Fabrication of Commercial-Scale Fiber-Reinforced Hot-Gas Filters by Chemical Vapor Deposition

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INTERIM REPORT

Lloyd R. White, Principal Investigator
Thomas M. Kafka, Program Manager

November, 1992

Report Prepared by
3M I&C New Products Department
3M Center, Bldg. 209-1W-24
St. Paul, MN 55144
under
Subcontract No. 93X-SB482C

for

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
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ABSTRACT

The goal of this work was to fabricate a filter for removal of particulates from gases at high temperature. Primary applications would be in advanced utility processes such as pressurized fluidized bed combustion or coal gasification combined cycle systems. Industrial applications also exist.

Filters were made following a two-step process: make a ceramic fiber preform and then coat it with silicon carbide by chemical vapor infiltration (CVD). A number of constructions were tried including ceramic felt, woven fabric, filament wound fabric, and ceramic felt/filament wound fabric. The most promising construction was felt/filament wound. For the sake of convenience, these are called CVD filters.

Filter specimens were fabricated and tested and results compared with a commercially-available ceramic candle filters which are made by bonding silicon carbide particles with a glassy phase. Filters made on this project are compared with candles below:

- CVD filters are light; weighing about 25% as much as candles. Because filters must be suspended from a metal plate that is exposed to temperatures up to 850°C, weight is an important parameter.
- CVD filters resist thermal shock. In a water cycle test, where a specimen is heated to 1000°C and then immersed in water, CVD filters showed less strength loss than candles.
- A CVD filter was heated to 850°C and subjected to repeated pulses of air at ambient temperature, a test which simulates actual service conditions. It withstood 100,000 pulses which is equivalent to a year of operation. Candles show similar behavior according to manufacturer's tests.

CVD filters made so far have deficiencies. The felt/filament wound structure had a filter surface of ceramic felt which was rough and not well-bonded to the filament wound fabric. Delamination was observed in some tests. Examination of the surface showed that CVD coating had closed many of the pores thereby reducing permeability. Examination of polished sections showed that the felt layer was thicker than needed.

These deficiencies can be corrected by modifying the fabricating procedure as follows. Three steps will be needed: make a preform, coat it with silicon carbide by chemical vapor infiltration, and then apply a filter surface. Preliminary experiments have been done in which chopped ceramic fibers have been deposited on, or a coating of particles has been painted on, a disc of ceramic/ceramic composite (Siconex™). Results of these studies are preliminary but suggest that by reducing fiber length and felt basis weight, surface roughness can be eliminated and better bonding of felt to substrate can be achieved. More work is needed in bonding filter surface to substrate and controlling porosity of the filter surface.

TABLE OF CONTENTS

Section	Page
ABSTRACT	i
1.0 INTRODUCTION	1
2.0 PREFORM-MAKING	2
2.1 Woven	3
2.2 Felt	4
2.3 Filament Wound	6
2.4 Felt/Filament Wound	7
3.0 CVD PROCESSING	7
4.0 CHARACTERIZATION	7
4.1 Permeability and Maximum Pore Size	8
4.1.1 Type A filters: SCI-101, 103, 104, & 105	9
4.1.2 Type B filters: SCI-201, 203, 204, & 205	11
4.2 Burst Strength and Thermal Shock Resistance	15
4.3 Observations of Polished Sections	20
5.0 BENCH-SCALE PREFORM STUDIES	22
5.1 Felt over Siconex™	23
5.2 Controlled Porosity Coatings	24
6.0 CONCLUSIONS	24
7.0 RECOMMENDATIONS	24
8.0 ACKNOWLEDGMENTS	25
9.0 REFERENCES	25

