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MICROWAVE SINTERING OF CONTINUOUS ZIRCONIA CERAMIC FIBERS

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ABSTRACT

Continuous yttria-stabilized zirconia ceramic fibers approximately 10-15 μm in diameter have been rapidly sintered by pulling them through a tuned, 2.45 GHz single-mode TE_{103} microwave cavity in ambient air. The resulting fibers were analyzed by X-ray diffraction, scanning electron microscopy, and single-filament tensile tests. They were found to be unsplit, to have a submicron grain structure and a tetragonal crystal structure, and to exhibit considerable strength and flexibility.

INTRODUCTION

Microwave sintering of continuous zirconia ceramic fibers in single-mode cavities is an attractive alternative to conventional resistance heating. Potential advantages of such microwave processing include its cold wall nature, speed, small size of equipment needed, ability to heat just a small portion of the total fiber length at any given time, possibility of precise control of input power vs. fiber temperature via optical sensors, and elimination of the need for massive and costly thermal insulation. The potential utility of continuous zirconia fibers is significant. Prospective applications include catalyst supports, refractories, structural ceramic composites, woven and nonwoven ultrahigh-temperature fabrics, and high-temperature filtration.

Although microwave processing of ceramic fibers offers potentially attractive advantages compared with conventional thermal processing, there are potential experimental difficulties which must be confronted. For the aluminum oxide-based ceramic filaments previously investigated [1,2], direct microwave heating to temperatures above 500°C was found to be complicated by their relatively low dielectric loss at ambient temperature, making them essentially transparent to 2.45 GHz microwaves at low temperatures. Although microwave heating of such low-loss ceramic oxides can be enhanced by increasing the electric field strength by using higher power levels or cavities with higher Q value, this approach generally fails because of thermal runaway as the oxide heats and its dielectric loss rapidly increases [3,4]. In an attempt to circumvent thermal runaway, a hybrid heating technique was developed whereby commercial Nextel™ alumina-based filaments (3M Company, St. Paul, MN) could be indirectly heated to 700°-900°C in a single-mode TE_{103} microwave cavity through lossy carbon coatings on the filament tow [2]. The lossy carbon did provide rapid transient heating, lasting 5-10 seconds, to a temperature near 900°C.

In the present study, attention has been directed to microwave-heating of zirconia fibers. There is considerable previous work on microwave sintering of zirconia-based, shaped monolithic parts. For example, yttria-stabilized zirconia powders pressed into the shape of 25mm x 6mm x 3mm bars and 4mm-diameter rods have been microwave-sintered in single-mode microwave applicators [5,6]. Larger zirconia parts isostatically pressed from powders have been microwave-sintered in multimode microwave furnaces using an indirect method involving a "picket fence" array of SiC rods surrounding the zirconia parts to be sintered [7]. There do not, however, seem to be any prior reports of attempts to microwave-sinter zirconia fibers. Effectively and stably coupling microwave power into continuously pulled 10-15μm-diameter zirconia fibers poses a significant challenge in comparison with microwave sintering of stationary bulk zirconia parts with dimensions some 2-3 orders of magnitude greater. It requires specialized apparatus and techniques, which will now be described.

EXPERIMENTAL

Continuous zirconia fiber tow containing 3 mole % yttria was prepared by a sol-gel route [8] and prefired conventionally in air at 600°C to drive off water, organics and volatiles. Fiber bundles approximately 50cm long were suspended down through a quartz sleeve into the 2.45 GHz TE_{103} microwave cavity sketched in Figure 1. This cavity system and associated microwave source has been previously described [1,2,9]. The 2.45 GHz microwave source is a 3 kW magnetron generator (Gerling Laboratories, Model GL119). The resonant TE_{103} rectangular cavity consists of a water-cooled stainless steel waveguide section with a coupling iris for the microwaves and an adjustable short to tune the cavity frequency. A variable stub tuner was located before the iris to minimize reflected power from the cavity. The loaded Q of this cavity was measured at 1200-1300.

