Light Weight Biomorphous Cellular Ceramics from Cellulose Templates

M. Singh and B.M. Yee[*]
QSS Group, Inc.
MS 106-5, NASA Glenn Research Center
Cleveland, OH 44135 (USA)

ABSTRACT

Bimorphous ceramics are a new class of materials that can be fabricated from the cellulose templates derived from natural biopolymers. These biopolymers are abundantly available in nature and are produced by the photosynthesis process. The wood cellulose derived carbon templates have three-dimensional interconnectivity. A wide variety of non-oxide and oxide based ceramics have been fabricated by template conversion using infiltration and reaction-based processes. The cellular anatomy of the cellulose templates plays a key role in determining the processing parameters (pyrolysis, infiltration conditions, etc.) and resulting ceramic materials. The processing approach, microstructure, and mechanical properties of the biomorphous cellular ceramics (silicon carbide and oxide based) have been discussed.

INTRODUCTION

In recent years, there has been a lot of interest in using biomimetic-based processing approaches to fabricate a variety of oxide and non-oxide based structural and functional materials [1]. Biomorphous ceramics from wood cellulose derived templates have attracted significant interest recently [2-16]. Wood consists of three major macromolecular constituents, namely cellulose, hemicellulose, and lignin. Typically, half of the dry weight of wood is cellulose, and hemicellulose and lignin comprise the other half (~25% each). The exact amount of these constituents changes with the specific nature and type of wood. These biopolymers have different molecular weights and serve distinct functions in the cellular anatomy. They are formed by the photosynthetic reaction within the needles or leaves of trees. The photosynthesis process uses sunlight to take carbon dioxide from air and convert it into oxygen and organic materials. The ceramic materials, fabricated via the pyrolysis and infiltration of wood cellulose-derived carbon templates, have very interesting microstructures and properties with numerous potential applications. Some of the potential applications of these materials include filters and catalyst supports, automotive components, tooling and wear components, armor, and lightweight porous ceramics for aerospace and ground based applications.

In previous publications, the microstructure and mechanical properties of a wide variety of ceramics made by the melt infiltration of liquid silicon into carbon templates have been reported [3-7]. The final ceramic materials show strong dependence on the density, microstructure, and cellular anatomy of starting wood precursors [3-16]. In addition, most of the final materials contain various amounts of residual silicon which has to be removed to obtain light weight cellular ceramics. In order to achieve the required porosity, post processing has to be carried out.

The main goal of this work was to evaluate the feasibility of fabricating porous silicon carbide structures using reactive gas infiltration. In addition, oxide sol infiltration has also been conducted to evaluate the feasibility of oxide and refractory carbide ceramics fabrication. In this paper, pyrolysis, ceramic fabrication approach, and final microstructures of a number of oxide and silicon carbide based ceramics have been reported.

EXPERIMENTAL PROCEDURES

In the present study, California North Coast redwood (*Sequoia sempervirens*) was investigated as a precursor carbon template for fabrication of biomorphous ceramics. Redwood is found only on the coasts of California and is among the tallest trees in the world. Most of the lumber is used for building and is moderately lightweight, moderately strong and stiff, and resistant to decay [17-18]. Blocks of redwood were dried in an oven at 135°C for several hours and then pyrolyzed up to 1000°C in an argon atmosphere. Pyrolysis is the decomposition of an organic material (in this case, the wood)

---

[*] Summer Intern, Currently at University of Illinois at Urbana Champaign, Urbana, Il

heated in an inert atmosphere to release volatiles, leaving behind a carbonaceous preform with cellular structures [19]. The dried wooden blocks measured 25 cm x 4 cm x 2 cm initially and after pyrolysis, porous carbon templates of about 0.25 cm thick were cut for infiltration.

A characterization of the pyrolysis process was performed using thermogravimetry (TG) and differential scanning calorimetry (DSC). These two techniques were executed simultaneously to measure the change in sample mass with temperature as well as changes in enthalpy that occur during pyrolysis. The Netzsch Thermische Analyse STA 409C was used in this process, with alumina powder as the reference sample. A small piece of redwood was heated in the thermal analyzer up to 1000°C in an inert atmosphere.