LIST OF FIGURES

Figure	Page
1. Steps in Making a Ceramic/Ceramic Composite Filter	3
2. Mandrel Used For Woven and Felt Preforms	4
3. Mandrel Used For Types A & B Preforms	6
4. Permeability, Maximum Pore Size, Burst Strength, Thermal Shock Tests	8
5. Permeability Of Central 18 Inches of SCI-101	9
6. Permeability Versus Delta P Across Filter, Filament Wound Preforms	11
7. Permeability Versus Delta P Across Filter, Felt/Filament Wound Preforms	12
8. Maximum Pore Size Versus Specimen Number Of Central 18 Inches Of SCI-205	13
9. Dependence Of Permeability On Amount Of Silicon Carbide Deposited During CVI; Type B Filter	14
10. Permeability Versus Weight Of SiC	15
11. Photograph Of Pulse Tester	17
12. Type B Filter; Burst Strength After Pulse Testing	18
13. Photographs Of The Pulse Tester Tube Sheet	19
14. Horizontal Cut Through a Type B Filter. Silicon Carbide Matrix Is White, Fiber Reinforcement Is Black	20
15. Felt Surface at 500X. Silicon Carbide Is White, Saffil™ Fibers Black, Nicalon™ Fibers Grey. Note Thickness Of Matrix.	21
16. Steps In Making A Ceramic Composite Filter	22

LIST OF TABLES

Table	Page
1. Permeability and Weight of Ceramic Fiber Felt Preforms	5
2. Properties of Fibers Used to Make Preforms	5
3. Maximum Pore Size, Central 18 Inches of SCI-101	10
4. Thermal Shock Resistance to Heat to 1000°C, Immerse in Water Cycles	16

1.0 INTRODUCTION

Since the oil crisis of 1973, more efficient coal to energy processes have been sought and pressurized fluidized bed combustion (PFBC) and coal gasification combined cycle (IGCC) are attractive technologies. Hot gas cleanup is needed for both PFBC and IGCC for turbine protection. High efficiency cyclones have been used but do not remove particles smaller than about five micrometers so that additional cleanup is needed in order to satisfy environmental constraints. Hot gas filtration using rigid ceramic filters will protect turbines and meet New Source Performance Standards (NSPS). Testing has demonstrated dust removal at high efficiency and at an acceptable pressure loss.^{1,2} Major concerns have been thermal shock caused by pulse-cleaning, chemical attack by alkali vapor and cleanability.

Dust has been captured upstream of gas turbines in either PFBC or IGCC in a fashion analogous to baghouse filtration where dust is collected on a filter and periodically removed by back-pulsing.

Rigid ceramic filters tested so far are called candles. They are shaped like large test tubes and are made from ceramic particles and fibers which are bonded with a glassy phase. The gas path through candles is 1.5 cm in length, and candles are fairly heavy, each one weighing about six kilograms.

Thicker ceramic structures are less tolerant of thermal shock than thinner ones, other things being equal, and lighter filters would be easier to support than heavier ones. Thinner filters should also offer less resistance to flow. The tubesheet from which filters are suspended is exposed to about 850°C and must be constructed of a refractory metal. The more weight it must support, the more expensive it will be and the more complicated will be its design.

The goal of the work reported here is to make a light, thin, rigid ceramic filter and the approach taken is to make it as a ceramic fiber reinforced ceramic matrix composite.

As engineering materials, ceramic/ceramic composites which have brittle matrices are very old, however mechanical behavior is less well understood than is the behavior of materials like fiberglass reinforced plastic (FRP). In composites such as FRP the matrix is much less stiff than the reinforcement, the bond between matrix and reinforcement is strong, and the strength of the composite is determined by the strength of the reinforcement.

Ceramic/ceramic composites which display toughness differ from FRP. In particular, the bond between reinforcement and matrix must be loose. Ceramic/ceramic composites with a tight bond between matrix and reinforcement have been observed to be brittle. In contrast, ceramic/ceramic composites with a loose bond between reinforcement and matrix have been observed to be damage-tolerant.^{3,4,5}

Conventional ceramics processing techniques such as hot pressing mixtures of ceramic particles and fibers do not produce good composites because fibers are damaged by

pressures and temperatures required in processing. Also, decoupling matrix from reinforcement is difficult. Chemical vapor infiltration (CVI) is a technique which avoids these problems. Making high temperature filters by CVI of fibrous substrates is a reasonable method of fabrication, especially since CVI lends itself to producing porous structures.⁶

To understand the advantages which this technology offers to the making of filters, it is helpful to review experience with candles.

Candle filters are constructed of large-grained silicon carbide particles bonded with a glassy phase. Large pores for relatively unimpeded flow of gas characterize the structure. The filtering surface is the outside of the tube and is a thin, porous layer of much finer-grained material reinforced with silica-alumina fibers. Thus the filter consists of an outer layer of fine pores over a structural support having much larger pores.