The waveguide section was equipped with two pairs of opposing orifices, as shown in Figure 2. The zirconia fibers were pulled through the pair of orifices aligned parallel with the electric field vector. The second pair of orifices, perpendicular to the electric field vector, provided for visual and optical pyrometric observation of the heated fibers. All orifices were located near the electric field maximum of the microwave standing wave. The motorized take-up wheel used to pull the filaments through the cavity is also shown in Figure 2. The continuous fiber bundles were continuously pulled by a slow-speed DC motor at a rate of 4.1 cm/min through the cavity, which was gradually powered up to ~200 watts to get ignition of the fibers, then backed off to ~10 watts to give stable heating. Temperature of the heated section of fibers was estimated by optical pyrometer (Leeds & Northrup Model 8622C) without correcting for the emissivity of the quartz sleeve. It typically took 12 minutes to continuously microwave-process an entire 50cm length of fibers in this way.

The microwave-sintered fibers were subsequently analyzed by scanning electron microscopy and X-ray diffraction. Single-filament tensile tests were performed on fibers prior to and after microwave sintering.

RESULTS AND DISCUSSION

The zirconia fibers reached intense white incandescence while within the cavity with relatively low levels of microwave power, and could be stably heated and controllably sintered in a continuous process. Temperature of the middle section of the microwave-heated zirconia fibers was estimated to range from 1325°-1360°C in one extreme case to 1000°-1100°C in a more moderate heating cycle. The latter temperature range is more in line with temperatures used to conventionally sinter zirconia fibers. In each case, the microwave-sintered zirconia fibers ended up white, flexible, and with appreciable strength. Single-filament tensile tests showed the initial fibers conventionally fired at 600°C to have an average tensile strength of 103,000 ± 6,900 psi (0.71 ± 0.05 GPa). After microwave sintering at about 1350°C, their average tensile strength was 93,000 ± 6,900 psi (0.64 ± 0.05 GPa), i.e. degraded from overfiring.

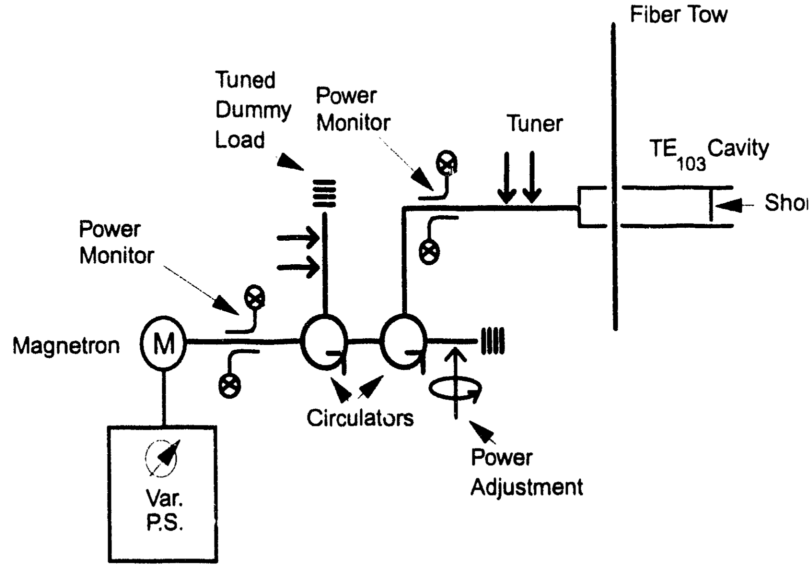

Figure 1. Schematic of the 2.45 GHz microwave system.