Several types of infiltration runs were carried out with different infiltrants to produce porous ceramics. Two types of oxides were used: low viscosity NYACOL® ZR50/20 pH 0.5 Zirconia sol and Nalco 1034A colloidal SiO_2 diluted with equal parts H_2O. The oxide infiltrations were performed in a Buehler Vacuum Impregnation chamber and dried in an oven at 90°C. Two different drying methods were employed for both infiltrants. After vacuum infiltration, the samples were either left in the infiltrant while drying or taken out and drained (dip coated) to determine the better method of producing a coated porous structure. They were then subjected to calcination at 400°C for one hour. This process was repeated up to 3 times, followed by firing at 1100°C for ZrO_2 and 1400°C for SiO_2. Finally, the samples were heat-treated at 1700°C for the ZrO_2 infiltrations and 1600°C for the SiO_2 infiltrations.

Porous silicon carbide was manufactured by infiltrating the carbon preforms with molten Si and heat treating the pieces to remove the excess silicon in a Centorr furnace, a process described in the literature [7, 11-12]. These samples were subsequently coated with either SiO_2 or ZrO_2 to create multiphase ceramics.

Biocarbon templates were also converted to porous SiC by a gas-phase reaction using silicon monoxide. The conversion of wood into cellular SiC has been achieved by a gas-phase reaction by E. Vogli, et al., but they used an equimolar mixture of Si/SiO_2 as their SiO(g) source [20]. In this research, Patinal® SiO pellets in a metastable solid state were used for infiltration because of the low vapor pressure required for vaporization. The reactive conversion of the carbon templates to porous silicon carbide occurred by the following reaction:

$$2C(s) + SiO(g) \rightarrow SiC(s) + CO(g)$$

The infiltration was performed in a Red Devil™ Webb #19 furnace up to 1500°C under vacuum for three hours. For infiltration, 4.0 g of SiO pellets were confined in a graphite ring placed in a graphite crucible. The preform was placed on top of the ring so that the infiltration can occur in the axial direction. A schematic of the setup is shown in Figure 1.

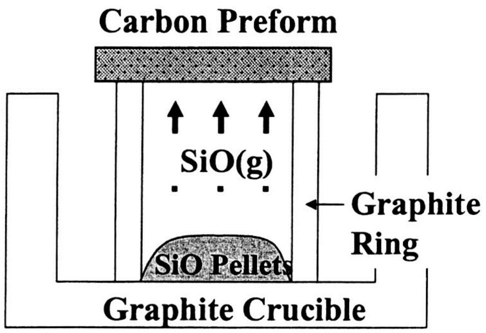

Fig. 1: Schematic of the SiO infiltration set-up.

The original pore structure of pyrolyzed redwood was analyzed by viewing a fresh fracture surface using the scanning electron microscope (SEM). Images were taken of two orientations of the carbon structures: perpendicular and parallel to the growth direction of the tree. The growth direction is equivalent to the longitudinal axis of the trunk. The SEM was also used for the analysis of the carbon preforms infiltrated with ZrO_2, SiO_2, and the porous SiC coated with ZrO_2 or SiO_2. Silicon and SiC were not readily distinguishable in the SEM images; therefore the samples infiltrated with only silicon were viewed with the light optical microscope (LOM). X-ray diffraction was also performed to verify the phases present in all of the infiltrated samples.

RESULTS AND DISCUSSION

Pyrolysis and Microstructure

The decomposition process during pyrolysis can be better understood by the thermal analysis curves. The TG and DSC curves are plotted on the same graph in Figure 2 to show that the decomposition occurred between 200°C and 500°C. The peaks in the DSC curve indicate that the reactions and gas evolutions during pyrolysis occur in the same temperature range as well as the endothermic and exothermic nature of the reactions. The initial loss of mass begins around 100°C, where any remaining moisture is removed and is completed by about 170°C. In the next step, the weight loss is attributed to the decomposition of hemicellulose and the release of volatiles from 190-280°C. A majority of the weight loss occurs due to the breakdown of cellulose and lignin between 280-500°C, leaving behind a carbonaceous preform. After 500°C, very little weight loss occurs, which can be seen in Figure 2 [14]. These two curves are quite similar for most types of wood, but DSC curves have slight variations from species to species due to varying chemical composition. Details on the reactions can be found in the literature [19].