From the standpoint of filtration, this is a desirable structure. It fosters cake filtration where dust forms a layer on the surface. Depth filtration, where dust is captured within the filter itself, is undesirable since such filters are difficult to clean.

During cleaning, a pulse of high pressure air is introduced into the center of the candle and the dust cake is removed by reverse flow. Pulse air is not heated and candles are exposed to thermal shock. Cleaning may be required as often as every two minutes, depending on dust load and dust characteristics, and a large number of cleaning pulses must be endured if filters are to last thousands of hours. Economics require filters to last in the neighborhood of 10,000 hours.

Examination of candles after 790 hours of PFBC service showed cracks due to thermal shock and tests showed significant loss in strength, at least for some of the candles.⁷ Evidence of chemical attack of the glassy, bond phase was not found. Nevertheless, it is a concern especially given the long life which filters must display, and the evidence of attack of refractories and ceramic fibers by alkali vapor which is in the literature.^{8,9,10}

The goal of the work described here has been to develop a filter, similar to a candle, but which is lighter, thinner, less sensitive to alkali attack, and less sensitive to thermal shock. Making such a filter from a ceramic fiber reinforced, ceramic matrix composite is the approach which has been followed.

2.0 PREFORM-MAKING

As indicated in Figure 1, filter-making is a two-step process: making a preform of ceramic fibers and then coating it by chemical vapor deposition (CVD). Preforms have been of woven fabric, ceramic fiber felt, filament wound fabric, and ceramic fiber felt over filament wound fabric. Phenolic resin is applied to the preform to rigidize it so that it can be suspended in a CVD reactor.

Figure 1. Steps in Making a Ceramic/Ceramic Composite Filter

2.1 Woven

Preforms were woven over the mandrel shown in Figure 2 by Woven Structures, Inc., Division of BP Chemicals, Compton, California. Fabric construction was discussed with their staff and the following was chosen based on needs for both strength and filtration properties along with their capability for weaving seamless tubing.

Warp count: 26 threads per inch

Filling count: 26 threads per inch

Warp thread: Nextel™ 312 600 denier 1/2

Filling thread: Nextel™ 312 600 denier 3/0, double served

Weave pattern: 5 harness satin, warp yarns on the outside

Figure 2. Mandrel Used For Woven and Felt Preforms

Weaving a “sock” around a cylindrical mandrel with a tapered section and a closed end requires some trimming of yarns at the taper and at the end. The sock was turned inside out after trimming to have the trimmed ends on the inside of the filter where they would not interfere with cleaning. It was desired to have the filling yarns on the outside filtering surface and this was also achieved by turning the fabric inside out.

The mandrel shown in Figure 2 was used as a fabric support while Borden SC1008 phenolic resin was applied to rigidize the preform.

2.2 Felt

Chopped ceramic fibers in aqueous suspension were formed into ceramic fiber felt preforms by vacuum slurry-forming at Refractory Products, Inc., Elgin, Illinois.

Nominal dimensions of felt preforms were the same as woven fabric except that thickness was about 1/4 inch.

Felts were bonded with Nalco 2327 colloidal silicon dioxide, an ammonium stabilized, low sodium binder.

Table 1 gives weights and permeabilities of preforms prepared from several different ceramic fiber mixtures. Table 2 lists properties of ceramic fibers used in preform-making.

TABLE 1. PERMEABILITY AND WEIGHT OF CERAMIC FIBER FELT PREFORMS

Perf. ID;	Fiberfrax™	Fiberfrax™	Fiberfrax™ / Nextel™	Fiberfrax™ / Nextel™	Saffil™ / Nicalon™	Saffil™ / Nicalon™	Fiberfrax™ / Nicalon™	Fiberfrax™ / Nicalon™
Wt.,g.:	569.5	624.4	650.0	698.0	444.5	455.3		607.5
Delta P (in. H ₂ O)	Permeability, feet/minute							
0.00								
0.05			0.164	0.164				
0.10	0.366	0.704	0.329	0.329	1.130	1.210	0.366	0.366
0.15		0.996	0.466	0.472	1.740	1.810		
0.20	0.676	1.220	0.629	0.632	2.340	2.390		0.822
0.25		1.420						
0.30	1.010						1.150	1.220
0.35								
0.40	1.330							1.680
	Permeability after resin coating, (feet/minute)							
0.00								
0.05								
0.10	0.393	0.521						
0.15								
0.20	0.777	0.960						

