

NASA/CR—2001-211202



Environment Conscious Ceramics (Ecoceramics): An Eco-Friendly Route to Advanced Ceramic Materials

M. Singh
QSS Group, Inc., Cleveland, Ohio

December 2001

The NASA STI Program Office . . . in Profile

Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program Office plays a key part in helping NASA maintain this important role.

The NASA STI Program Office is operated by Langley Research Center, the Lead Center for NASA's scientific and technical information. The NASA STI Program Office provides access to the NASA STI Database, the largest collection of aeronautical and space science STI in the world. The Program Office is also NASA's institutional mechanism for disseminating the results of its research and development activities. These results are published by NASA in the NASA STI Report Series, which includes the following report types:

- **TECHNICAL PUBLICATION.** Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA's counterpart of peer-reviewed formal professional papers but has less stringent limitations on manuscript length and extent of graphic presentations.
- **TECHNICAL MEMORANDUM.** Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.
- **CONTRACTOR REPORT.** Scientific and technical findings by NASA-sponsored contractors and grantees.

- **CONFERENCE PUBLICATION.** Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or cosponsored by NASA.
- **SPECIAL PUBLICATION.** Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.
- **TECHNICAL TRANSLATION.** English-language translations of foreign scientific and technical material pertinent to NASA's mission.

Specialized services that complement the STI Program Office's diverse offerings include creating custom thesauri, building customized data bases, organizing and publishing research results . . . even providing videos.

For more information about the NASA STI Program Office, see the following:

- Access the NASA STI Program Home Page at <http://www.sti.nasa.gov>
- E-mail your question via the Internet to help@sti.nasa.gov
- Fax your question to the NASA Access Help Desk at 301-621-0134
- Telephone the NASA Access Help Desk at 301-621-0390
- Write to:
NASA Access Help Desk
NASA Center for AeroSpace Information
7121 Standard Drive
Hanover, MD 21076

NASA/CR—2001-211202



Environment Conscious Ceramics (Ecoceramics): An Eco-Friendly Route to Advanced Ceramic Materials

M. Singh
QSS Group, Inc., Cleveland, Ohio

Prepared for the
11th International Symposium on Ultra-High Temperature Materials
sponsored by the Japan Ultra High Temperature Materials Institute
Tajimi, Japan, September 6-7, 2001

Prepared under Contract NAS3-00145

National Aeronautics and
Space Administration

Glenn Research Center

December 2001

Acknowledgments

The author would like to thank Mr. Richard Dacek for help in experimental work and Mr. J. Douglas Kiser for critically reading the manuscript. Technical assistance of Dr. Jon Salem in performing fracture toughness measurements is also acknowledged.

Available from

NASA Center for Aerospace Information
7121 Standard Drive
Hanover, MD 21076

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22100

Available electronically at <http://gltrs.grc.nasa.gov/GLTRS>

Environment Conscious Ceramics (Ecoceramics): An Eco-friendly Route to Advanced Ceramic Materials

M. Singh
QSS Group, Inc.
Cleveland, Ohio 44135
msingh@grc.nasa.gov

Abstract

Environment conscious ceramics (Ecoceramics) are a new class of materials, which can be produced with renewable natural resources (wood) or wood wastes (wood sawdust). This technology provides an eco-friendly route to advanced ceramic materials. Ecoceramics have tailorable properties and behave like ceramic materials manufactured by conventional approaches. Silicon carbide-based ecoceramics have been fabricated by reactive infiltration of carbonaceous preforms by molten silicon or silicon-refractory metal alloys. The fabrication approach, microstructure, and mechanical properties of SiC-based ecoceramics are presented.

Introduction

Since the dawn of human civilization, there has always been a delicate balance between the various activities of mankind that utilize resources while expanding the human frontiers and the need to have minimum influence on the ecosystem. The first two hundred years of the industrial revolution essentially solved the problem of production. However, the massive production of goods also generated tremendous amounts of by-products and wastes. In the new millennium, in order to sustain a healthy life in harmony with nature, it will be extremely important to develop various materials, products, and processes that minimize any harmful influence on the environment.