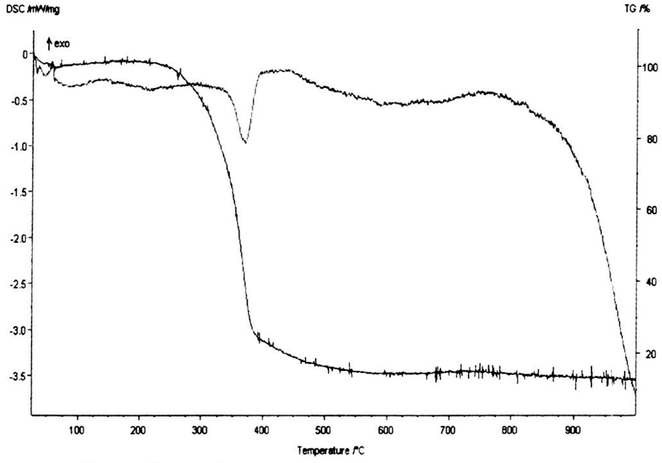

Fig. 2: Thermal analysis curves for redwood.

After pyrolysis, the blocks retained their original shape but underwent a change in volume. The total volume decreased by about 55%. The heating rates are crucial to the integrity of the pyrolyzed blocks, and each type of wood requires different rates that are dependent on the wood's density [21]. After the templates were cut, the average geometric density was 0.25 g/cm^3.

The microstructure of pyrolyzed redwood is shown in Figs 3a and b in the view that is perpendicular and parallel to the growth direction. Redwood is classified as softwood since it has a uniform cell structure. The cells provide easy access for infiltration fluids in the same way that they transport sap and water through the tree.

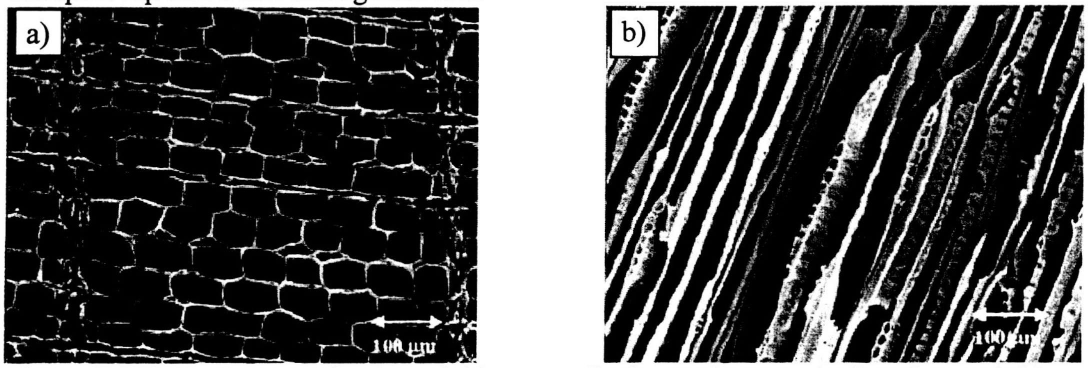

Figure 3. Microstructure of redwood (a) perpendicular to the growth direction and (b) parallel to the growth direction.

Oxide Infiltration

The microstructures of porous carbon templates after one ZrO_2 infiltration are shown in Figures 4a and b. As expected, the ZrO_2 accumulation increased as the number of infiltrations increased. This is also reflected in the densities of the samples after each infiltration (Figure 5). The mass gain from each infiltration was consistently about 0.3 g when the samples were left in the infiltrant while drying and the mass would decrease by 7% after firing. When the samples were dip-coated, the mass gain from infiltrations increased by 0.14 g each time, while the final mass after firing would decrease by varied amounts. Dip-coating the template seems to be the ideal method for drying when trying to obtain a porous structure coated with oxide. The x-ray diffraction results indicated that tetragonal ZrO_2 was present in the structures in Figure 6. As the number of infiltrations increased, the peak intensities increased. After heat treating at 1700°C, zirconium carbide was formed, verified by the x-ray diffraction scan in Figure 7. The resulting structure was extremely soft and weak, possibly due to the reaction and release of oxygen.