TABLE 2. PROPERTIES OF FIBERS USED TO MAKE PREFORMS

Property	Fiberfrax™	Nextel™ 312 chopped	Nicalon™ chopped	Saffil™
Composition, % by wt.				
Al ₂ O ₃	51.9	62		96-97
B ₂ O ₃		14		
SiO ₂	47.9	24		3-4
Si			54.3	
O			11.8	
C			30	
Density, g/cc	2.73	2.75	2.55	3.3
Diameter, micrometer	2-3	11	10-15	3
Fiber lengths, mm	NA	3.1	3	NA
Use temp., °C	1260	1200	1200	1600

Permeability can be controlled to some extent by varying fiber composition. Incorporating either chopped Nextel™ or Nicalon™ into Fiberfrax™ did not change permeability but a mixture of Saffil™ and chopped Nicalon™ had much higher permeability.

Although not needed for rigidizing, phenolic resin was applied to preforms prior to CVD coating to furnish a carbon interface between ceramic fiber reinforcement and silicon carbide matrix.

2.3 Filament Wound

New mandrels were prepared and are shown in Figure 3.

Figure 3. Mandrel Used For Types A & B Preforms

Preforms were wound at Structural Composites Ind., Pomona, California, according to patterns which are designated A and B for the sake of convenience. Both patterns consisted of three plies laid up to provide strength both axially and radially and, in the case of A, controlled porosity of the outer surface. Pattern A was CVD coated directly and pattern B was first coated with ceramic felt before CVD coating.

Fabric braided from Nextel™ 312 yarn was inserted between plies one and two at the flange. In service a filter is suspended from the flange and this part of it must be strong. It must support the weight of the filter and the dust cake and, more importantly, resist forces introduced by pulse cleaning. Woven fabric was inserted between plies one and two at the closed end to block openings in the filament wound fabric which were undesirably large.

2.4 Felt/Filament Wound

Preforms of pattern B were coated with ceramic fiber felt at Refractory Products, Inc., Elgin, Illinois.

Felts of various composition can be deposited. The composition carried into CVD coating was 50% Saffil™, 50% chopped Nicalon™, 3 mm length. Sizing on chopped Nicalon™ was removed before felting.

3.0 CVD PROCESSING

Silicon carbide matrix was deposited on preforms by chemical vapor deposition (CVD) at Delta G Corp., Sun Valley, California. The preform was suspended in a graphite reactor which was within a vacuum envelope. The graphite reactor was induction heated. Methyltrichlorosilane (MTS) was the silicon carbide precursor and was admitted to the reactor together with hydrogen. Woven fabric, ceramic fiber felt, filament wound fabric, and felt/filament wound fabric preforms were CVD coated.

4.0 CHARACTERIZATION

A filter which will be effective in PFBC or IGCC service must collect dust at high efficiency, must be durable, and must be cleanable. The goal of characterization is to identify an effective filter.

A performance test at simulated PFBC or IGCC conditions is needed to establish credibility and such a test was planned. However, no candidates that would merit such a test were produced. Filters which showed good strength and resistance to thermal shock were produced but they had deficiencies in filtering ability or cleanability.

Tests which were done and observations of polished sections are described below. Tests were of two kinds: permeability and pore size determinations which can be related to filtration performance and strength measurements made both before and after subjecting test specimens to thermal shock. A scheme used for sampling filters for before and after thermal shock testing is shown in Figure 4.

Figure 4. Permeability, Maximum Pore Size, Burst Strength, Thermal Shock Tests

4.1 Permeability and Maximum Pore Size

A commercially available rigid high temperature filter, made by Schumacher, Crailsheim, Germany, and marketed in the United States by Selee/Schumacher, Hendersonville, North Carolina, has the following permeability specification:

Initial pressure drop = 6 ± 2 mbar, flow rate of 200 m/hr

This can be expressed as:

Maximum permeability = $200 \text{ m/hr} / 4 \text{ mbar} = 50 \text{ m/hr/mbar}$

Minimum permeability = $200 \text{ m/hr} / 8 \text{ mbar} = 25 \text{ m/hr/mbar}$

This manufacturer's specification has been used as a benchmark for testing filter specimens.