Ceramics have continued to play a key role in revolutionizing industry. Silicon carbide-based ceramics have been utilized since the beginning of the 20th century as heating elements. However, tremendous growth in research and development activities in this area has occurred in the last fifty years. These materials have high strength, good oxidation and corrosion resistance, high thermal conductivity, and good thermal shock resistance. A number of manufacturing approaches have been used to fabricate these materials including hot pressing/hot isostatic pressing, sintering, reaction bonding/reaction forming, polymer pyrolysis, and chemical vapor deposition. Hot pressing and sintering approaches require significant consumption of energy while CVD and polymer pyrolysis techniques generate liquid and gaseous chemical by-products. The reaction bonding technique typically utilizes silicon carbide and carbon powder combined with polymer binders while resin/pore former derived preforms are used in the reaction forming

techniques. The production of silicon carbide powder is energy consuming. The pyrolysis of resin systems produces chemical by-products, which have to be collected for disposal.

Environment conscious ceramics (Ecoceramics) are a new class of materials, which can be fabricated with renewable resources (wood) and wood waste material (wood sawdust). Wood is a "lignocellulosic" material 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. Wood has been known to be one of the best and most intricate engineering materials created by nature and known to mankind [1–2]. In addition, natural woods of various types are available throughout the world. On the other hand, wood saw dusts are generated in abundant quantities by sawmills. The environment conscious ceramic materials, fabricated via the pyrolysis and infiltration of natural wood-derived preforms, have tailorable properties with numerous potential applications. The experimental studies conducted to date on the development of materials based on biologically derived structures indicate that these materials behave like ceramic materials manufactured by conventional approaches [3–9]. These structures have been shown to be quite useful in producing porous or dense materials having various microstructures and compositions.

In this study, natural wood has been used to fabricate SiC ceramics through a process of pyrolysis and silicon infiltration as described in previous publications [7 and 10]. The natural internal channels of wood allow the silicon infiltration, and result in a network of SiC after the reaction with carbon. In this work, the microstructure and mechanical properties of SiC fabricated from African Bubinga wood is presented in detail.

Ecoceramics Technology

A schematic of the Ecoceramics fabrication process is given in Fig. 1. The wood pieces were dried in an oven and pyrolyzed in a furnace up to 1000 °C in a flowing argon atmosphere to create carbonaceous preforms. The weight and dimensional changes were recorded after pyrolysis. The pyrolyzed preforms were infiltrated with silicon in a graphite element furnace under vacuum. The infiltration time and temperature depend on the melting point of the infiltrants and dimensions and properties of the preforms. For silicon infiltration, porous preforms were infiltrated at 1450 °C for 30 minutes. A wide variety of wood specimens (softwood and hardwood) and wood saw dusts were used for the fabrication of carbonaceous preforms. These results will be reported elsewhere [11–12]. The ecoceramic technology has been used to fabricate complex shaped parts from the machined wood or carbon specimens shown in Fig. 2.

Although a wide variety of ceramic materials were fabricated using this approach, detailed microstructural characterization and the mechanical properties of SiC fabricated by the infiltration of molten silicon into a pyrolyzed African Bubinga wood preform will be presented. After the infiltration, specimens were machined for microstructural and mechanical property studies. Samples were cross-sectioned and polished for metallographic studies. Microstructural characterization was performed on the as-fabricated and tested samples using optical and scanning electron microscopy. The final product has a cellular structure with elongated areas of SiC and Si.

