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**The Development of a Porous Silicon
Nitride Crossflow Filter**

**Final Report
September 1988 - September 1992**

September 1992

Work Performed Under Contract No.: DE-AC21-88MC25022

**For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia**

**By
Allied-Signal Aerospace Company
AiResearch Los Angeles Division
Torrence, California**

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ABSTRACT

This report summarizes the work performed in developing a permeable form of silicon nitride for application to ceramic crossflow filters for use in advanced coal-fired electric power plants. The program was sponsored by the Department of Energy Morgantown Energy Technology Center and consisted of a design analysis and material development phase and a filter manufacture and demonstration phase.

The crossflow filter design and operating requirements were defined. A filter design meeting the requirements was developed and thermal and stress analyses were performed. Material development efforts focused initially on reaction-bonded silicon nitride material. This approach was not successful, and the materials effort was re-focused on the development of a permeable form of sintered silicon nitride (SSN). This effort was successful. The SSN material was used for the second phase of the program, filter manufacture and evaluation.

Four half-scale SSN filter modules were fabricated. Three of the modules were qualified for filter performance tests. Tests were performed on two of the three qualified modules in the High-Temperature, High-Pressure facility at the Westinghouse Science and Technology Center. The first module failed on test when it expanded into the clamping device, causing dust leakage through the filter. The second module performed well for a cumulative 150-hr test. It displayed excellent filtration capability during the test. The blowback pulse cleaning was highly effective, and the module apparently withstood the stresses induced by the periodic pulse cleaning. Testing of the module resumed, and when the flow of combustion gas through the filter was doubled, cracks developed and the test was concluded.

1. INTRODUCTION AND SUMMARY

1.1 INTRODUCTION

This final report summarizes the work performed during the U.S. Department of Energy (DOE) Morgantown Energy Technology Center (METC) Contract DE-AC21-88MC25022, titled "Membrane Filter Technology, Silicon Nitride Crossflow Filters."

The overall program had as its objective the development of a high-temperature ceramic filter using a porous version of silicon nitride for use in the gas cleanup systems of advanced coal-burning power plants. The program was conducted by Allied-Signal Aerospace Company, AiResearch Los Angeles Division. Westinghouse, as a subcontractor, provided the testing and evaluation of the filter elements at their existing test facility. The program was organized around a six-task effort encompassing the design, development, fabrication, test, and evaluation of silicon nitride filters for the defined application. These tasks are as follows:

- (a) Test plan
- (b) Modeling and structural analysis
- (c) Determination of optimum filter properties
- (d) Filter element manufacture
- (e) Filter evaluation
- (f) Management and documentation

The overall program ran approximately 48 months, which included the time required for fabrication, testing, and evaluation of half-scale filters. The revised program schedule is shown in Figure 1-1 in terms of the tasks listed in the WBS. The program schedule was revised in September 1991 to reflect additional time required for material development.

The initial phase of the program comprised task 2, modeling and structural analysis, and task 3, determination of optimum filter properties. Task 2 provided for the actual filter element thermal design and the structural analysis of the design employing the properties of the material developed in task 3. Task 3 involved the development of the material and the determination of the physical properties used in the filter design analysis. Thus, the design and materials development tasks represented iterative efforts to define a material system and filter design that will meet the prescribed design requirements.

The initial baseline technical approach was the development of a porous form of reaction-bonded silicon nitride (RBSN). However, when difficulties emerged (see para. 1.2.4 for detail) with the porous RBSN during the development effort, several approaches were investigated in parallel to provide an alternative to the baseline approach. These alternative approaches included various formulations of sintered silicon nitride (SSN), holes punched in fully dense RBSN plates, and the use of various

PROGRAM SCHEDULE

IG-00311-G

Figure 1-1. Revised Program Schedule

foaming agents to produce porous silicon nitride structures. With the exception of the foaming agents, the alternative approaches investigated yielded material systems offering promise as crossflow filter materials.