Permeability was measured on whole filters and on one-inch long sections cut from whole tubes using a modified Frazier technique (ASTM D737-75). Maximum pore size was measured using ASTM method E128-89.

4.1.1 TYPE A FILTERS: SCI-101, 103, 104, & 105

Figure 5 shows permeability for the central 18 inches of SCI-101. Permeability ranged from about 2 to 4 m/hr/mbar. Maximum pore size is in Table 3 and values varied from about 100 to 400 micrometers. The manufacturer's specification for the pore size in the filtering surface of the Schumacher filter is 10 micrometers.

Figure 5. Permeability Of Central 18 Inches Of SCI-101

TABLE 3. MAXIMUM PORE SIZE, CENTRAL 18 INCHES OF SCI-101

Section Number	Maximum Pore Size (micrometer)
1	177
2	96
3	121
4	209
5	144
6	209
7	209
8	209
9	209
10	230
11	192
12	192
13	209
14	288
15	192
16	384
17	384

These data show that permeability must be composed of a relatively small number of large pores, and this would not be an efficient filter. SCI-101 was a Type A, filament wound structure with filtering surface made from a layer of texturized yarn subsequently coated by CVD.

Figure 6 shows that permeability measured on entire type A filters varied from 8.5 to 19.7 m/hr/mbar which is substantially greater than the values in Figure 5. Therefore, the permeability of the entire filter is greater than permeability of the central portion which implies that the ends are more permeable than the center. Similar results were obtained on Type B filters.

Figure 6. Permeability Versus Delta P Across Filter, Filament Wound Preforms

4.1.2 TYPE B FILTERS: SCI-201, 203, 204, & 205

Permeability of four type B filters, SCI-201, 203, 204, and 205, is shown in Figure 7. These filters had permeabilities of 25 to 73 m/hr/mbar which is in the range of the Schumacher candle. Strength testing and examination of polished sections were focused on these kinds of filters because they showed more promise.

Figure 7. Permeability Versus Delta P Across Filter, Felt/Filament Wound Preforms

Figure 8 shows maximum pore size versus specimen number for the central 18 inches of SCI-205. These values were determined from one-inch sections and ranged from about 100-240 micrometers. However, this is misleading. The filter surface was rough with projections scattered over it. These projections had large openings at their tips, i.e. they were like miniature volcanoes. The test method involved pressurizing a specimen under water and observing when bubbles first begin to be emitted by the largest pore. In all cases, the largest pore was at the tip of a projection. Hence, if surface roughness can be eliminated, lower maximum pore size is likely to be achieved.

Figure 8. Maximum Pore Size Versus Specimen Number Of Central 18 Inches Of SCI-205

Figure 9 shows the weight of silicon carbide and permeability versus distance along the axis for SCI-205. Silicon carbide weight and permeability were determined from one-inch sections. Note the increase in permeability at both ends which is correlated with the decrease in weight. Evidently, differences in coating had a strong effect on permeability.

Figure 9. Dependence Of Permeability On Amount Of Silicon Carbide Deposited During CVI; Type B Filter

Figure 10 shows that the outside of the bottom half of the filter was more heavily coated than the upper half. This is most likely due to the flow pattern of gas in the CVD reactor and better uniformity can be achieved by controlling flow patterns during processing.

Figure 10. Permeability Versus Weight Of SiC

4.2 Burst Strength and Thermal Shock Resistance

Burst strength was used to characterize filters. Other strength tests such as "C" ring crush were considered and some measurements were made. But, results were difficult to interpret and much more variable than were burst data. Similar behavior has been observed with ceramic/ceramic composite made by CVD coating silicon carbide onto ceramic fabric (Siconex™).

Resistance to thermal shock was measured using two different tests: a water cycle test described briefly below and air pulse tests. The latter simulate cleaning in actual filter service except that pressure was atmospheric. Cleaning at high pressure will generate higher thermal stress than at lower pressure because heat transfer rates will be higher. Nevertheless, pulse tests at atmospheric pressure more closely reflect the thermal shock which filters must endure than does the water cycle test which is much more severe.