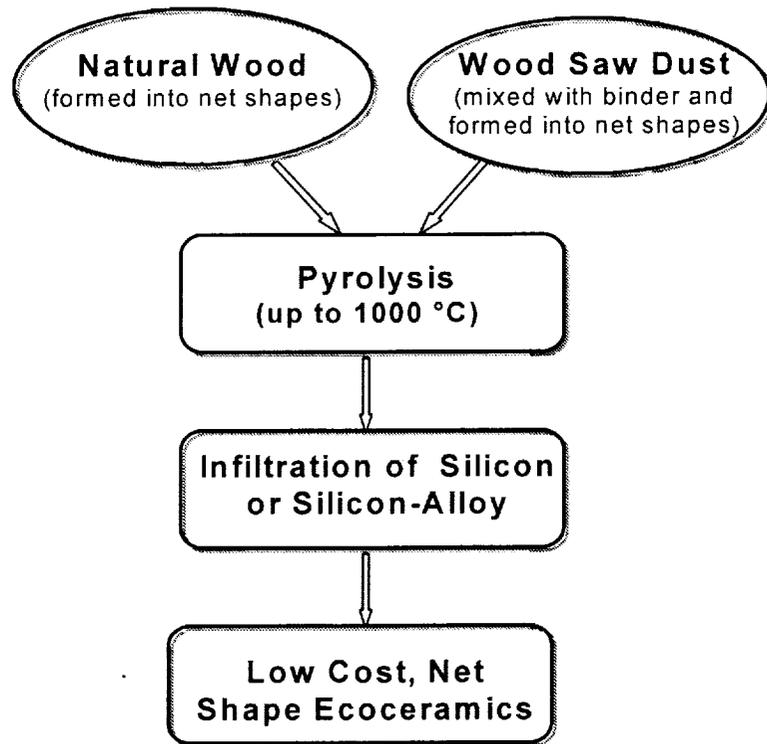


Fig. 1: Schematic of the Ecoceramics fabrication process.

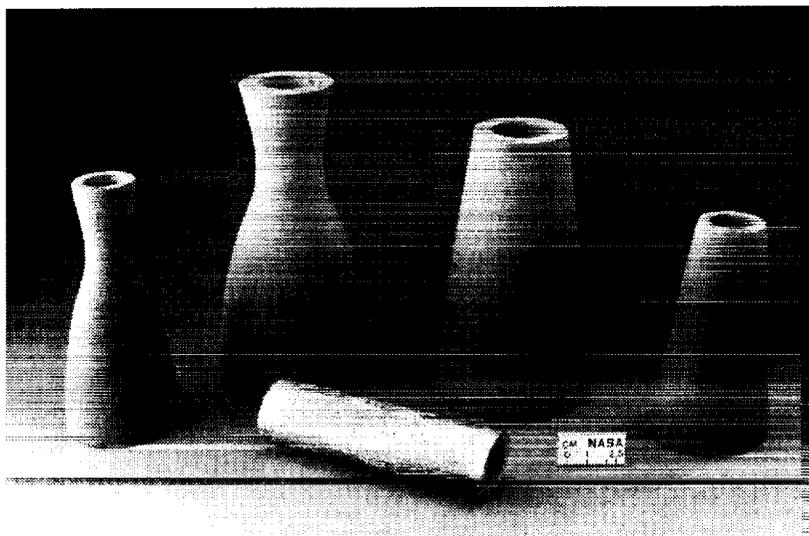


Fig. 2: Photograph showing different shapes fabricated by ecoceramics technology.

Ecoceramics Properties

A wide variety of wood (softwood and hardwood) specimens were pyrolyzed and infiltrated in this program. Scanning electron micrographs of fracture surfaces of some wood-derived porous preforms are given in Fig. 3. These micrographs show a wide variation in the microstructure and density of the carbonaceous preforms, due to structural differences between various types of wood. The variation of preform microstructure and properties can be utilized to produce final materials with controlled microstructure, composition, and phase morphologies. The pyrolysis shrinkage, composition, and final density of preforms vary greatly depending on the type of wood. The preform density and microstructure control the composition and microstructure of final materials.

