Direct Observation of Preceramic and Organic Binder Decomposition in 2-D Model Microstructures

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Preceramic and organic binder decomposition processes were studied during thermolysis to determine how the physico-chemical properties of the binder affected the microstructural development of the ceramic component. Specifically, the behavior of two organic polymers, poly(methyl methacrylate) (PMMA) and a cross-linked poly(methyl methacrylate) (x-PMMA), and two preceramic polymers, polycarbosilane (PCS) and vinylic polysilane (VPS) was observed as a function of temperature. Binder-filled two-dimensional (2-D) model microstructures were fabricated to simulate ceramic green bodies whose pores were completely filled with binder. Examination of these 2-D samples by hot-stage optical microscopy enabled direct observations of pore development and changes in polymer morphology during binder thermolysis. These observations revealed that the mass transport processes involved during thermolysis, as well as the developing microstructural features, depend on the properties of the binder system during thermal decomposition. The organic polymers were investigated because of their chemical similarity and markedly different physical behavior upon heating. It was shown that thermoplastic polymers (e.g., PMMA) are influenced by capillary forces during thermolysis, while thermosetting polymers (e.g., x-PMMA) do not flow within these porous microstructures. Both of the preceramic polymers displayed a range of physical behavior over the temperatures studied. The decomposition chemistry and weight loss at a given temperature combined with the associated physical behavior had a dramatic effect on the final distribution of the pyrolyzed product (amorphous silicon carbide and glassy carbon) formed during thermolysis. The pyrolysis product formed from PCS was observed to segregate to the smaller pore channels in the 2-D microstructures, while the pyrolysis product formed from VPS was observed to be homogeneously distributed in these model microstructures. This work offers guidelines to improve the microstructural homogeneity of ceramic–ceramic composites derived from particulate–preceramic polymer green bodies.

I. Introduction

APPLICATION of preceramic polymers (e.g., organosilicon polymers) as binders for ceramic processing has received

recent attention.[1-6] Unlike conventional organic binders that are removed prior to densification, preceramic polymers decompose to form amorphous–covalent ceramics[7] which are incorporated into the matrix. Hence, these polymers offer a novel synthesis route for producing a wide variety of ceramic–ceramic composites (e.g., silicon carbide–alumina, silicon carbide–silicon carbide, and silicon carbide–silicon nitride).[2,4,8] The strengths of pyrolyzed preceramic polymer–ceramic composites have been reported by Rogers *et al.*[2] to be as high as 430 MPa. In addition, numerous advantages such as increased green density, reduced shrinkage, and improved strength of the pre-sintered ceramic part[2,4,9-11] have also been reported for ceramic bodies containing preceramic binders.

Several organosilicon polymers have been developed which form nonoxides, silicon carbide (SiC) plus excess carbon or silicon nitride (Si_3N_4), upon decomposition.[12-15] Polycarbosilane (PCS) and vinylic polysilane (VPS) are representative of those preceramic polymers that have been proposed in the literature for use as binders. Each of these polymers decomposes in an inert atmosphere to first form an amorphous nonoxide (approximately 1000°C) and then crystalline SiC plus excess carbon (above 1200°C) with final yields between 50 and 60 wt% of their initial weight.

The distribution of the pyrolysis residue that develops as preceramic polymers decompose in a particulate-filled matrix determines whether the advantages listed above are realized. The preceramic binder system must meet several requirements: (1) give high yields of ceramic pyrolysis product, (2) decompose to give a uniform distribution of this product, and (3) produce minimal defects during the formation of ceramic product. Many researchers have focused on organosilicon polymer synthesis with the goal of increasing pyrolysis yields; however, relatively little is known about the effects of the binder's physical and chemical properties on the final microstructure of the composite or its performance properties.

Previous research has shown that the physico-chemical properties of organic binders have a marked effect on their distribution, and, hence, the pore development that occurs in tape-cast ceramic components during binder thermolysis.[16,17] Based on their physico-chemical properties, organic polymers are easily separated into two groups: thermoplastic and thermosetting polymers, each of which behaves differently in porous networks during decomposition. The physico-chemical changes that preceramic polymers undergo during decomposition are generally more complicated than that of organic binders and often encompass both thermoplastic and thermosetting behavior. The purpose of this research is two-fold: (1) to determine the effects of these changes on microstructural development and (2) to develop a knowledge base that can be used to improve the design of these novel polymers.

In this paper, we report *in situ* observations of binder distribution processes and porosity development for two organosilicon polymers (PCS and VPS) and, for comparative purposes,

two acrylate-based organic binders during their decomposition in two-dimensional model microstructures. The organic polymers were included in this work to illustrate the behavior characteristic of pure thermoplastic and thermosetting polymers. These observations will serve as a basis for interpreting the more complicated behavior expected for the preceramic polymers studied. The 2-D structures were fabricated to model the porous network formed between densely packed particles in green components. This approach has several advantages over traditional methods (e.g., scanning electron microscopy, SEM) of characterizing ceramic components. The main advantage is that direct observations of the polymer distribution within the pore channels can be made at any point during decomposition. An additional advantage is derived from the ease with which the polymer and ceramic phases can be distinguished in this approach. By comparison, relatively little contrast exists between these phases using SEM at high magnification. Hence, this approach also addresses a deficiency in the analytic capabilities currently relied upon by other investigators in this area.