Table 4 gives burst strength for A, B, and the Schumacher product (labeled Monolithic in the table). Burst strength was measured by pressurizing a rubber bladder confined inside a ring-shaped sample and determining the pressure at which the sample broke. The burst strength of all filters shown in Table 4 far exceeds internal pressures which could be created in either PFBC or IGCC service.

TABLE 4. THERMAL SHOCK RESISTANCE TO HEAT TO 1000°C, IMMERSE IN WATER CYCLES

Filter A		Filter B		Monolithic	
No. of cycles	Burst Press. psi (bar)	No. of cycles	Burst press. psi (bar)	No. of cycles	Burst Press. psi (bar)
0	538 (37)	0	457 (32)	0	>870 (60)
1	369 (25)	1	240 (16)	1	136,155 (9,10)
2	207 (14)	2	85 (5.9)	2	Did not determine
4	122 (8.4)	4	88,135 (6.1,9.3)	4	Too weak to measure
8	143 (9.9)	8	Did not determine Delamination of outer layer after 2 cycles	8	Too weak to measure

Table 4 shows the effect of thermal shock created by immersing a specimen heated to 1000°C into water, a very severe test. Strength loss occurred for all filters but was most severe for Monolithic. B suffered delamination of the outer layer of felt.

Water cycle tests are so severe that they may be unrealistic and a tester was used to assess damage caused by cleaning pulses. This pulse tester consisted of a heated enclosure in which a filter was suspended and air was passed through it from outside to inside. Periodically, a cleaning pulse was sent down the axis of the filter. Figure 11 is a picture of the pulse tester.

Figure 11. Photograph Of Pulse Tester

A filter of type B was pulse tested for about 1000 hours. Temperature was 850-900°C, air flow was 16-18 SCFM (27-31 cu. m/hr), pressure drop across the filter was 20-24 inches of water (50-60 mbar), pulse reservoir pressure was 80-90 psig (5.5-6.2 bar) and pulse duration was 0.1 second. Pulse frequency was twice per minute and was set at that value because measurements of temperature indicated that equilibration between pulses required about thirty seconds. The total number of pulses applied to the test specimen was 100,000 which corresponds to one year of service if filters are cleaned once every five minutes.

Figure 4 shows how the filter specimen was prepared for pulse testing. The central eighteen inches were cut out and used to determine properties of new material. The top and bottom portions of this same filter were attached using a ceramic composite sleeve (Siconex™) and a ceramic adhesive to form a shorter filter. This was installed in the pulse tester.

The filter was removed after 40,000 pulses and inspected visually. No damage was detected and it was returned to the tester. Visual inspection after 100,000 pulses showed a crack along the axis of the filter about three inches long that traversed the joint at the center where the top and bottom had been cemented together. This crack may have been an artifact of the test due to greater thickness in the area of the cemented joint.

Figure 12 shows burst strength of the pulse-tested filter. Air pulsing, exposure to temperature, or both have weakened it but it was strong enough to withstand pulsing, i. e. the filter did not break during testing. The spike in burst strength at 30-35 inches, near the bottom of the test specimen, is not understood and may be due to the dynamics of pulse cleaning.

Figure 12. Type B Filter; Burst Strength After Pulse Testing

Photographs of the tube sheet of the pulse tester are in Figure 13 and show how the filter was secured. Direct contact between a metal hold-down disc and the top was used and did not damage the top of the filter. This is important because it indicates that installation will be easier than with other kinds of rigid, ceramic filters where direct metal to filter contact causes breakage.

Figure 13. Photographs Of The Pulse Tester Tube Sheet

4.3 Observations of Polished Sections

Figure 14 is a micrograph of a polished section of a horizontal cut through the axis of a Type B filter. Silicon carbide shows up as white and Nextel™ or Saffil™ fibers are black. Nicalon™ shows up as grey. Plies 1-3 of the filament wound fabric show clearly as does the felt layer.

Figure 14. Horizontal Cut Through a Type B Filter. Silicon Carbide Matrix Is White, Fiber Reinforcement Is Black

Note the gap between the felt layer and the filament wound substrate. The felt must be well-bonded to the underlying fabric to avoid delamination.