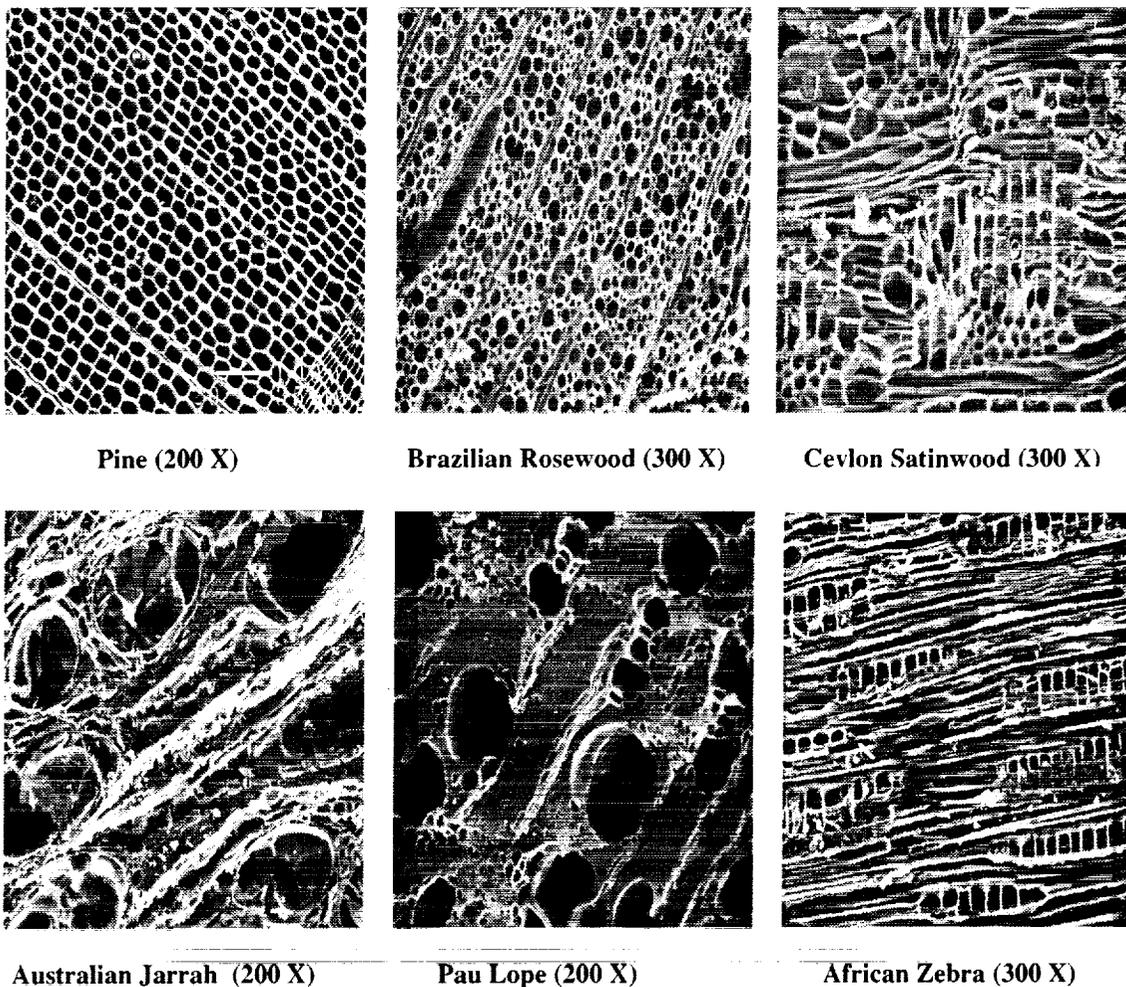


Fig. 3: Microstructure of porous carbon obtained from the pyrolysis of different types of wood.

Microstructure and mechanical properties of a wide variety of wood specimens have been investigated and reported in other publications [7–12]. The African Bubinga wood is from the Leguminosae family of woods and has other common names as Essingang (Cameroon), Ovang,

Kevazingo (Gabon), and Waka (Zaire) [13]. The wood species of this group are found in equatorial Africa from Nigeria through Cameroon to the Congo region. It is found near rivers and lake shores and swampy inundated forests. The tree height is approximately 130 to 150 feet and typically trunk diameters are three to six feet. It is heartwood pink or red brown wood with fine and even texture, with straight or interlocked grains, with a density of 0.65 to 0.78 gm/cm³.