II. Experimental Procedure

(1) Binders

PCS (NICALON™ X9-6348, Lot PL-79, Dow Corning, Midland, MI, marketed for Nippon Carbon, Tokyo, Japan) and VPS (Y-12044, Lot 509110305586, Union Carbide, Specialty Chemicals Division, Tarrytown, NY) were obtained from commercial sources, as was the poly(methyl methacrylate) (PMMA) (Aldrich Chemical, Milwaukee, WI) used in this study. PCS, a powder at room temperature, had an average molecular weight of 1580 g/mol as measured cryoscopically in benzene.[5] Elemental analysis[5] showed that this polymer contained 49.14% Si, 41.73% C, 7.83% H, and 0.71% O (neutron activation), which is in good agreement with the values reported by Hasegawa et al.[18] VPS had an average molecular weight of 1040 g/mol, which was also measured cryscopically in benzene.[5] VPS was a viscous fluid at room temperature, while PMMA was a finely divided powder. A cross-linked acrylate-based polymer (x-PMMA) was synthesized from a solution consisting of 80% methyl methacrylate (Aldrich), 19% ethylene glycol dimethacrylate, and 1% benzoyl peroxide by weight. Cross-linking was initiated by heating this solution in a nonoxidizing atmosphere to a slightly elevated temperature (60°C).

(2) 2-D Model Microstructures

A schematic view of the 2-D samples is shown in Fig. 1. There were three steps involved in the preparation of these samples: (1) patterning the substrates, (2) filling the channels (or pores) with binder, and (3) bonding the top glass cover. Circular glass cover slides (diameter = 22 mm) were used as substrates. They were processed by a standard photolithography technique,[19] described briefly in Table I, to produce etched channels on their surface. The resulting channel depth was approximately 5 μm, and their widths ranged from 20 to 200 μm.
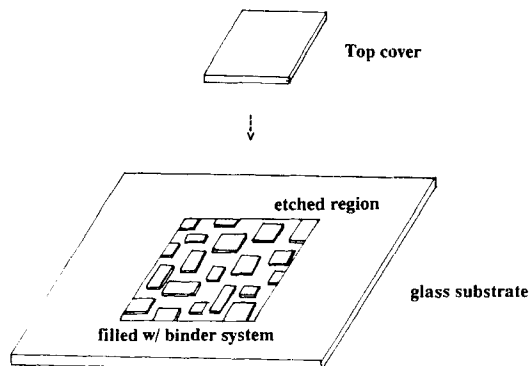

Fig. 1. Fabrication process for binder-filled 2-D model microstructures.

The channel-filling procedure was dependent on the polymer's properties. To fill the channels with x-PMMA, a syringe was used to place a droplet of solution onto the etched region of each substrate. A top glass cover was then placed upon each of these filled channels (see Fig. 1), and the samples were heated above 60°C for 12 h to polymerize (or cure) the mixture. The procedure used to form the PCS and VPS samples was similar to that used for x-PMMA. An appropriate amount of PCS was dissolved in toluene to form a 10% polymer solution by weight. A droplet of either PCS–toluene solution or pure VPS was placed onto the etched region of each substrate and then covered. The as-prepared PCS samples contained residual toluene, which was removed during subsequent heat treatment. For the PMMA samples, a small amount of the polymer was placed on top of the etched region of each substrate and heated to a temperature above its softening point (≈100°C). At this temperature, the PMMA flowed to uniformly fill the pore channels. These samples were then covered and cooled to 25°C.

(3) Microstructural Observation

Decomposition of the 2-D samples filled with PMMA and x-PMMA was observed using hot-stage (Linkam THM 600, United Kingdom) optical microscopy (Olympus, Lake Success, NY). These samples were heated to 300°C at 10°C/min in air, and optical micrographs were taken during the heating cycle. This technique could not be used for the preceramic polymers, due to their sensitivity to oxygen during decomposition. Therefore, the 2-D samples filled with PCS and VPS were fired in an atmosphere-controlled furnace that was evacuated and back-filled twice with gettered argon ($P_{O_2} \approx 10^{-13}$ atm) prior to heating. Samples were heated from room temperature to 225°C at a heating rate of 1.3°C/min, held at this temperature for 3 h, and then heated to different final temperatures (T_{max}) at a heating rate of 0.3°C/min. Following each heat treatment, optical micrographs were taken of these samples.