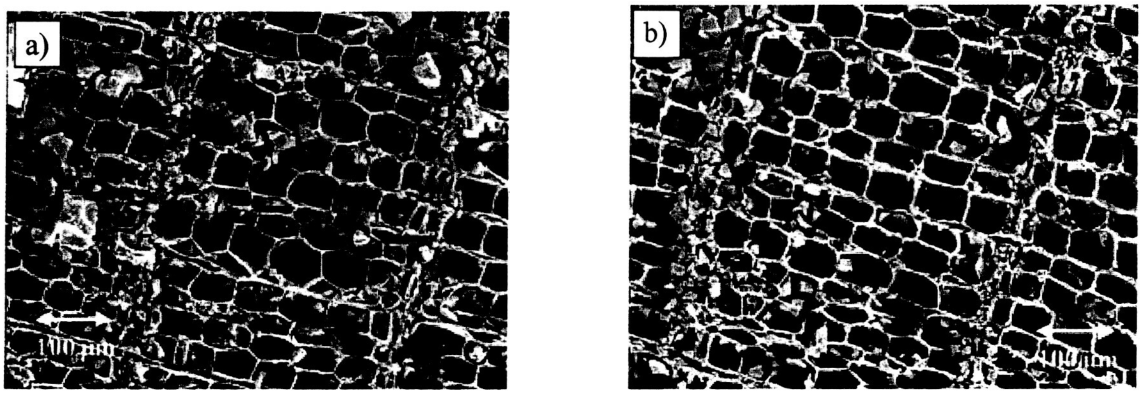

Figure 4. Microstructure of redwood infiltrated with ZrO_2 one time by (a) leaving the sample in the infiltrant while drying and by (b) dip coating.

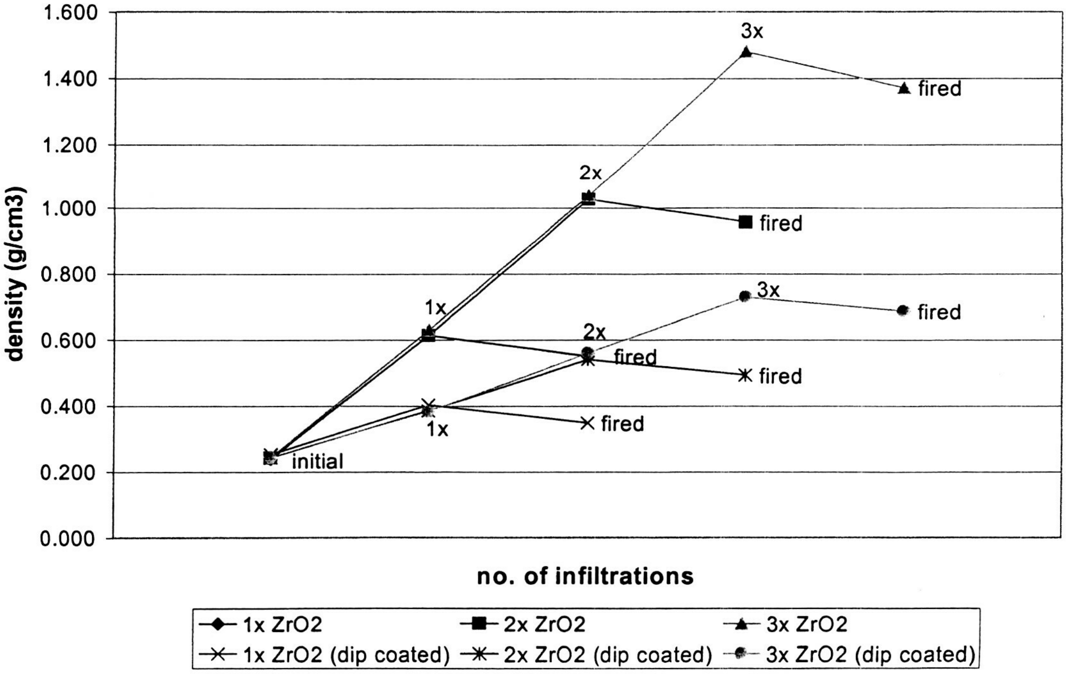

Figure 5. Plot of the densities of pyrolyzed redwood infiltrated with ZrO_2.

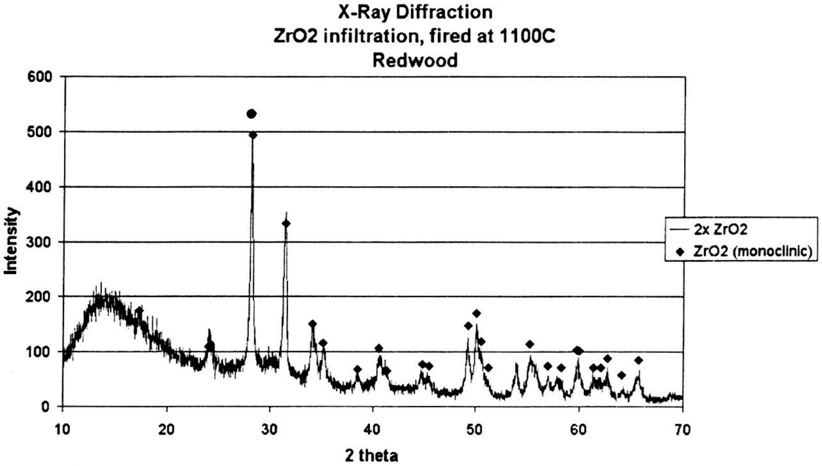

Figure 6. X-ray diffraction plot of pyrolyzed redwood infiltrated with ZrO_2 two times.