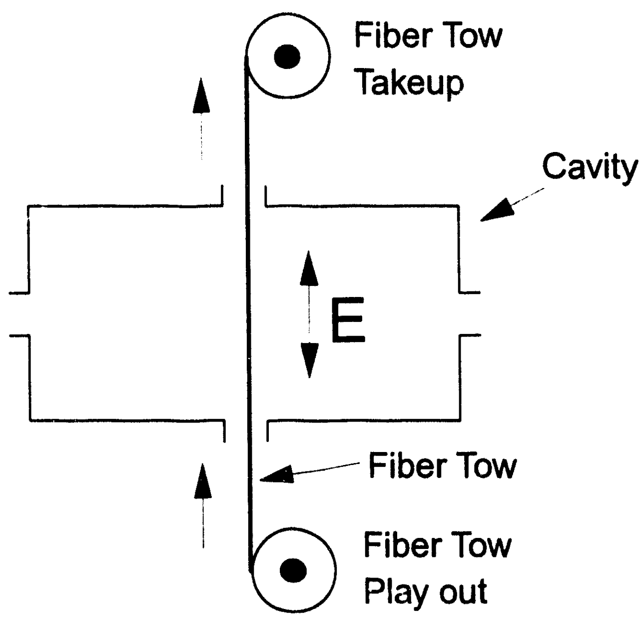

Figure 2. Schematic cross-sectional view of the TE_{103} cavity, showing the relative position of the filament tow.

This is consistent with the behavior of conventionally fired yttria-stabilized zirconia fibers, whose strength decreased at firing temperatures of 1300°C and above [8]. After microwave sintering at about 1100°C, the average tensile strength was 108,000 ± 40,000 psi (0.74 ± 0.28 GPa). After microwave sintering at about 1050°C, the average tensile strength was 148,000 ± 29,000 psi (1.02 ± 0.20 GPa). Optimally conventionally sintered similar yttria-stabilized zirconia fibers show tensile strengths up to 1.5 GPa, but their firing cycle involves slow heatup and as much as a two-hour soak at maximum temperature [8].

Scanning electron microscopic analyses showed the microwave-sintered fibers to have a thin, dense-looking skin, to be intact with no cracking or axial splitting, and to have submicron grain sizes, thereby resembling conventionally sintered zirconia fibers. Four representative scanning electron photomicrographs are shown in Figures 3a-d. The individual submicron grains are apparent in Figure 3a. The intact, uncracked nature of the fibers is evident in Figure 3b. The thin, dense-looking skin is visible in each of the four Figures 3a-d. X-Ray diffraction analyses revealed the only crystalline phase present to be tetragonal zirconia.

The results of this initial investigation indicate that it is indeed possible to rapidly microwave-sinter zirconia fibers in a continuous process. Further study with more accurate temperature measurement and stricter process control are necessary to optimize the process and improve the mechanical properties of the fibers.

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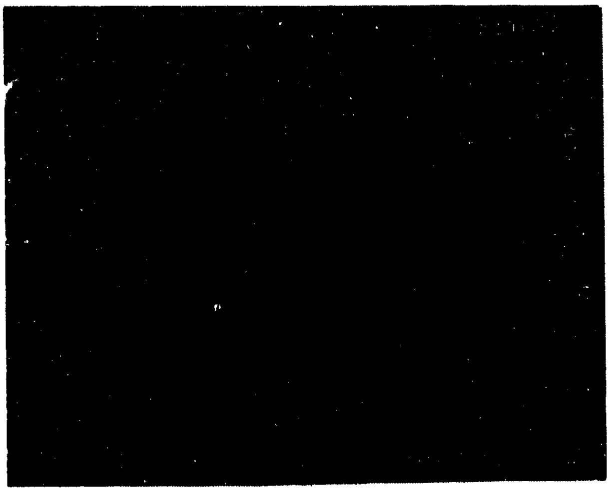
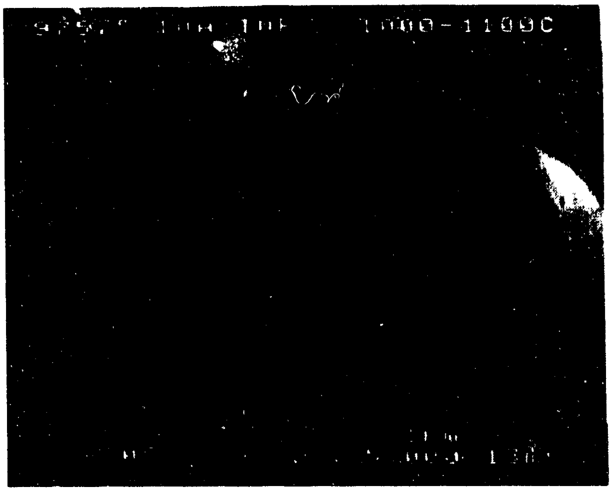
REFERENCES