All efforts to produce a porous form of RBSN material were unsuccessful. The problem was thought to be the formation of α - Si_3N_4 , a fibrous form of Si_3N_4 that forms preferentially in the pores of the material during the nitriding process. This fibrous material severely impedes the air flow through the material. Extensive efforts to inhibit the formation of α - Si_3N_4 or once formed, to remove it from the pores of the material, were only partially successful. Heat treating the RBSN material at high temperatures in an effort to oxidize the fibrous α - Si_3N_4 yielded an adequately permeable structure, but the resulting material was so highly oxidized that it would not be a satisfactory filter material.

In view of the difficulties encountered with the RBSN material, the technical effort was refocused on developing a permeable form of SSN. This was accomplished successfully. A new baseline material was developed having the required flow vs pressure drop characteristics and adequate strength for the envisioned filter application. This material system was used for the fabrication and demonstration of half-scale filter elements in the remaining portion of the program.

This report details all the work performed on task 2, modeling and structural analysis, and task 3, optimum filter properties (materials development). Both the initial RBSN efforts and the later SSN development are reported. The manufacture and evaluation of filter modules utilizing the new baseline SSN material is also presented. A summary of the work effort is presented in para 1.2.

1.2 SUMMARY

1.2.1 Requirements

The requirements for the ceramic crossflow filter consist of steady-state as well as transient operation during startup, shutdown, and a reverse-flow pulse used to clean the filter. The steady-state operation requirements are shown in Table 1-1 for two typical environments associated with advanced coal-burning electric power plants. The transient operation defined was associated with the Westinghouse test facility. The test facility simulates a typical power plant gas exhaust stream to evaluate filtering devices. The steady-state and transient pressures, temperatures, and time relationships were used in the subsequent thermal and stress analysis to determine the adequacy of the filter design to perform in its design environment.

TABLE 1-1		
REFERENCE REQUIREMENTS FOR FILTER DESIGN – NORMAL OPERATION		
Parameter	Oxidizing Environment	Reducing Environment
Temperature, °F	1500 to 1650	1000 to 2000
Pressure, psia	70 to 250	150 to 1000
Particle loading, ppm	100 to 10,000	100 to 10,000
Particle removal efficiency, percent	99.99	99.99
Operating lifetime, hr	16,000	16,000
Maximum clean pressure drop* at 10 ft/min face velocity**, in. H ₂ O	5	5
Maximum actual face velocity, ft/min	10	10
Minimum surface area, sq ft	1.25	1.25
Maximum pressure drop prior to cleaning, psi	2	2
* For new filter element		
** At standard conditions		

1.2.2 Filter Design

The crossflow filter designed by AiResearch is shown in Figure 1-2. The filter consists of a series of porous ceramic plates arranged in layers so that alternate layers act as flow passages for dirty (unfiltered) and clean (filtered) gas streams. The dirty gas enters both faces of the filter, is turned 90 deg and diffuses through the porous filter plates, and exits from the filter through the clean-gas flow passages. The particles in the gas stream are collected on the surface of the dirty-side plates. When the accumulation of the particles is severe enough to cause a significant pressure drop, a reverse-flow pulse is used to dislodge the filter cake which has accumulated on the filter surface. In operation, the filter is oriented to permit this cake to fall from the filter to a collection area for subsequent removal.

B-16129-1

Figure 1-2. Crossflow Filter Design

The plates comprising the filter are shown in Figure 1-3. The plates are formed in the green state with integral fins on one side. The fin geometry is different for the clean and dirty sides as shown on the plate drawings. The plates have identical plan form dimensions. The clean-side fins are 0.05 in. high, five per in., approximately 6 in. long, and an average thickness of 0.03 in. The actual fin root-to-tip thickness varies somewhat to aid in removal of the plate from the compression molding die. Each plate has eight fins and two 0.125-in.-thick header bars defining nine flow passages. The flow passage average dimension is 0.17 by 0.05 in.

Figure 1-3. Filter Plates

The dirty-side fins are 0.05 in. high, three per in., approximately 2 in. long, and an average thickness of 0.03 in. Each plate has 15 fins and 2 header bars defining 16 flow passages. The flow passage average dimension is 0.303 by 0.20 in. The fin patterns and dimensions of each plate are shown in Figure 1-3.