III. Results and Discussion

The redistribution of the acrylic polymers (PMMA and x-PMMA) in the 2-D microstructure during thermal decomposition was observed by optical microscopy using a hot stage to control the temperature. Figures 2 and 3 depict representative optical micrographs (50×) as a function of temperature for the 2-D samples filled with PMMA and cross-linked PMMA, respectively. The pore development that occurred as these polymers decomposed was markedly different and was illustrative of the two different behavior regimes.
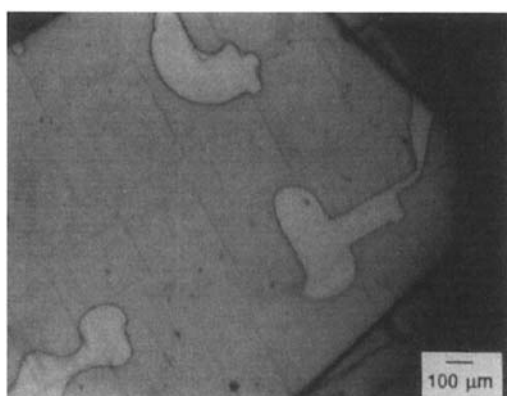
Previous observations showed that, under slow heating rates, the distribution of thermoplastic polymers in ceramic green bodies is controlled by capillary forces.[16,17] PMMA is a thermoplastic polymer, which melts upon heating and depolymerizes over a narrow temperature range to produce its monomer, methyl methacrylate (MMA). Figure 2 shows that bubbles formed in the PMMA as it was being heated. These bubbles grew rapidly to the edge of the cover (or free surface), where they rapidly decreased in size. Once bubbles ceased to form, the distribution of the remaining polymer was governed by capillary forces. The cessation of bubble generation may be linked to the reduction in diffusion distance (or increase in removal rate) as large pores penetrated into the 2-D microstructure.

The formation of bubbles dominates the transport of volatile species (e.g., MMA), if the removal rate of volatile species is slower than their generation rate, allowing the local vapor pressure of MMA to exceed 1 atm.[20,21] The fast heating rate (10°C/min) used in this study promoted the rapid generation of monomer, and, thus, bubble formation. It is expected that at much lower heating rates, bubble formation would not occur and only capillary forces would influence this process.
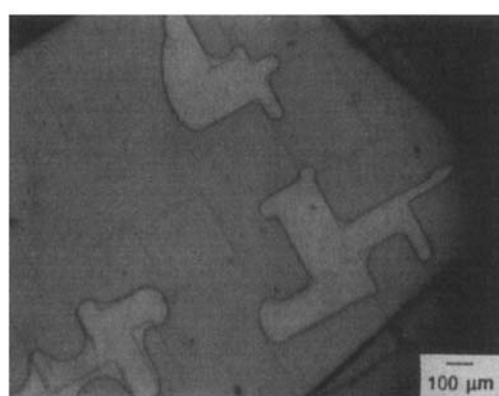
Cross-linked PMMA (x-PMMA) is a thermosetting resin. Instead of forming bubbles or being redistributed by capillary forces, cracks were observed to form (≈250°C) during x-PMMA decomposition, as illustrated in Fig. 3. These cracks

Table I.   Procedure for Fabrication of 2-D Microstructures

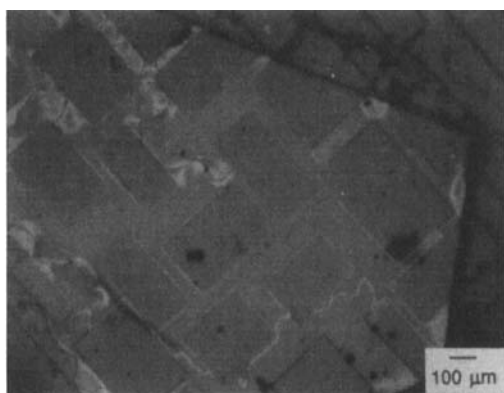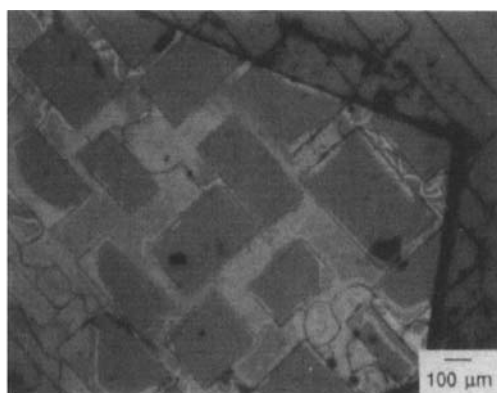| Step	Description
1. Clean	Immerse substrates in a 1:1 solution of sulfuric acid and hydrogen peroxide (≈ 300 s), then rinse in deionized water and allow to dry overnight at 120°C
2. Apply photoresist	Cover top surface of substrate with resist (positive photoresist 820, KTI Chemical, Sunnyvale, CA) and spin coat at 5000 rpm for 30 s.
3. Prebake	Heat substrates coated with resist at 90°C for 30 min.
4. Expose	Expose prebaked substrates to UV light (contact aligner) for 40 s.
5. Develop	Develop exposed pattern by immersing substrates in a 1:1 solution of DI water and positive resist developer (positive photoresist developer, KTI) for 120 s, then rinse in DI water.
6. Postbake	Heat patterned substrates at 120°C for 30 min.
7. Etch	Etch postbaked samples for 0.5 h, using a buffered oxide etchant, then rinse in DI water.
8. Clean	Remove photoresist with acetone and then clean (refer to Step 1).