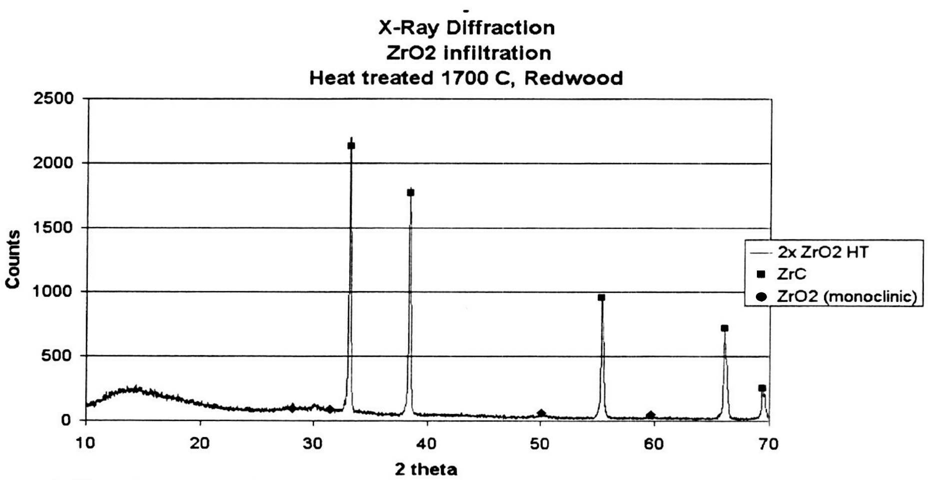

Figure 7. X-ray diffraction plot of pyrolyzed redwood infiltrated with ZrO_2 two times and heat-treated at 1700°C.

Figures 8 a and b show the microstructure of the preforms infiltrated with SiO_2 one time. There were no consistent increases in mass after each infiltration and they appeared to have accumulated the maximum amount of SiO_2 after the second infiltration when the preform was left in the infiltrant. After firing the sample with three infiltrations, a large amount of the carbon and SiO_2 came off and resulted in the dramatic decrease in density in Figure 9. Due to the relatively lower density of SiO_2, the overall mass gain and subsequent density increase was less than that exhibited by ZrO_2 infiltrations. The x-ray diffraction scans indicated that some SiC was produced from firing the SiO_2 infiltrated samples at 1400°C. However, after heat treating at 1600°C, three unknown broad peaks were observed in the scans.

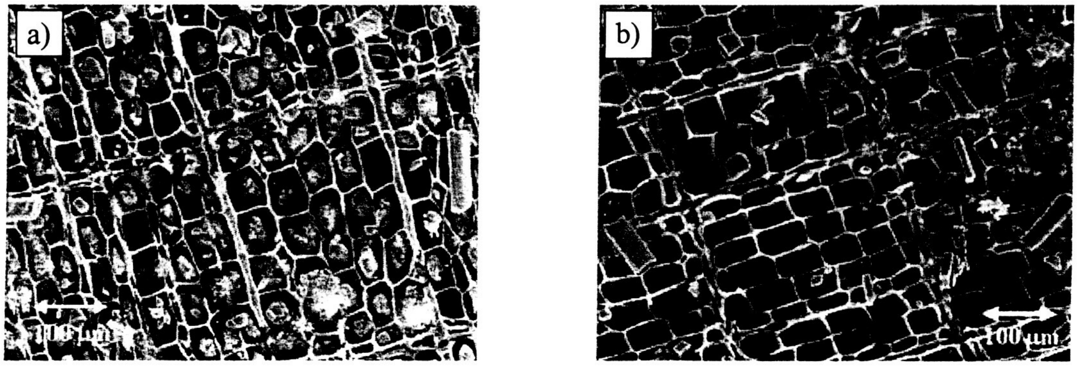

Figure 8. Microstructure of redwood infiltrated with SiO_2 one time by (a) leaving the sample in the infiltrant while drying and by (b) dip coating.