1.2.3 Thermal/Structural Analysis

The thermal and structural analysis methodology was developed in parallel with the materials development effort. To aid in the analytical development, the known physical properties of heat exchanger grade RBSN were used for the initial investigation. This initial investigation encompassed a coarse-grid finite-element model of a filter plate (Figure 1-4). The coarse-grid model was used to analyze the startup and pulse-cleaning modes of operation. The startup transient was quite benign. The pulse-cleaning transient produced more severe thermal gradients. A typical temperature/time history for the pulse-cleaning operation is shown in Figure 1-5. The coarse model was used to establish the location of the maximum thermal gradient. A more detailed model was made of this area, where maximum stress levels were anticipated. The critical area is shown on the plate in Figure 1-6. The finite-element model of this region is shown in Figure 1-7.

The thermal analysis performed on the coarse-grid model utilized the physical properties of heat exchanger grade RBSN. This type of material has a porosity of about 18 percent. It became obvious during the initial material development activity that a much higher porosity would be required for the filter material. This would result in

Figure 1-4. Thermal Grid of Ceramic Filter Model

a significant change in relevant physical properties, especially elastic modulus, density, and thermal conductivity (see para. 4.2 for greater detail). These properties were estimated for a 60 percent porous material and used in the fine-grid thermal and stress analysis.

The thermal analysis was performed for the cleaning-pulse conditions. The results of the thermal analysis were used as input to the stress analysis performed using essentially the same model (see Figure 1-7). The predicted stresses at 0.45 sec (the end of the pulsing period) are shown in Figure 1-8. The maximum stress level is approximately 3.6 ksi. The highest stresses are at the fin-to-flange interface regions across the thickness of the filter.

The structural analysis results indicate that moderately high thermal stresses are generated during the cleaning-pulse period, compared to the measured material strength (see para. 1.2.4). The stresses result from the application of ambient-temperature cleaning air to the filter, which is at a uniform temperature of 1600°F.

It would appear to be desirable to reduce the pulse-cleaning thermal stresses. This can be accomplished in a number of ways such as the use of a heated blowback

Figure 1-5. Plate Temperatures Along Section B-B

Figure 1-6. Detailed Region of Ceramic Filter Plate Shown on Model of Clean-Side Fins

tank, provision for sufficient accumulator volume between the pulsing air valve and the filter element, or the use of a regenerator between the pulsing air valve and the filter element.

1.2.4 Materials Development

In the initial materials development effort, a great number of formulations and process variables were investigated to obtain a satisfactory form of RBSN that yielded the appropriate permeability and exhibited adequate strength characteristics. A batch formulation containing 25 wt% polystyrene as a pore former was found to give about three times the required flow rate following binder removal, but the flow rate dropped to 0 following nitriding. The problem is thought to be that α -silicon nitride, a fibrous form of silicon nitride, forms in the pores of the material during the nitriding process. This formation inhibits the flow of air through the material. A heat treatment of the nitrided material in air was found to increase the flow to the targeted level. The characteristic biaxial strength of the material was 4.3 ksi. Consequently, a RBSN formulation employing 25 wt% polystyrene microspheres and subjected to this postprocessing heat treatment was recommended as the initial baseline material for manufacturing the demonstration filter elements.

The heat treatment was supposed to consolidate this alpha phase preferentially, due to the high surface area of the alpha phase. However, later tests revealed that the heat treatment resulted in converting a good part of the Si_3N_4 to SiO_2 , making the RBSN unsuitable as a filter material. As a result of these findings, further work on the filter manufacture was suspended pending resolution of the materials problem.

To resolve this problem, AiResearch formulated a program to investigate various methods to inhibit the growth of, and/or to remove, the α -silicon nitride that formed in the pores of the material during the nitriding step of the process. In addition to pursuing the RBSN approach, an alternative approach was investigated in parallel. This alternative approach involved the use of sintered silicon nitride (SSN). In this material system, pure silicon nitride powder is employed with various binders, pore formers, and sintering aids to form the desired component. The binders and pore formers are thermally decomposed and the part is sintered to its final shape and density. This program was presented to the DOE, whose concurrence was received to proceed. The methods and results of this investigation are summarized below.