(A)   **(B)**

Fig. 2.   Optical micrographs of PMMA-filled 2-D samples heated at 10°C/min in air: (A) $T = 291$°C and (B) $T = 297$°C.

(A)   **(B)**

Fig. 3.   Optical micrographs of cross-linked PMMA-filled 2-D samples heated at 10°C/min in air: (A) $T = 264$°C and (B) $T = 278$°C.

initiated randomly within the pore structure and then were observed to propagate along the channels (or pores). As thermolysis progressed, these cracks widened until they matched the width of the channels. The volume change which occurred during decomposition was apparently accommodated by fracture of the x-PMMA.
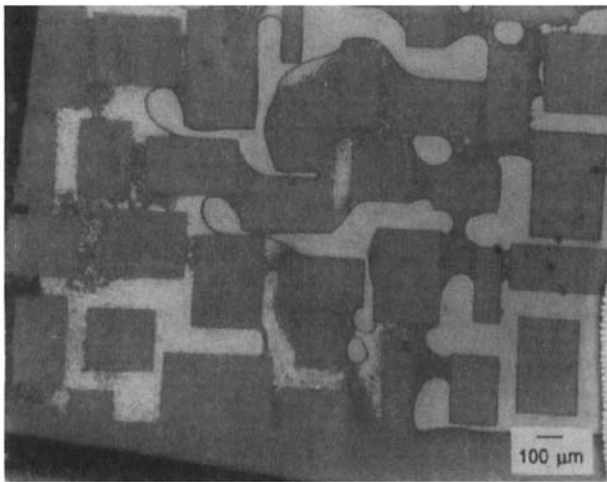
Direct observations of the distribution of preceramic polymers, PCS and VPS, in the 2-D model microstructures were made by optical microscopy at intermittent points during their decomposition in an inert atmosphere. Comparison of Figs. 4–7 indicates many differences exist between the microstructural

development that occurs during pyrolysis of these two organo-silicon polymers. As we will discuss, most of these differences can be related to the chemical changes that occur during the thermal decomposition of these polymers, which dictate whether they will exhibit thermoplastic or thermosetting behavior at a given temperature during decomposition.
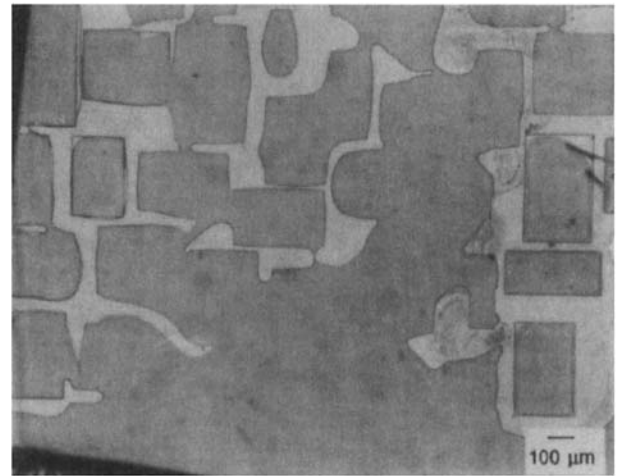
Figures 4 and 5 show optical micrographs (50× and 200×, respectively) of the 2-D samples filled with PCS and heated to various temperatures. At 25°C, the PCS-filled sample contained residual solvent, since it was dissolved in toluene to aid in the channel-filling process. Pores developed as the residual solvent
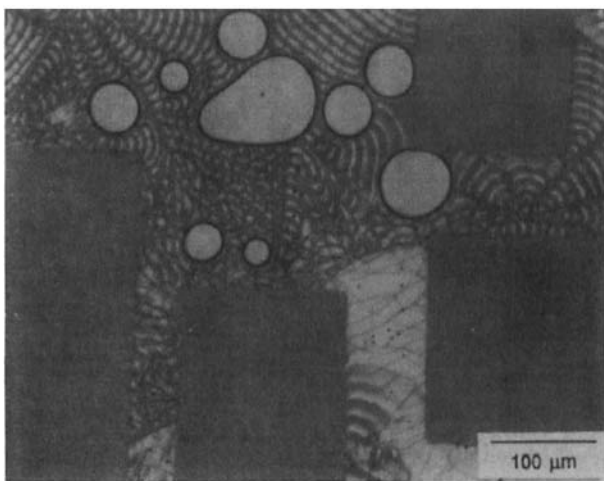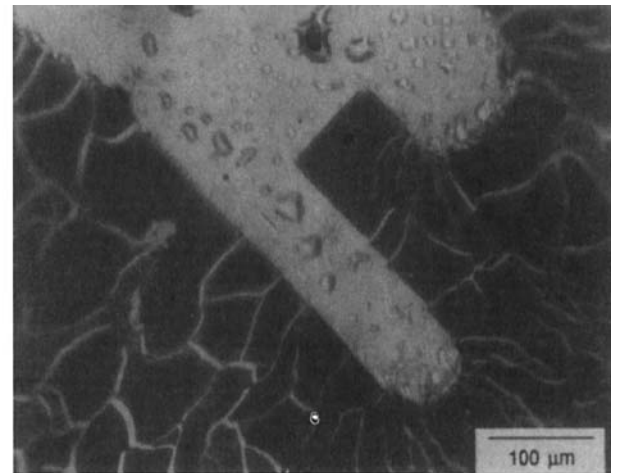
(A)