Figure 15 shows the felt layer at high magnification. Note the thickness of the silicon carbide layer on the chopped fibers. To maximize filtration efficiency one must minimize fiber diameter in the filtering surface and CVD coating the felt defeats that purpose. Also, it appears from Figure 14 that silicon carbide coating has covered pores in the surface thus reducing permeability and filtering efficiency. Filters need to be made differently to avoid these problems.

Figure 15. Felt Surface At 500X. Silicon Carbide is White, Saffil™ Fibers Black, Nicalon™ Fibers Grey. Note Thickness Of Matrix.

5.0 BENCH-SCALE PREFORM STUDIES

Figure 16 is a schematic which shows a fabrication procedure that should overcome the deficiencies noted above. Three steps are involved: making a preform, coating it with silicon carbide, and then applying a filtering surface. The first two steps are identical to or simple extensions of procedures developed already. The third step, applying a filtering surface, needs more work. Bench-scale tests were done to identify techniques for putting a thin, controlled porosity surface on a ceramic composite substrate and achieving a good bond between them.

Figure 16. Steps In Making A Ceramic Composite Filter

Discs of Siconex™ were cut from flat plates of CVD coated, woven fabric and were used as substrates for coating with filtering surfaces.

5.1 Felt over Siconex™

Basis weight of the felt in Type B filters was about 130 g/sq meter. Based on photomicrographs such as Figure 14, thinner felt should provide complete coverage. Roughness on the preform surface should also be reduced by a thinner felt. Finally, fiber length of the Nicalon™ used in Type B filters was 3 mm and reducing the fiber length should reduce the gap between substrate and filtering surface, thus leading to better bonding and reduced tendency to delaminate.

The first step in creating a felt over Siconex™ filter was dispersing fibers in aqueous media. Difficulty was encountered in achieving uniformity with tightly bonded clumps of fibers being observed. Several dispersing aids were tried including Arquad 2C-75 and Aromox DM16 from Akzo Chemicals Inc. and Aerosol OT from American Cyanamid. Aerosol OT was the most effective, but it was impossible to disperse all clumps using dispersants only. Clumps were observed with both chopped Nicalon™ and chopped Nextel™ yarns.

While inspecting the chopped fibers, it appeared that clumps were present in the material before dispersing, i.e. they were present initially and not formed by flocculation of fibers that had been completely dispersed. When agglomerates are present initially, mechanical energy is required to disperse them.¹¹ Vigorous mixing using a Waring blender was ineffective and introduced abraded metal into the suspension but application of ultrasonic energy was effective.

Fibers were suspended in solutions of Methocel A4M with viscosity of about 50 centipoise to which a drop of dispersant had been added.

A filtering surface of chopped fibers was formed by filtering a dilute suspension through a Siconex™ disc on a Buchner funnel. A bead of silicone cement was applied to the periphery of the disc, allowed to dry, and used to seal it against the wall of the Buchner funnel. Vacuum source was a laboratory aspirator. Non-uniform coverage was observed. A pad of needled polyester felt was placed under the disc in an effort to make the flow more uniform with limited success.

Slurry-forming on cylindrical preforms had been relatively straightforward and it was not clear why difficulties were encountered on test coupons. It may have been due to lower vacuum levels than used in slurry-forming and low permeability of the Siconex™ discs.

Nevertheless, enough work was done both on Siconex™ discs and on sheets of fabric clamped against the wire of a handsheet maker to show that reducing fiber length leads to more intimate contact with the underlying surface. Also, thinner felts did not have uneven surfaces like the ones observed on type B filters. Therefore, reducing fiber length and felt basis weight should lead to smoother, better-bonded filter surfaces.

5.2 Controlled Porosity Coatings

A different kind of surface was applied which consisted of silicon carbide particles, with and without starch particles, suspended in aqueous aluminum phosphate. Several different particle sizes of silicon carbide were used in the range of 8 to 70 micrometers. Starch particle size was from 20 to 40 micrometers. The suspension had the consistency of a thin paste and was painted on the substrate. Starch particles were included as burn-out material in an effort to control porosity. After drying, the coupon was fired at 1000°C in air to remove burn-out material and to develop inorganic bonds from aluminum phosphate. The resultant coating was thin and well-bonded to the substrate.

Permeability of fired coupons was low, the most permeable being less than 4 m/hr/mbar which is an order of magnitude lower than the Schumacher specification. Nevertheless, this approach has merit if porosity can be controlled.