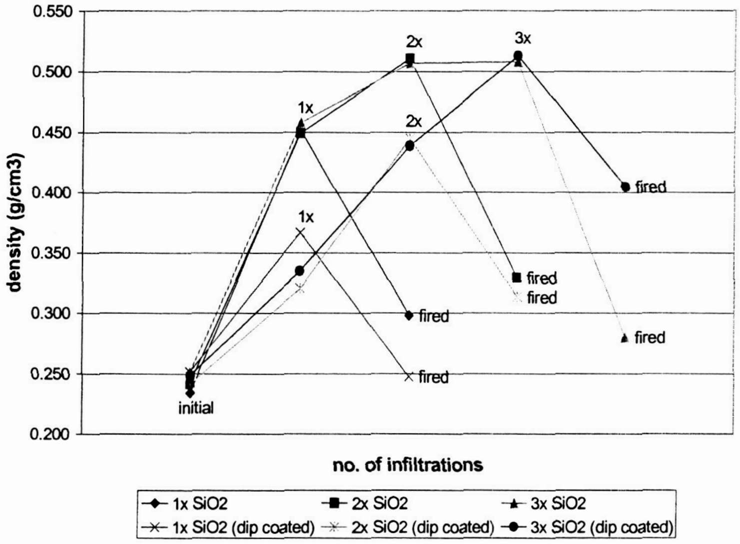

Figure 9. Plot of the densities of pyrolyzed redwood infiltrated with SiO_2

Melt Infiltration

A stronger biomorphous SiC was produced by the infiltration of molten silicon that reacted with the carbon to produce SiC. To remove the excess silicon remaining in the pores, the samples were heat treated at 1550°C for 4 hours. Figures 10a and b show the SiC structure before and after heat treatment. The dark gray outlines are SiC and the light gray areas are excess silicon remaining in the pores. After the initial infiltration, the geometric density was around 2.4 g/cm^3 and decreased to 2.0 g/cm^3 after heat treatment at 1550°C for 4 hours. The porous SiC samples were also coated with ZrO_2 and SiO_2. SEM observations indicate that the oxides crystallized on the SiC structure.

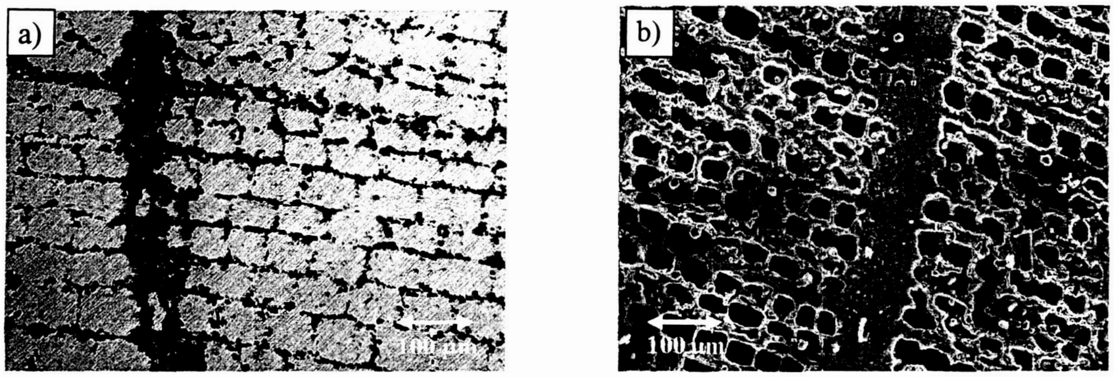

Figure 10. Microstructure of pyrolyzed redwood (a) infiltrated with molten silicon (LOM) and (b) heat-treated at 1550°C to remove excess silicon (SEM).

Gas Phase Infiltration

Porous SiC was also created by the infiltration of silicon in the gas phase. This was verified by the x-ray diffraction scan in Figure 11, which indicated that SiC was the only phase present. The density increased from 0.25 g/cm^3 to 0.30 g/cm^3 after the reaction. This biomorphic ceramic retained the original pore structure of redwood better than the molten silicon infiltrations. However, Figure 12 (b) shows that cracks formed in the struts due to the reaction of SiO with carbon and the release of CO.