1.2.4.1 Reaction-Bonded Silicon Nitride

Several approaches were investigated to remove and/or inhibit the formation of fibrous α -silicon nitride. High-pressure nitriding experiments were conducted using the initial baseline RBSN formulation. At higher N_2 pressures, the formation of the alpha-phase should be suppressed. Also the temperature ramping rate was increased in these experiments, as it has been reported in literature that the alpha phase formation is suppressed at temperatures above 1400°C . However, there was a moderate amount of α - Si_3N_4 on the material following each of these experiments, and the flow rate through the material was 0.

A series of heat treatments in air (oxidation) of the initial baseline material at various times and temperatures was performed. The oxidized material was removed by a hydrofluoric acid etch, and the flow and weight loss of the samples were measured. In another type of experiment, processed samples were heated in vacuum to remove the alpha phase from the pores. It was concluded from these experiments that in order to achieve the desired flow rate, the material weight loss would be greater than 20 percent. The bulk material would therefore be unacceptably degraded.

The third type of experiment on RBSN material was a postnitriding sinter to consolidate the fibers blocking the pores. These experiments included as-nitrided samples and samples which were vacuum-infiltrated with sintering aids. No change in appearance or in flow rate was observed following this type of experiment (conducted with various hold times at temperatures up to 1650°C).

It was concluded that none of these approaches to producing an RBSN filter yields satisfactory results. Obtaining adequate permeability by any of these methods would cause the RBSN to degrade significantly.

1.2.4.2 Sintered Silicon Nitride

Fine sintered silicon nitride (SSN) powder with sintering aids and various pore formers was processed. Screening tests (flow and strength measurements) were performed on these experimental SSN batches. One formulation, containing polystyrene pore former, was selected as the new baseline filter material.

The new baseline SSN formulation was fine-tuned to give the best combination of flow and strength. Samples of the fine-tuned batch were processed in two sintering runs, and results of measurements on those samples are shown in Table 1-2. The average flow and characteristic strength of these samples are higher than those of the initial baseline RBSN material. The high degree of interconnected porosity is evident in the micrograph in Figure 1-9.

TABLE 1-2
COMPARISON OF BASELINE SSN SAMPLES
PROCESSED IN TWO SINTERING RUNS

Sintering Run Number	Average Flow, ft/min	Standard Deviation, ft/min	Characteristic Biaxial Flexure Strength, ksi	Weibull Modulus	Average Bulk Density, g/cc	Standard Deviation, g/cc	Average Total Porosity, percent	Standard Deviation, percent
1	14.2	2.6	5.0	5.5	0.87	0.03	73.5	1.3
2	11.5	1.0	5.6	8.6	0.90	0.02	72.9	0.7

Figure 1-9. A High Degree of Interconnected Porosity Is Seen Through the Cross-Section of a Baseline SSN Filter Disc

The baseline SSN material was pressed on a fin tool die with excellent results. The pressed material was successfully processed with moderate linear shrinkage (approximately 11 percent) and a minimum of distortion, as shown in Figure 1-10. The bonding strength is relatively high. Attempts to break the bond between layers resulted in fractured layers (as well as some broken bonds). This indicates that the bond may be as strong as the parent material.

X-ray diffraction analysis performed on processed baseline SSN material indicates that the material is composed of about 85 vol% β - Si_3N_4 . The remainder is a phase composed of silicon nitride and sintering aids.

1.2.5 Filter Manufacture

The SSN formulation described in para. 1.2.4.2 was adopted as the baseline material for the filter element fabrication and demonstration phase of the program. The filter element manufacture activities included approval of the filter design (presented in para. 1.2.2), design and procurement of compression molding tools, and fabrication of elements according to the schematic shown in Figure 1-11. A detailed flow chart for the manufacturing process is shown in Figure 1-12.

Four elements were completed, and three of those were used for filter qualification. Of those, two that were checked for dimensional tolerances, flaws and cracks, permeability, and strength were selected for filter capability testing.