(B)

(C)

Fig. 4. Optical micrographs of PCS-filled 2-D samples heated in argon: (A) $T = 25°C$, (B) $T = 300°C$, and (C) $T = 550°C$.

(A)

(B)

Fig. 5. Optical micrographs of PSC-filled 2-D samples heated in argon: (A) $T = 300°C$ and (B) $T = 700°C$.

was removed, due to capillary redistribution of the remaining binder solution. Drying cracks formed in the regions around these developing pores. By 300°C, the solvent was completely removed, and regions containing drying cracks, open porosity, and entrapped bubbles were present in the microstructure.

The behavior of PCS in the temperature range between 25° and 300°C is similar to that observed for PMMA. It is believed that bubbles formed as the boiling point of toluene was exceeded. The drying cracks healed as PCS was heated above 350°C. Above this temperature, PCS softens and begins to flow
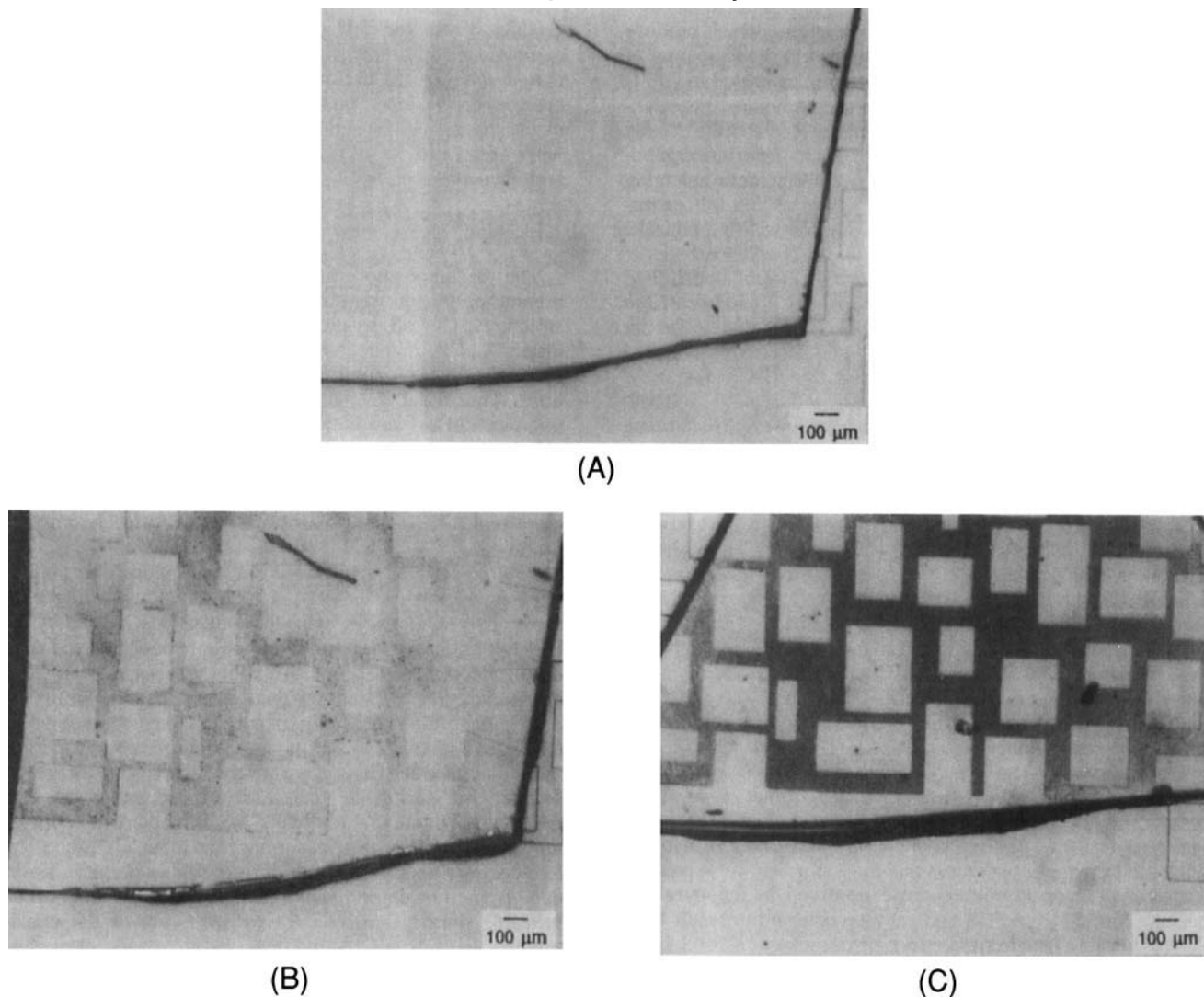
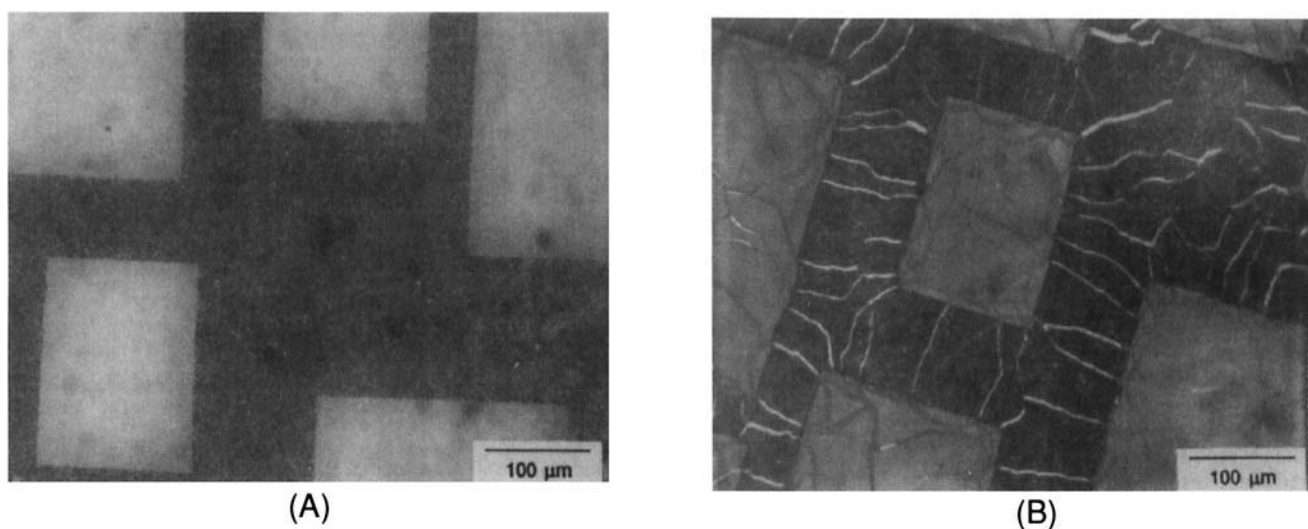**Fig. 6.** Optical micrographs of VPS-filled 2-D samples heated in argon: (A) $T = 25°C$, (B) $T = 450°C$, and (C) $T = 550°C$.