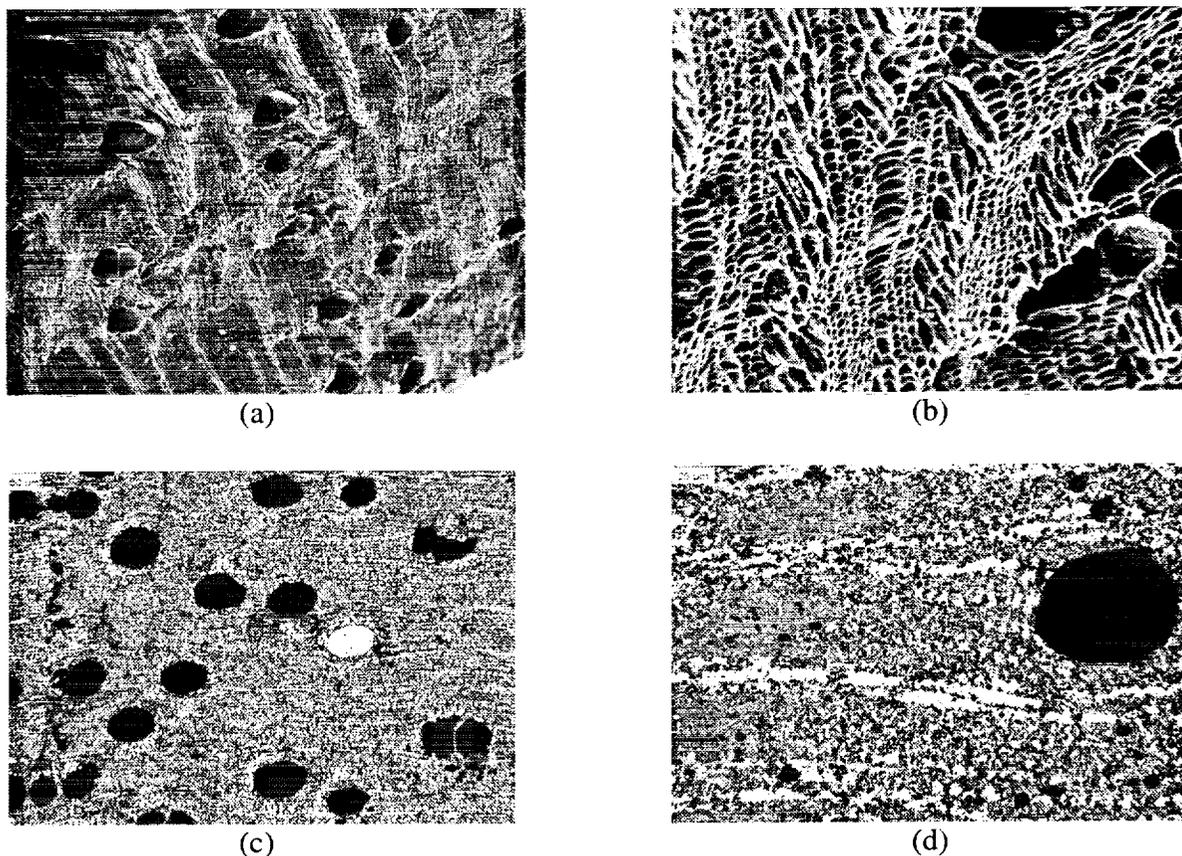


Fig. 4: SEM micrograph of (a) and (b) porous carbon performs (50 and 200 X); (c) and (d) as-fabricated SiC (50 and 200 X) from African Bubinga (white: Si, gray: SiC, black: pores).

Scanning electron micrographs of fracture surfaces of pyrolyzed African Bubinga wood are shown in Figs. 4 (a) and (b). This microstructure shows a heterogeneous pore size distribution (large and small pores). Microstructures of the silicon carbide based materials obtained after silicon infiltration are shown in Figs. 4 (c) and (d). In these micrographs, silicon carbide regions are gray and silicon regions are white. This material also contains porosity (black regions). The density of silicon carbide ceramics characterized in this study was 2.54 gm/cm³.

After the melt infiltration, flexure bars were machined from the infiltrated plates. Four-point flexural strength testing was carried out using MIL-STD-1942 (MR) configuration B specimens with 20 mm inner and 40 mm outer spans. Flexure tests were conducted at room temperature,

800, 1200, and 1300 °C in air. Three specimens were tested at each temperature. After testing, fracture surfaces were examined by optical and scanning electron microscopy to identify the failure origins. The room and high temperature flexural strengths of the as-machined materials are shown in Fig. 5. The average flexural strength of as-machined specimens was 213.3 ± 26.6 MPa (RT), 227.2 ± 9 MPa (800 °C), 217.7 ± 8.3 MPa (1200 °C), and 205.7 ± 17.9 MPa (1300 °C). The flexure strength has been compared with a commercially available reaction bonded silicon carbide material (Cerastar RB-SiC). The flexural strength data shows that there is no significant strength loss in these materials up to 1300 °C and it is comparable to commercial RB-SiC materials.