6.0 CONCLUSIONS

Ceramic composite filters which are thin, light and tough can be made. Reinforcement by continuous fibers is needed to avoid brittleness. Preliminary testing indicates that direct metal to filter contact does not damage the top of the filter which simplifies installation. However, examination of the filter surface of felt/filament wound structures shows that much of it has been closed over by the CVD coating. Also, the surface was rough and subject to delamination.

7.0 RECOMMENDATIONS

Ceramic composite filters can be improved by:

- Applying a thin filter surface to a ceramic/ceramic composite substrate.
- Making such filter surfaces as thin as possible and bonding them as tightly as possible to the underlying substrate.

This basic approach is sketched in Figure 16 and some specific filter surfaces are indicated there and summarized here along with techniques for applying them.

- Filter surface A: Filament wind yarn with controlled spacing between the individual filaments in the yarn.
- Filter surface B: Slurry-form chopped fibers from aqueous suspension onto the substrate.
- Filter surface C: Coat ceramic particles onto the substrate and control porosity by addition of burn-out material.

Techniques for bonding filter surfaces to substrates are indicated below:

- Light CVD coating of silicon carbide
- Application of inorganic sols, such as the precursors for Nextel™ fibers, followed by firing to develop inorganic bonds
- Application of inorganic bonding agents, such as colloidal silica or monoaluminum phosphate, followed by firing to develop inorganic bonds.

The substrate for a filter made by any of the approaches indicated above will be the same as those tested on this program. Therefore, good strength, toughness, and thermal shock resistance should be observed. The approaches for forming filter surfaces which are outlined above should lead to good filtration performance so that the final product should have both durability and the ability to filter dust effectively.

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9.0 REFERENCES

1. T. E. Lippert, M. A. Alvin, D. M. Bachovchin, G. B. Haldipur, R. A. Newby, and E. E. Smelzer, Development and Commercialization of Hot Gas Filtration Systems. In Proceedings of the 1991 International Conference of Fluidized Bed Combustion, Montreal, Canada, 1073-1080, April 21-24, 1991. ASME, NY, NY
2. John Stringer, A. J. Leitch, and R. K. Clark, The EPRI Hot Gas Filter at Grimethorpe: What worked, What Broke and Where Do We Go Now? In Proceedings of the 1991 International Conference on Fluidized Bed Combustion, Montreal, Canada, 971-984, April 21-24, 1991. ASME, NY, NY
3. M. J. Chappell and R. S. Millman, The Fabrication Of Ceramic-Coated Carbon Fibre Duplex Elements, J. Material Sci., 1933-1948, (1974)
4. L. Boyne, J. Hill and K. Turner, CVD Strengthening of Carbon Fibre-Glassy Carbon Composites, in the Proceedings of the Conference on Chemical Vapor Deposition, 5th International Conference, 577-588, (1975)

5. J. Aveston, G. A. Cooper and A. Kelly, Single and Multiple Fractures, in the Properties of Fibre Composites, Conference Proceedings Nat. Physical Lab., IPC Science and Technology Press LTD Surrey, England, 15-25, (1971)
6. D. P. Stinton, R. S. Lowden, and Ramsey Chang, Ceramic Engineering & Science Proceedings, vol. 9, no. 9-10, p. 1233-1244, 1988
7. John Stringer, et. al., op. cit.
8. John Sawyer, R. J. Vass, N. R. Brown, and J. J. Brown, Corrosion and Degradation of Ceramic Particulate Filters in Direct Coal-Fired Turbine Applications, presented at the Gas Turbine and Aeroengine Congress and Exposition, June 11-14, 1990, Brussels, Belgium
9. J. E. Oakey and G. P. Reed, The Behavior of High Temperature Filter materials in Hot Gasifier and Combustor Atmospheres, I. Chem. E. Symposium Series No. 99, 421-444, 1986
10. P. Dietrichs and W. Kronert, The Effect of Different Gas Atmospheres on Ceramic Fibre Materials, Interceram, p. 223-236, NR.3, 1982
11. Parfitt, G. D., Dispersion of Powders in Liquids, 3rd edition, p.3, (1981) Elsevier Applied Science Publishers, New York, NY

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