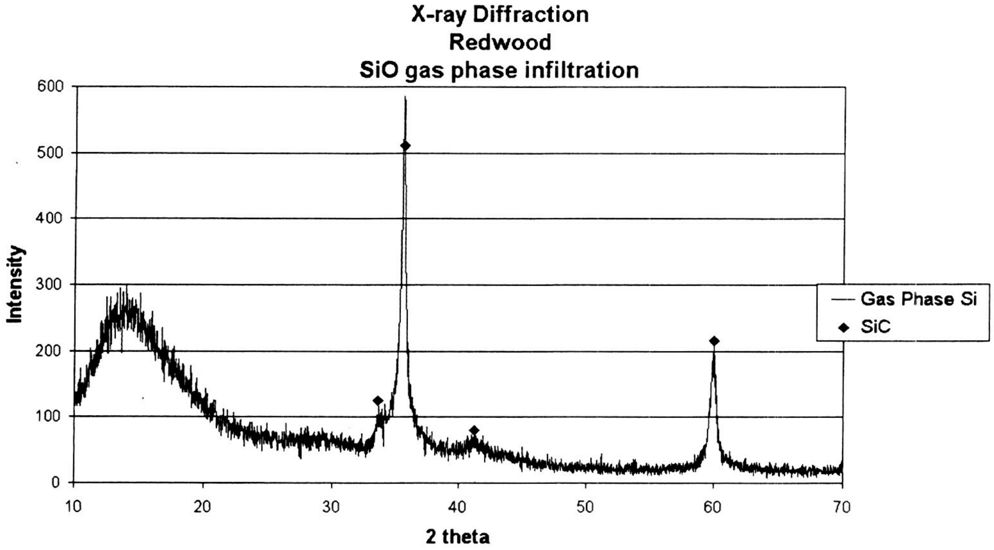

Figure 11. X-ray diffraction scan of biocarbon preform infiltrated with gaseous SiO to form SiC.

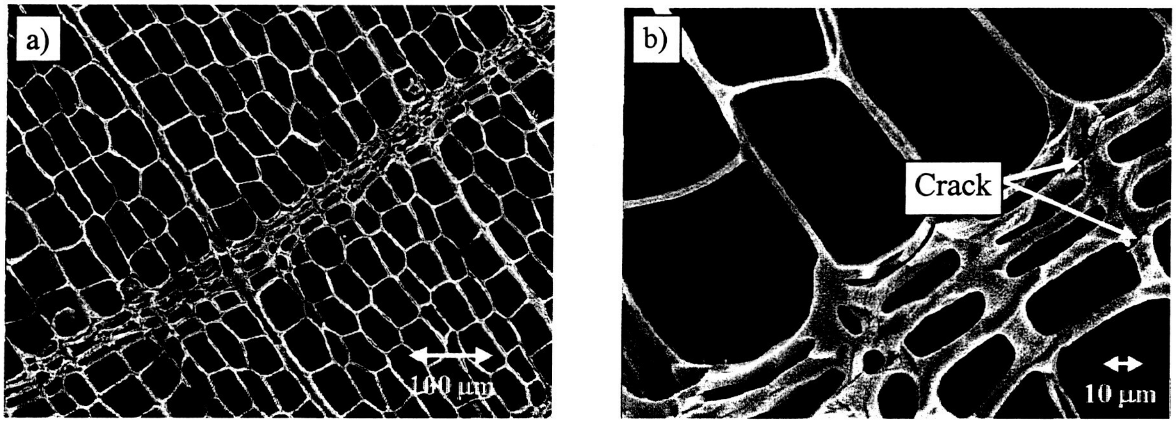

Figure 12. Microstructure of pyrolyzed redwood (a) infiltrated with gaseous SiO and (b) enlarged to show that cracks formed in the struts of the growth rings.

CONCLUSIONS

Highly porous, low-density SiC materials are achievable by reacting biomorphic carbon with gaseous silicon monoxide. Porous ceramics were also obtained by infiltrating carbon templates from wood precursors with ZrO_2, SiO_2, and molten silicon. These ceramic materials have a consistent microstructure that resembles the microstructure of the wood preform. The low cost, flexibility to fabricate complex shapes, and the availability of unique microstructures in nature makes this fabrication technique very promising for producing materials suitable for structural and lightweight applications.

ACKNOWLEDGEMENTS

The authors would like to thank Mr. Richard Dacek, Mr. Ralph Garlick, and Mr. John Setlock for their help in experimental work. The critical reviews of the manuscript by Mr. James D. Kiser are also acknowledged.

