
- ⁴³P. Colombo, R. Silbergliitt and G.A. Danko, "Microwave Joining of SiC," Advanced Industrial Materials Annual Review Meeting, Jackson Hole, Wyo., June 23, 1998.
- ⁴⁴C.A. Lewinsohn and S. Elangovan, "Progress in Seals for Solid Oxide Fuel Cells," U.S. Dept. of Energy Phase I SBIR DE-FG03-02ER83385.
- ⁴⁵C.R. Bearinger, R.C. Camilletti, G. Chandra, T.E. Gentle and L.A. Haluska, U.S. Pat. No. 5 904 791, 1999.
- ⁴⁶A. Kojima, S. Hoshii and T. Muto, "Characteristics of Polysilazane Compound and Its Application as Coating for Carbon Material," *J. Mater. Sci. Lett.*, **21**, 757–60 (2002).
- ⁴⁷J. Bill and D. Heimann, "Polymer-Derived Ceramic Coatings on C/C–SiC Composites," *J. Eur. Ceram. Soc.*, **16**, 1115–20 (1996).
- ⁴⁸C. Duston, S. Seghi, R. Watts and B. Carney, "Strength Enhancement and Application Development of Carbon Foam for Thermal Management Systems," USAF/ML SBIR Contract No. F33615-03-M-5039 and U.S. Dept. of Energy Grant No. DE-FG02-03ER83627.
- ⁴⁹W. Yang, L. Zhang, H. Ji, L. An, et al., "Si₃N₄ Nanobelts Grown by Pyrolysis of Polyureasilazane with Iron Catalyst," *J. Am. Ceram. Soc.*, **466** (2005).
- ⁵⁰J. Wan, M.J. Gasch and A.K. Mukherjee, "Consolidation and Crystallization of Si₃N₄/SiC Nanocomposites from a Poly(urea-silazane) Ceramic Precursor," *J. Mater. Res.*, **16** [11] 3274–86 (2001).
- ⁵¹M. Kamperman, C.B.W. Garcia, P. Du, H. Ow and U. Wiesner, "Ordered Mesoporous Ceramics Stable up to 1500°C from Diblock Copolymer Mesophases," *J. Am. Chem. Soc.*, **126**, 14708–709 (2004).