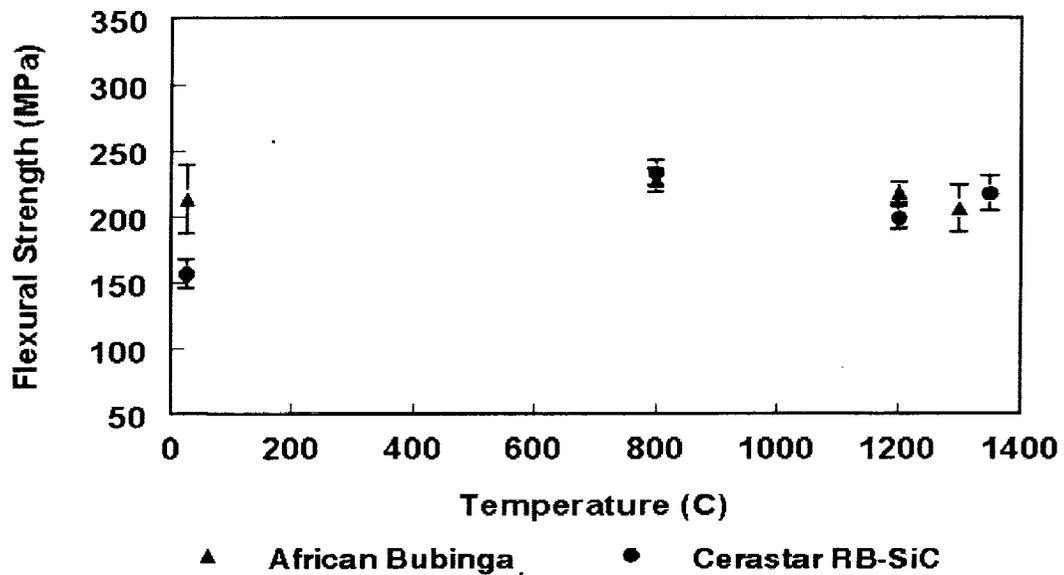


Fig. 5: Flexural strength of ecoceramic made from African Bubinga as a function of temperature.