REFERENCES

1. Mark, J.E. and Calvert, P.D., Biomimetic, hybrid and in-situ composites, Mater. Sci. and Engg., 1994, C1, 159.
2. Ota, T., Takahashi, M., Hibi, T., Ozawa, M. and Suzuki, H., Biomimetic process for producing SiC wood, J. Am. Ceram. Soc., 1995, **78**, 3409-3411.

3. Greil, P., Lifka, T. and Kaindl, A., Biomorphic silicon carbide ceramics from wood: I and II, J. Eur. Ceram. Soc., 1998, **18**, 1961-1983.
4. Griel, P., Biomorphic ceramics from lignocellulosics, J. Eur. Ceram. Soc., 2001, 21 105-118.
5. Shin, D.-W., Park, S.S., Choa, Y.-H., and Niihara, K., Silicon/silicon carbide composites fabricated by infiltration of a silicon melt into charcoal, J. Am. Ceram. Soc., 1999, **82**, 3251-54.
6. Nagle, D.C. and Bryne, C.R., Carbonized wood and materials formed there from, US Patent 6, 124, 028, 2000.
7. Singh, M., Environment conscious ceramics (Ecoceramics), Ceram. Sci. Engg. Proc., 2000, 21 (4) 39-44.
8. Martínez-Fernández, J., Valera-Feria, F.M. and Singh, M., High temperature compressive mechanical behavior of biomorphic silicon carbide ceramics, Scripta Materialia, 2000, 43, 813-818.
9. Martínez-Fernández, J., Valera-Feria, F.M., Domínguez Rodríguez, A. and Singh, M., Microstructure and Thermomechanical characterization of bimorphic silicon carbide-based ceramics, pp. 733-740 in *Environment Conscious Materials; Ecomaterials*. Edited by H. Mostaghaci, Canadian Institute of Mining, Metallurgy, and Petroleum. Quebec, Canada, 2000.
10. Qiao, G., Ma, R., Cai, N., Zhang, C. and Jin, Z., Mechanical properties and microstructure of Si/SiC materials derived from native wood, Mater. Sci. Engg., 2002, A 323, 301-305.
11. Singh, M., Environment conscious ceramics (Ecoceramics)", NASA/TM-2001-210605, NASA Glenn Research Center, Cleveland, OH, 2001.
12. Singh, M., Ecoceramics: ceramics from wood, Advanced Materials and Processes, 2002, 160 (3), 39-41.
13. Singh, M., and Yee, Bo-Moon, "Environment Conscious, Biomorphic Ceramics from Pine and Jelutong Wood Precursors", Ceramic Engg. and Science Proceedings, Vol. 23, 4 (2002) 719-726.
14. Singh, M., and Salem, J.A., Mechanical properties and microstructure of biomorphic silicon carbide ceramics fabricated from wood precursors, J. Eur. Ceram. Soc., Vol. 22, N0. 14-15 (2002) 2709-2718.
15. Varela-Feria, F.M., Martinez-Fernandez, J., Arellano-Lopez, A.R., and Singh, M., Low density biomorphic silicon carbide: microstructure and mechanical properties, J. Eur. Ceram. Soc., Vol. 22, N0. 14-15 (2002) 2719-2726.
16. Munoz, A., Martinez-Fernandez, J., and Singh, M., High temperature compressive mechanical behavior of joined biomorphic silicon carbide ceramics, J. Eur. Ceram. Soc., Vol. 22, N0. 14-15 (2002) 2727-2734.
17. *Wood Handbook- Wood as an Engineering Material*, Forest Products Laboratory, USDA Forest Service, Madison, WI, General Technical Report, FPL-GTR-113, 1999.
18. *Concise Encyclopedia of Wood and Wood-Based Materials*, A.P. Scniewind, Ed., Pergamon Press, NY, 1989.
19. Sinha, S., Jhalani, A., Ravi, M.R., and Ray, A., Modeling of pyrolysis in wood: a review, J. Solar Energy Society of India, 2000, 10 (1) 41-62.
20. E. Vogli, J. Mukerji, C. Hoffman, R. Kladny, H. Sieber, and P. Greil. "Conversion of Oak to Cellular Silicon Carbide Ceramic by Gas-Phase Reaction with Silicon Monoxide." J. Am. Ceram. Soc., Vol. 84, No. 6, 2001, pp. 1236-1240.
21. C.E. Byrne, D.C. Nagle. "Carbonization of Wood for Advanced Materials Applications." Carbon Vol. 35, No. 2, 1997, pp. 259-266.