Fig. 7. Optical micrographs of VPS-filled 2-D samples heated in argon: (A) $T = 550°C$ and (B) $T = 700°C$.

as its viscosity decreases. Upon heating to 550°C (refer to Fig. 4(C)), the pore development was more extensive in the 2-D microstructure as compared to Fig. 4(B), due to the elimination of volatile decomposition products generated as PCS decomposed. Between 350° and 550°C, no major chemical changes

occur, since only low-molecular-weight polycarbosilanes are removed as PCS is heated.[14,18,22] In this temperature range, PCS is a thermoplastic and behaves similarly to PMMA, whose distribution can be influenced either by capillary forces or by bubble formation processes. As PCS is heated above 550°C, it

begins to cross-link via condensation reactions which produce hydrogen and methane and eventually lead to the formation of amorphous SiC and excess carbon. In samples heated to 700°C (refer to Fig. 5(B)), cracks formed to accommodate the reduction in volume associated with the material loss and the density increase associated with the transformation from an organometallic polymer to an amorphous covalent ceramic material. The pyrolyzed microstructure at 700°C was clearly inhomogeneous; it contained both empty pores and those filled with the desired pyrolysis product.

Figures 6 and 7 show optical micrographs (50× and 200×, respectively) of the 2-D samples filled with VPS and heated to various temperatures. At 25°C, VPS was distributed uniformly in these 2-D channels because, as a liquid precursor, it flowed easily to fill the pore space. Upon heating, VPS polymerizes between 140° and 250°C to form an infusible solid.[13,15] Schmidt et al.[23] showed that this solid forms as the result of cross-linking through vinyl polymerization. Some cross-linking through hydrosilylation reactions involving the Si-H and vinyl groups also occurs.

The first changes in the 2-D microstructure were observed between 450° and 550°C when the binder-filled channels began to darken and microporosity developed. In addition, cracks formed near the edges of the covered region, but they did not propagate into the interior regions. These changes are believed to result from the chemical rearrangement VPS undergoes in this temperature range. Schilling[13] and Schmidt et al.[23] have reported that an insertion reaction occurs between 350° and 550°C, in which the polysilane ($=$ SiMeSiMe $=$) rearranges to form a polycarbosilane, ($=$ Si(H)CH$_2$Si(H) $=$).