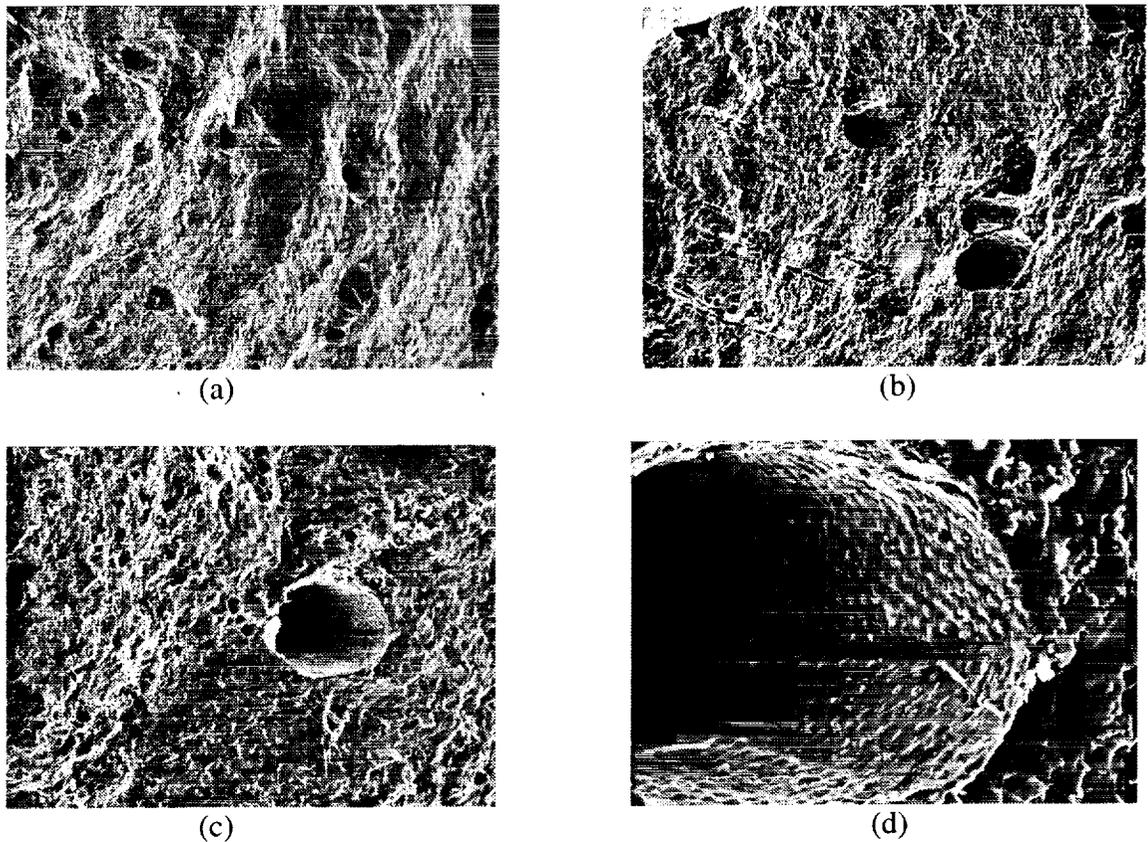


Fig. 6: SEM micrographs showing the fracture surfaces of specimens tested at room temperature (a) 50X and (b) 200X; and at 1300 °C (c) 200X and (d) 800X.

The SEM fractographs of flexure tested specimens are shown in Figs. 6(a)–(d). The fractographs show interesting features. The porosity in these materials was believed to act as the failure origins. Some of these pores were also filled with silicon (Fig. 6(b)). Fractographs of specimens tested at 1300 °C (Fig. 6(d)) show the internal surfaces of pores.

Two of the test methods standardized by ASTM [14] were applied in an attempt to measure the fracture toughness of these materials: the CN (chevron-notch) and the SEPB (Single-Edged-Pre-cracked-Beam) methods. Neither method yielded valid results. In the case of the chevron-notch, stable crack extension, which is required for a valid result, was not obtained. For the SEPB method, the Vickers's indentations that are used to start the through-section pre-crack did not emanate starter-cracks from the indentation corners. This is likely due to the porosity of the material. As a result, a through-section pre-crack for fracture toughness measurement could not be generated without failing the test specimen. Due to the limited number of specimens available, the CN and SEPB techniques could not be investigated in detail in order to determine a solution. Although C 1421 [14] contains a third test method (the surface crack in flexure), the lack of starter-crack formation at indentation sites implied that the technique would not work, and it was not pursued.

In order to measure the fracture toughness, the SEVNB (Single-Edged-V Notched-Beam) method was employed [15]. This technique involves cutting a narrow notch with a small root radius (< 0.020 mm) into a flexure test specimen. The notch tip is sufficiently sharp to produce fracture toughness measurements in general agreement with techniques employing sharp cracks for some ceramics [15]. The fracture toughness of the ecoceramic made from African Bubinga measured 2.6 ± 0.5 MPa m^{1/2} (3). Casual observation of the specimen indicated an increase in the fracture toughness with a decrease in the porosity visible on the test specimen surface. The standard deviations are relatively large and may be a result of density variations in the materials. The fracture toughness values for this material are similar to that measured with ASTM C 1421 for other types of silicon carbide [16].

Conclusions

Environment conscious SiC-based ceramics have been fabricated from renewable natural resources. These ceramic materials have a consistent microstructure that resembles the microstructure of the wood preform. They behave as a silicon carbide-based cellular solid, reaching very high strengths. 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.