1. G. J. Vogt and W. P. Unruh, "Microwave Hybrid Heating of Alumina Filaments," in Microwaves: Theory and Application in Materials Processing II, edited by D.E. Clark, W.R. Tinga, and J.R. Laia, Jr. (Ceram. Trans. **36**, Westerville, OH, 1993) pp. 297-306.
2. G. J. Vogt and W. P. Unruh, "Processing Aerosols and Filaments in a TM_{010} Microwave Cavity at 2.45 GHz," in Microwave Processing of Materials III, ed. by R. L. Beatty, W. H. Sutton, and M. F. Iskander (Mater. Res. Soc. Proceedings **269**, Materials Research Society, Pittsburgh, PA, 1992) pp. 245-250.
3. W. H. Sutton, "Microwave Processing of Ceramic Materials," Am. Ceram. Soc. Bull., **68** (2) 376-86 (1989).
4. W. H. Sutton in Microwave Processing of Materials III, op. cit., pp. 3-20.
5. J. Wilson and S. M. Kunz, "Microwave Sintering of Partially Stabilized Zirconia," J. Am. Ceram. Soc. **71** (1), C-40-C-41 (1988).
6. Y.-L. Tian, B.-S. Li, J.-L. Shi, Y.-P. Xu, J.-K. Guo, and D.-S. Yen, "Microwave Sintering of Y_2O_3 (3%)-ZrO_2 (TZP)," in Microwaves: Theory and Application in Materials Processing, edited by D.E. Clark, F.D. Gac, and W.H. Sutton (Ceram. Trans. **21,** The American Ceramic Society, Westerville, OH, 1991) pp.577-84.



3a.

3b.



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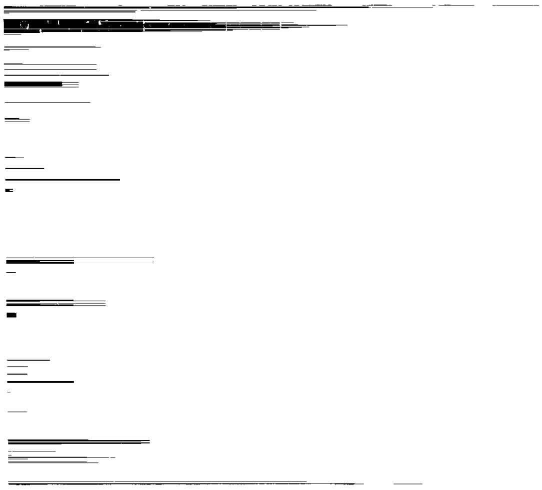

3d.

Figure 3. Scanning electron photomicrographs of representative, microwave-sintered, continuous, yttria-stabilized zirconia ceramic fibers.

7. M. A. Janney, C. L. Calhoun, and H. D. Kimrey, "Microwave Sintering of Solid Oxide Fuel Cell Materials: I, Zirconia-8mol% Yttria," J. Am. Ceram. Soc. **75** (2), 341-46 (1992).
8. E. F. Funkenbusch and T. T. Tran, "Zirconium Oxide Fibers and Process for Their Preparation," U.S. Patent No. 4,937,212 (26 June 1990).
9. D. E. Christiansen and W. P. Unruh, "Use of a TM_{010} Microwave Cavity at 2.45 GHz for Aerosol and Filament Drying,")," in Microwaves: Theory and Application in Materials Processing, op. cit., pp. 597-604.

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