Upon heating above 550°C, VPS undergoes condensation reactions (similar to PCS) leading to the formation of amorphous SiC. In the pyrolyzed microstructure heated to 700°C (refer to Fig. 7(B)), the product was uniformly distributed within the channels, but cracks and microporosity were present. These cracks are similar to those observed in the pyrolysis product formed from PCS and are also believed to result from the volume decrease associated with material loss as well as the transformation from an organometallic polymer to an amorphous covalent ceramic material.

The main limitation of this study is that the "pore" dimensions in the 2-D model microstructures are approximately two orders of magnitude greater than the pores present in green ceramics formed from spherical, submicrometer powders. Another important difference is that the 2-D network of pores does not quantitatively represent the percolative transition of three-dimensional pore networks;[24] nonetheless, it appears reasonable to assume that the microstructural features on the scale of the particles are adequately represented by these model samples based on previous observations.[16,17] The binder is subjected to similar resistance to flow and capillary stress on the scale of the particles for both 3-D and 2-D networks; however, the magnitudes of both these forces depend on the representative particle size. The resistance to flow is proportional to the inverse of the particle size squared, while the driving force is proportional to the inverse of the particle size. Thus, the change in dimensionality and the larger absolute pore size must be considered when using these 2-D results to predict the behavior of binders within the porous network of ceramic green bodies.

The observations reported in this work provide basic guidelines which relate the physico-chemical properties of organic and preceramic binders to their resulting distribution in porous microstructures during decomposition. These results are significant for both types of binders. For organic binders, their distribution during thermolysis has important implications on the kinetics of binder removal. We have shown previously[25] that capillary redistribution of organic binders (i.e., plasticized poly(vinyl butyral)) in ceramic green tapes enhances their removal by greater than two orders of magnitude to the removal times predicted based solely on diffusion. For preceramic binders, the distribution which developed during pyrolysis had important implications on the final distribution of the ceramic pyrolysis product within the 2-D porous network. The general trends exhibited for thermoplastic and thermosetting polymers suggest that, to optimize the uniformity of the pyrolyzed product within ceramic components, one must first distribute them uniformly in the green microstructure and then form a cross-linked network prior to significant pyrolysis to "freeze" in this homogeneity.

IV. Conclusions

The decomposition of preceramic and, for comparison, organic polymers was directly observed in 2-D model microstructures. Our observations indicate the distribution of polymeric binders in ceramic green bodies is dependent on the binders' physico-chemical properties and processing conditions. The initial distribution of liquid binders in the model microstructures was homogeneous, while the distribution of solid polymers depended upon the method used to introduce them to these structures. In our work, for example, drying defects resulted, due to solvent evaporation when solid polymers (e.g., PCS) were dissolved in solvent to improve their fluidity.

Polymers which are fluid during decomposition may form bubbles, a source of defects, if volatile products are generated too quickly. Otherwise, their distribution is governed by capillary forces. In contrast, infusible polymers do not redistribute during decomposition due to capillarity, but instead develop microcracks as volatile material is eliminated. Similar processes were also observed to occur during preceramic polymer decomposition. However, the behavior of these polymers is more complex and diverges from the behavior of their organic counterparts during the final stage of decomposition. Rather than being completely removed, preceramic polymers produce a pyrolysis product that must transform to an amorphous covalent ceramic material of significantly higher density. The residue from preceramic polymers cross-links and becomes infusible during pyrolysis. The distribution of the pyrolysis product depends greatly on whether a large amount of decomposition occurs prior to the cross-linking step. In either case, cracks were observed to form in the pyrolyzed residues during the final stage of decomposition to accommodate the volume shrinkage associated with the elimination of volatile decomposition products and with the increasing density of the residue as it transformed to a ceramic material.

References

[1]R. W. Rice, "Ceramics from Polymer Pyrolysis, Opportunities, and Needs—A Materials Perspective," *Am. Ceram. Soc. Bull.*, **62** [8] 889–92 (1983).

[2]J. J. Rogers, J. Semen, and D. Y.-F. Yu, "Silicon Carbide and Silicon Nitride Structural Ceramics Derived from a Preceramic Polymer Binder," *Ceram. Eng. Sci. Proc.*, **10** [7–8] 833–36 (1989).

[3]K. B. Schwartz, D. J. Rowcliffe, and Y. D. Blum, "Microstructural Development in Si$_3$N$_4$/Polysilazane Bodies during Heating," *Adv. Ceram. Mater.*, **3** [4] 320–23 (1988).

[4]S. Yajima, T. Shishido, and K. Okamura, "SiC Bodies Sintered with Three-Dimensional Cross-linked Polycarbosilane," *Am. Ceram. Soc. Bull.*, **56** [12] 1060–63 (1977).

[5]M. S. Spotz, "Organosilicon Polymers as Preceramic Binders for Silicon Carbide"; Ph.D. Thesis. Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, January, 1990.

[6]B. E. Walker, Jr., R. W. Rice, P. F. Becher, B. A. Bender, and W. S. Coblenz, "Preparation and Properties of Monolithic and Composite Ceramics Produced by Polymer Pyrolysis," *Am. Ceram. Soc. Bull.*, **62** [8] 916–23 (1983).

[7]G. D. Soraru, F. Babonneau, and J. D. Mackenzie, "Structural Concepts of New Amorphous Covalent Solids," *J. Non-Cryst. Solids*, **106**, 256–61 (1988).

[8]R. P. Boisvert and R. J. Diefendorf, "Polymeric Precursor SiC Matrix Composites," *Ceram. Eng. Sci. Proc.*, **9**, 873–89 (1988).

[9]S. Yajima, "Special Heat-Resisting Materials from Organometallic Polymers," *Am. Ceram. Soc. Bull.*, **62** [8] 893–903 (1983).

[10]K. B. Schwartz and D. J. Rowcliffe, "Modeling Density Contributions in Preceramic Polymers/Ceramic Powder Systems," *J. Am. Ceram. Soc.*, **69** [5] C-106–C-108 (1986).

[11]B. C. Mutsuddy, "Use of Organometallic Polymer for Making Ceramic Parts by Plastic Forming Techniques," *Ceram. Int.*, **13**, 41 (1987).

[12]R. M. Laine and F. Babonneau, "Preceramic Polymer Routes to Silicon Carbide," *Chem. Mater.*, **5**, 260–79 (1993).

[13]C. L. Schilling, Jr., "Polymeric Routes to Silicon Carbide," *Br. Polym. J.*, **18** [6] 355–58 (1986).

[14]S. Yajima, Y. Hasegawa, J. Hayashi, and M. Imura, "Synthesis of Continuous Silicon Carbide Fibre with High Tensile Strength and High Young's Modulus, Part I. Synthesis of Polycarbosilane as Precursor," *J. Mater. Sci.*, **13**, 2569–76 (1978).

[15]D. Seyferth, G. H. Wiseman, and C. Prud'Homme, "A Liquid Silazane Precursor to Silicon Nitride," *J. Am. Ceram. Soc.*, **66** [1] C-13–C-14 (1983).

[16]M. J. Cima, J.A. Lewis, and A. D. Devoe, "Binder Distribution in Ceramic Greenware during Thermolysis," *J. Am. Ceram. Soc.*, **72** [7] 1192–99 (1989).

[17]J. A. Lewis and M. J. Cima, "Direct Observation of Binder Distribution Processes in 2-D Porous Networks during Thermolysis"; pp. 583–90 in Ceramic Transactions, Vol. 12, *Ceramic Powder Science III*. Edited by G. L. Messing, S. Hirano, and H. Hausner. American Ceramic Society, Westerville, OH, 1990.

[18]Y. Hasegawa, M. Imura, and S. Yajima, "Synthesis of Continuous Silicon Carbide Fibre, Part II. Conversion of Polycarbosilane Fibre into Silicon Carbide Fibres," *J. Mater. Sci.*, **15**, 720–28 (1980).

[19]B. G. Streetman, *Solid State Electronic Devices*. Prentice-Hall, Englewood Cliffs, NJ, 1980.

[20]P. Calvert and M. J. Cima, "Theoretical Models for Binder Burnout," *J. Am. Ceram. Soc.*, **73** [3] 575–79 (1990).

[21]C. Dong and H. K. Bowen, "Hot-stage Study of Bubble Formation during Binder Burnout," *J. Am. Ceram. Soc.*, **72** [6] 1082–87 (1989).

[22]Y. Hasegawa and K. Okamura, "Synthesis of Continuous Silicon Carbide Fibre, Part III. Pyrolysis Process of Polycarbosilane and Structure of the Products," *J. Mater. Sci.*, **18**, 3633–48 (1983).

[23]W. R. Schmidt, L. V. Interrante, R. H. Doremus, T. K. Trout, P. S. Marchetti, and G. E. Maciel, "Pyrolysis Chemistry of an Organometallic Precursor to Silicon Carbide," *Chem. Mater.*, **3**, 257–67 (1991).

[24]E. A. Holm and M. J. Cima, "Zero-Shrinkage Whisker Fraction in Ceramic Matrix–Ceramic Whisker Composites"; pp. 319–30 in *Processing Science of Advanced Ceramics*, Materials Research Society Symposium Proceedings, Vol. 155. Edited by I. A. Aksay, G. L. McVay, and D. R. Ulrich. Materials Research Society, Pittsburgh, PA, 1989.

[25]J. A. Lewis and M. J. Cima, "Diffusivities of Dialkyl Phthalates in Plasticized Poly(vinyl butyral) Films: Impact on Binder Thermolysis," *J. Am. Ceram. Soc.* **73** [9] 2702–707 (1990).   □