References

- [1] "Wood Handbook- Wood as an Engineering Material," Forest Products Laboratory, USDA Forest Service, Madison, WI, General Technical Report, FPL-GTR-113 (1999).
- [2] "Concise Encyclopedia of Wood and Wood-Based Materials," A.P. Scniewind, Ed., Pergamon Press, NY (1989)
- [3] J.E. Mark and P.D. Calvert, "Biomimetic, Hybrid and In-situ Composites," Mater. Sci. and Engg., C1, 159 (1994).
- [4] T. Ota, M. Takahashi, T. Hibi, M. Ozawa, and H. Suzuki, "Biomimetic Process for Producing SiC Wood," J. Am. Ceram. Soc., **78**, 3409 (1995).
- [5] P. Greil, T. Lifka, and A. Kaindl, "Biomorphic Silicon Carbide Ceramics from Wood : I and II, J. Europ. Ceram. Soc., **18**, 1961 (1998).
- [6] D.-W. Shin, S.S. Park, Y.-H. Choa and K. Niihara, "Silicon/Silicon Carbide Composites Fabricated by Infiltration of a Silicon Melt into Charcoal," J. Am. Ceram. Soc., **82**, 3251 (1999).
- [7] M. Singh, "Environment Conscious Ceramics (Ecoceramics)," Ceram. Sci. Engg. Proc., 21 [4] 39-44 (2000).
- [8] J. Martínez-Fernández, F.M. Valera-Feria and M. Singh, "High Temperature Compressive Mechanical Behavior of Biomorphic Silicon Carbide Ceramics," Scripta Materialia, 43 813-818 (2000).
- [9] J. Martínez-Fernández, F.M. Valera-Feria, A. Domínguez Rodríguez and M. Singh, "Microstructure and Thermomechanical Characterization of Biomorphic 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] M. Singh, "Environment Conscious Ceramics (Ecoceramics)", NASA/TM—2001-210605, NASA Glenn Research Center, Cleveland, OH.
- [11] M. Singh, Structural Ceramics and Ceramic Composites for High Temperature Applications, Engineering Foundation Conference, Seville, Spain, 2001.
- [12] M. Singh, Unpublished work (2001).
- [13] Wood Technical Fact Sheet, USDA Forest Service, Madison, WI.
- [14] ASTM C 1421-99 "Standard Test Method for the Determination of Fracture Toughness of Advanced Ceramics at Ambient Temperatures," J.A Salem, M.G. Jenkins and G.D. Quinn under jurisdiction of ASTM committee C 28 on Advanced Ceramics, in Annual Book of ASTM Standards, V. 15.01, ASTM, West Conshohocken, Pennsylvania (2000).
- [15] J.J. Kübler, "Fracture Toughness of Ceramics using the SEVNB Method: From a Preliminary Study to a Standard Test Method," *Fracture Resistance Testing of Monolithic and Composite Brittle Materials, ASTM STP 1409*, J. A. Salem, G. D. Quinn, and M. G. Jenkins, Eds., American Society for Testing and Materials, West Conshohocken, PA, 2002.
- [16] J.A. Salem, L. Ghosn, M.G. Jenkins and G.D. Quinn, "Stress Intensity Factor Coefficients for Chevron-Notched Flexure Specimens and a Comparison of Fracture Toughness Methods," *Ceramic Engineering and Science Proceedings*, Vol. 20, No. 3, pp. 503-512 (1999).

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (<i>Leave blank</i>)	2. REPORT DATE December 2001	3. REPORT TYPE AND DATES COVERED Final Contractor Report	
4. TITLE AND SUBTITLE Environment Conscious Ceramics (Ecoceramics): An Eco-Friendly Route to Advanced Ceramic Materials		5. FUNDING NUMBERS WU-251-30-07-00 NAS3-00145	
6. AUTHOR(S) M. Singh		8. PERFORMING ORGANIZATION REPORT NUMBER E-13048	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) QSS Group, Inc. 21000 Brookpark Road Cleveland, Ohio 44135		10. SPONSORING/MONITORING AGENCY REPORT NUMBER NASA CR-2001-211202	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Washington, DC 20546-0001		11. SUPPLEMENTARY NOTES Prepared for the 11th International Symposium on Ultra-High Temperature Materials sponsored by the Japan Ultra High Temperature Materials Institute, Tajimi, Japan, September 6-7, 2001. Project Manager, S.R. Levine, Materials Division, NASA Glenn Research Center, organization code 5130, 216-433-3276.	
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unclassified - Unlimited Subject Category: 27 Available electronically at http://gltrs.grc.nasa.gov/GLTRS This publication is available from the NASA Center for AeroSpace Information, 301-621-0390.		12b. DISTRIBUTION CODE	
13. ABSTRACT (<i>Maximum 200 words</i>) Environment conscious ceramics (Ecoceramics) are a new class of materials, which can be produced with renewable natural resources (wood) or wood wastes (wood sawdust). This technology provides an eco-friendly route to advanced ceramic materials. Ecoceramics have tailorable properties and behave like ceramic materials manufactured by conventional approaches. Silicon carbide-based ecoceramics have been fabricated by reactive infiltration of carbonaceous preforms by molten silicon or silicon-refractory metal alloys. The fabrication approach, microstructure, and mechanical properties of SiC-based ecoceramics are presented.			
14. SUBJECT TERMS Ecoceramics; Melt infiltration; Preforms; Wood; Silicon carbide		15. NUMBER OF PAGES 15	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT