

Polycrystalline Ceramic Fibers by Extrusion

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Submicron powders of several technically interesting advanced ceramics have been conventionally extruded as fibers and hollow fibers. Alumina, partially stabilized zirconia, silicon nitride, silicon carbide, lanthanum strontium manganate, lead zirconate titanate and a silicon carbide/zirconium diboride particulate composite have each been blended with thermoplastic or aqueous binders and extruded. The green extrudates have diameters ranging between 50 and 150 μm and polyethylene-base 150 μm diameter fibers can be drawn down at elevated temperature to approximately 40 μm diameter. Hollow fibers with 150 μm outer and 90 μm inner diameter can also be fabricated. Green fibers have been processed into chopped fiber felts for use as gas distributors/current collectors in an experimental solid oxide fuel cell (SOFC) and the first attempts at producing simple textile structures have been successful. The fibers, tubes and felts have been successfully debound and sintered and characterization of the sintered PSZ fibers, for example, has revealed a density in excess of 99% and tensile failure stresses up to 1.0 GPa for 78 μm diameter fibers.

Key words: Extrusion, Fibers, Felts, Textile structures

I. Introduction

The demand for high performance ceramic fibers is increasing steadily for use in a diverse range of applications, including fiber reinforcement, catalytic converters, thermal insulation, microtechnology and fluid and gas filtration. This has resulted in a tremendous number of processes being developed with which to produce high quality material.¹⁾ The majority of these methods are extremely complex, usually involving the formation of fibers from aqueous and gaseous precursors by way of a diversity of chemical and physical reactions. The goal of this work was to develop a method to fabricate continuous polycrystalline fibers of several technologically interesting ceramics, including silicon nitride (Si_3N_4), silicon carbide (SiC), alumina (Al_2O_3), partially stabilized zirconia (PSZ), lanthanum strontium manganate (LSM), lead zirconate titanate (PZT), and a particulate composite of zirconium diboride and SiC (ZBSC). The desired fibers were successfully fabricated by means of extrusion using synthesized and commercially available submicron powders plastisized with either thermoplastic or aqueous binder systems.

II. Experimental Procedure

The powders used in this work are listed in Table 1. The synthesized powders were conditioned via wet milling, sieving, air-classifying (Type MZR50, Alpine AG, Germany), and spray drying (Minor "Hi-Tec", Niro A/S, Denmark) while the commercial powders, with exception of those

constituting the ZBSC composite, were used directly without conditioning. Each powder was characterized for particle size (light scattering; Mastersizer X, Malvern Instruments Ltd, UK), bulk density (helium pycnometry; AccuPyc 1330, Micrometrics Instrument Corp., USA), morphology (scanning electron microscopy; JSM-6300F, JEOL Corporation Ltd., Japan) and specific surface area (BET; Automated BET Sorptometer, Porous Materials Inc., USA).

Table 2 lists the polymeric binders selected for the study which were analyzed for characteristic temperatures (thermogravimetric and differential thermal analysis (TGA/DTA); STA 409, Netzsch-Gerätebau GmbH, Germany) and bulk density (helium pycnometry).

The extrusion pastes were prepared in an electrically heated/water cooled mixing head equipped with roller blades attached to an instrumented torque rheometer (Rheomix 3000, Rheocord 9000; HAAKE Mess-Technik GmbH, Germany). The thermoplastic pastes were mixed at 150°C while the water-based pastes were mixed at room temperature. Mixing was performed at a constant 30 RPM. A lightly loaded paste was first prepared and then ceramic powder was incrementally added to increase the powder loading up to the highest possible value over a maximum run time of 2 hours. Temperature and torque were monitored throughout the procedure and a given paste was considered sufficiently homogenized when the measured torque remained constant with time.

A laboratory increasing-core single-screw extruder attached to the same torque rheometer was used to extrude the pastes (Rheomix 202HF; HAAKE Mess-Technik GmbH,

Table 1. Ceramic Powders

Material	Si ₃ N ₄	SiC	Al ₂ O ₃	PSZ	(La _{0.8} Sr _{0.2}) _{0.98} MnO ₃	PZT	ZBSC
Source	commercial	commercial	commercial	commercial	EMPA	commercial*	EMPA**
Additives (wt %)	1.4 MgO 3.6 Al ₂ O ₃	3.0 C 0.5 B	—	5.4 Y ₂ O ₃	—	—	—
$\rho_{\text{theor.}}$ (g/cm ³)	3.18	3.21	3.98	6.08	6.50	8.08	4.80
d ₅₀ (μm)	0.78	0.67	0.30	0.25	0.88	0.88	0.59
SSA (m ² /g)	12.3	20.5	11.1	11.1	7.0	2.0	9.6

*Supplied by the Active Materials and Structures Lab, Massachusetts Institute of Technology, USA.

**Commercial powders conditioned at EMPA.

Table 2. Binder Systems

Designation	PEW	HOS	PEG4K, PEG10K	MEC
Type	thermoplastic	thermoplastic	aqueous	aqueous
Source	EMPA	commercial	commercial	commercial
Composition	polyethylene/wax mixture	polyolefin/wax mixture	Polyethyleneglycol PEG4K: Mn 4000+ 70 wt% DI H ₂ O PEG10K: Mn 10,000+ 85 wt% DI H ₂ O	Methylcellulose Mn 86,000+ 85 wt% DI H ₂ O

Germany). The aqueous feedstocks were forced onto the screw by a hydraulic ram and extruded at room temperature. The cooled thermoplastic feedstocks were first manually crushed and then fed into the extruder via a vibratory funnel and extruded between 140 and 160°C. Sapphire dies of 150, 100 and 50 μm diameter fixed in steel mountings were used either singly or in 3- or 7-die clusters. Incorporated into the system between the screw end and the die land was a sieve containing numerous 100 μm dies which served to remove any large particles or agglomerates not removed during powder conditioning or destroyed during compounding. A schematic of the fiber extrusion setup and a micrograph of the sapphire dies are shown in Fig. 1. Extrusion pressures with a single 150 μm die were generally below 7.5 MPa for the water-based pastes and between 15 and 25 MPa for the thermoplastic pastes. The extrusion rate for a single die was typically on the order of 0.03 to 0.05 cm³/min, which for a 150 μm diameter die corresponds to 2 to 3 m/min of fiber.

As shown in Fig. 1, single fibers were wound directly onto a variable speed rotating drum while the fiber bundles were first drawn away from the dies by a compressed air venturi before being picked up on the drum. By increasing the rotating speed of the drum the fibers could, depending on the binder system, be drawn down in diameter before solidifying. Inserting a fine steel wire into the die permitted 150 μm diameter hollow fibers with a 90 μm inner diameter to be extruded.

The resulting fibers were prepared for debinding and sintering as single strands and in the case of LSM and

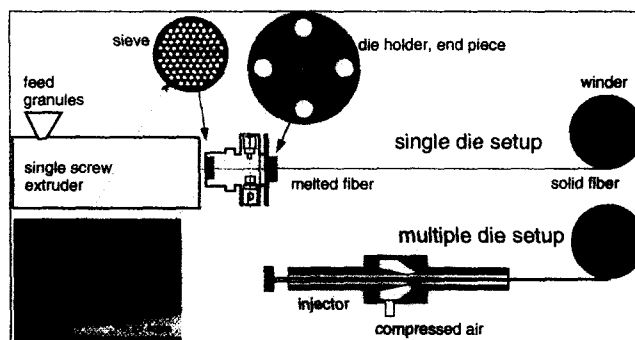


Fig. 1. Schematic representation of the fiber extrusion and drawing process (Inset: sapphire dies).

PSZ plastisized with PEW as disk-shaped felts. The felts were fabricated by chopping the green fibers to a length of approx. 10 mm and dispersing them in an aqueous 1% cellulose solution at room temperature. The resulting fiber slurries were then axially filter pressed and the filter cakes completely dried under ambient conditions. Continuous LSM single fibers were also rolled back off the pick-up drums onto a special spindle which produced a simple textile structure.

Thermal decomposition of the binder was achieved at temperatures up to 500°C in air, or in the case of SiC and ZBSC under nitrogen. With exception of the PZT fibers¹, pressureless sintering was performed according to schedules optimized by dilatometry (802 S, BÄHR-Gerä-

¹Sintering schedule provided by Active Materials and Structures Lab, MIT, Boston, USA.

tebau GmbH, Germany) for green samples made of the same powders, but formed by processes other than extrusion (slip casting, pressing, etc.). The Al_2O_3 , LSM, PZT, and PSZ fibers were sintered under air, while SiC and ZBSC were sintered under argon and Si_3N_4 under nitrogen. The sintered fibers were characterized for bulk density (helium pycnometry), microstructure (SEM) and in the case of PSZ for tensile strength (Zwick 1478, Zwick GmbH, Germany). The gauge length of the tensile test specimens was 10 mm and the tests were performed at room temperature under strain controlled conditions with a crosshead speed of 0.1 mm/min.

III. Results and Discussion

All the powders considered were successfully extruded as 150 μm diameter fibers with at least one of the chosen binder systems. Two examples are shown in Figs. 2 and 3. The mixtures attempted and their respective powder loadings are summarized in Table 3. Hollow fibers, such as the one depicted in Fig. 4, were extruded only with mixtures using the PEW binder, the other binder systems not having been attempted to date. Drawing the fibers down in diameter was possible only with the PEW binder system. The drawing process requires that the binder system be inherently stretchable, which is the case with the structurally simple and hence flexible linear polyethylene molecules present in this binder. Furthermore, the binder must be chemically compatible

with the ceramic and present in sufficient concentration to ensure fiber integrity during drawing, and the PEW system with powder loadings between 50 and 58 vol% appears to be uniquely suitable in these respects with the powders considered. The other binder/ceramic combinations are apparently unoptimized in one or more of these areas and consequently break rather than draw down



Fig. 2. Textile structure of green 150 μm diameter LSM/PEW fibers.

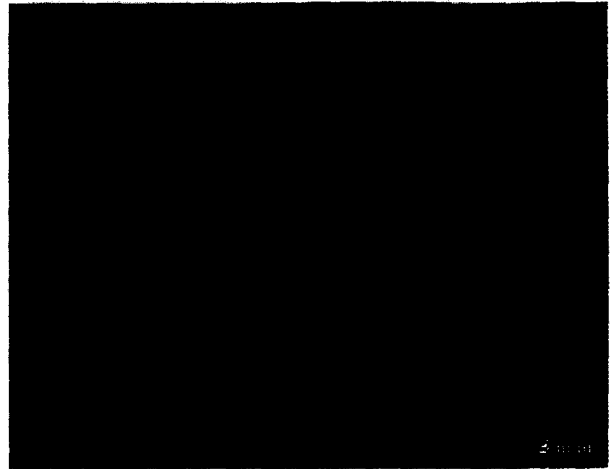


Fig. 3. SEM micrograph of green 150 μm -, 100 μm and 50 μm diameter SiC/HOS fibers.

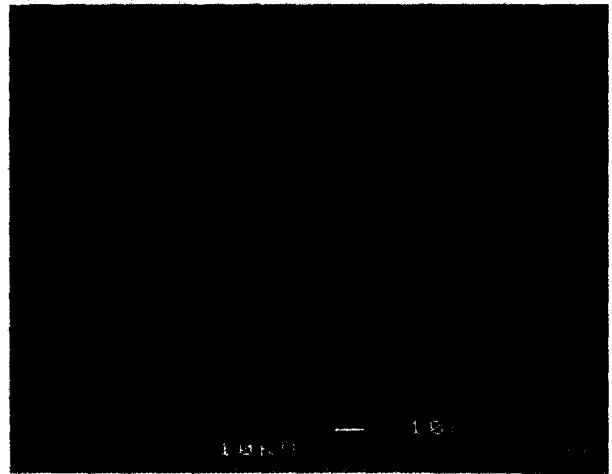


Fig. 4. SEM micrograph of a sintered hollow LSM/PEW fiber.

Table 3. Attained Powder Loadings

	Si_3N_4 (vol%)	SiC (vol%)	Al_2O_3 (vol%)	PSZ (vol%)	LSM (vol%)	PZT (vol%)	ZBSC (vol%)
PEW	55.1	55.1	×	53.4	58	50	55
HOS	59.7	54.1	×	×	×	-	-
PEG4K	47.5	-	50.0	-	×	-	-
PEG10K	-	52.5	-	42.0	×	-	-
MEC	49.0	52.0	51.5	42.3	×	-	-

×: not successful, -: not attempted.

when a tensile stress is applied. Drawing of the LSM/PEW fibers was extensively studied and at the optimum drawing temperature, 40 μm was determined to be the minimum achievable fiber diameter, regardless of the starting diameter of the fiber. The reason for this is unclear, but it may be related to strain hardening of the polyethylene melt brought about by localized crystallization of stretched polymer chains in the uncontrolled temperature gradient outside of the die.

Obstruction of the dies with agglomerates and large particles was a serious problem with the 50 μm dies. Substituting 50 μm dies for the 100 μm dies in the sieve helped to reduce the frequency of the blockages, but the penalty was a large reduction in throughput. The powder conditioning prior to compounding must be further optimized to eliminate the problem.

A further difficulty encountered with the 50 μm dies was the separation of the binder from the ceramic under high pressures. This phenomenon was very pronounced with the aqueous pastes at pressures approaching 10 MPa and pointed to an unoptimized interaction chemistry between the binders and the ceramic powder surfaces. The relatively low powder loadings achieved for these systems add weight to this argument. Detailed analyses of the powder surfaces and their interactions with the respective polymeric binders, as proposed by Roosen and Seitz,² for example, should help to better match the binder systems with the ceramic powders.

The best average results for the physical characterization of the solid cross-section sintered fibers are presented in Table 4. Despite using submicron powders of high sinterability, the bulk densities achieved for the SiC and Al_2O_3 material were unsatisfactory. The low density of 7.4 g/cm^3 for the PZT fibers, compared with 8.1 g/cm^3 for the raw powder, and the fact that microscopy revealed the fibers to be practically fully dense indicate that lead was lost from the material during the sintering process. As expected, pressureless sintering of the Si_3N_4 fibers was not successful, the material decomposing at elevated temperatures. Sintering this material under elevated nitrogen pressure has not yet been attempted.

First attempts at producing textile structures using PEW-plastisized green fibers were successful, as shown in Fig. 2. While the PEW-based fibers were the only fibers

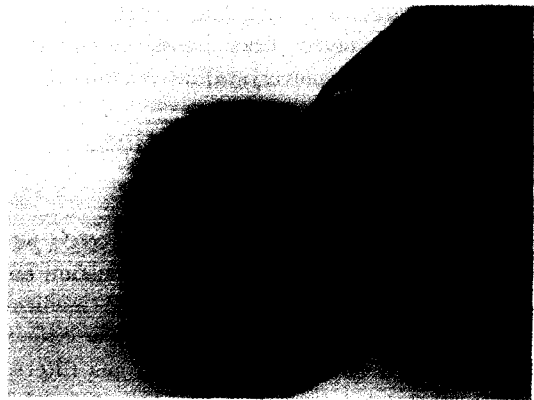


Fig. 5. Sintered LSM/PEW felt ready for testing in an experimental solid oxide fuel cell.

possessing sufficient green strength to permit such post-extrusion handling, their tensile strength was still too low to permit continuous weaving with an automated loom. Textile structures have yet to be sintered.

LSM and PSZ felts containing a mixture of chopped fibers with diameters between 40 and 150 μm have been sintered and the former material has been tested in an experimental SOFC.³ A representative disk with approximately 35 vol% fiber content is shown in Fig. 5. Mechanical tests revealed that, on average, the fibers in these felts are too thick to exhibit any appreciable elasticity in the sintered state and, as a result, the felts are relatively stiff and brittle. It remains to be determined whether using only 40 μm fibers is sufficient to impart acceptable elasticity on the felts, or if it is necessary to reduce the fiber diameter below the current minimum of 40 μm into the range of 20 to 10 μm .

IV. Summary

The goal of fabricating ceramic fibers using a conventional extrusion approach was successfully reached. While the general procedure has been proven, the powder conditioning and the chemical compatibility between the ceramic powder surfaces and the binder systems must be improved to aid the extrudability and the processability of the fibers. In this respect, the polyethylene/wax binder proved to be the best binder composition, but even with

Table 4. Properties of Sintered Fibers

Fiber	Si_3N_4	SiC	Al_2O_3	PSZ	LSM	PZT	ZBSC
Binder system	-	PEW	PEG4K	PEW	PEW	PEW	PEW
$\rho_{\text{theor.}}$ (g/cm^3)	-	3.06	3.93	6.08	6.40	7.4	4.80
$\rho_{\text{theor.}}$ (%)	-	96.1	98.7	100	99.0	92.8	100
Radial shrinkage (%)	-	-15	-15	-22	-25	-25	-
Tensile failure stress (GPa)	-	-	-	0.8 ($\text{Ø}118 \mu\text{m}$) 1.0 ($\text{Ø}78 \mu\text{m}$)	-	-	-

this system, the green strength and drawability must be improved to permit better fiber handling and the fabrication of truly flexible polycrystalline ceramic fibers.

V. Possible Applications

The fibers extruded in this work can be envisaged in a variety of applications. Hollow ZrO₂ fibers could be used as microscopic gas sensors in internal combustion engines or as microscopic hypodermic needles in medical applications. Alternatively, bundles of hollow SiC fibers could be envisaged as high-temperature gas filters. The PZT fibers were fabricated with the intention of incorporating them as actuating elements in an active fiber composite for vibration damping applications. The ZBSC composite combining high wear resistance and electrical conductivity was developed specifically as a material for spark erosion electrodes, and vanishingly small electrodes manufactured from extruded fibers are considered possible. Considering that powders of superconducting ceramics are also available in the required submicron grades, the extrusion of such fibers for applications such as superconducting magnets, for example, should be possible.

Acknowledgments

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