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Figure 1-10. Uniform Shrinkage from Processing Is Displayed in Pressed and Bonded Finned Disc Stacks

1.2.6 Filter Evaluation

The high-temperature, high-pressure (HTHP) test facility located at the Westinghouse R&D site has been operated over the past 8 years to evaluate the performance and operating characteristics of high-temperature gas-cleaning systems. Figure 1-13 shows a schematic of the flow loop and identifies the major equipment items. In this system, fuel is combusted with excess air, and reentrained ash is injected to produce a high-temperature, particle-laden gas flow.

Two filters (Modules 2 and 4) were tested at the Westinghouse HTHP gas-cleaning test facility. The actual conditions and the time at each condition are shown for the two modules in Tables 1-3 and 1-4. Module 2 performed effectively during the filter conditioning period; dust was steadily collected, and the filter was sufficiently cleaned by blowback pulsing at regular intervals. Module 2 failed during the baseline series, when it expanded into the clamping device. Cracks developed, allowing dust to pass into the exhaust stream. Module 4 performed very well through the filter conditioning and baseline test series for a cumulative 150 hr period. The flow was doubled through the filter to induce higher stress, which led to crack development in the module. The test ended after a cumulative 170 hr period in the HTHP test unit.

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Figure 1-11. Ceramic Filter Element Fabrication

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Figure 1-12. Process Flow Sheet for SSN Filter Elements

Figure 1-13. HTHP Gas-Cleaning Test Facility at Westinghouse

TABLE 1-3						
TEST CONDITIONS FOR MODULE 2 HTHP FILTER TESTING						
Test Series	Time at Condition, hr	Actual Flow, ft ³ /min	Startup Thermal Gradient, °F/min	Pulse Intensity/ Duration	Temperature, °F	Comment
1	10	9.5	< 10	0.25 psi/ 0.2 sec	1275	Filter conditioning period
2	30	13.5	< 10	0.25 psi/ 0.2 sec	1440	Baseline

TABLE 1-4						
TEST CONDITIONS FOR MODULE 4 HTHP FILTER TESTING						
Test Series	Time at Condition, hr	Actual Flow, ft ³ /min	Startup Thermal Gradient, °F/min	Pulse Intensity/ Duration	Temperature, °F	Comment
1	10	9.5	< 10	0.25 psi/ 0.2 sec	1290	Filter conditioning period
2	140	13.5	< 10	0.25 psi/ 0.2 sec	1440	Baseline
3	20	27	10	0.25 psi/ 0.2 sec	1520	High stressing conditions

TABLE 1-5			
SSN FILTER POSTTEST ANALYSIS MATRIX			
Evaluation	Filter Specimen	Analytical Technique	Data
Filter morphology	Channel surface and cross section	Scanning electron microscope (SEM), energy dispersive X-ray analysis (EDAX)	Gross physical changes such as pore size, sintering, glass phase formation, qualitative chemical changes (reaction surface effects)
Ash deposits	Dirty channel filter surface	Atomic absorption (AA), emission spectroscopy, X-ray	Elemental composition, trace and minor elements, compound identification, eutectic formations
Filter blinding	Dirty channel filter surface and cross section	Microprobe	Specific elemental profile, ash
Material strength	Sliced section	Four-point bend	Modulus of rupture

2. SYSTEM REQUIREMENTS

System requirements have been specified for two types of operating environments—oxidizing and reducing. A typical oxidizing environment might be a pressurized fluidized bed combustor, and a typical reducing environment might be an integrated gasifier combined cycle.

The effect of these typical operating environments on the silicon nitride material proposed for the filter elements is expected to be minimal. Material property degradation of silicon nitride is being studied in a companion program performed by Westinghouse for the DOE.

For convenience, filter operation can be divided into three categories: normal operation, startup/shutdown operation, and cleaning-pulse operation. These categories are discussed in the following paragraphs.

2.1 NORMAL OPERATION

Normal operation occurs when the filter element attains steady-state temperature conditions and is operating in the filtering mode. The requirements for this condition are summarized in Table 2-1. Note that the face velocity is based on the active filter area. The required gas volumetric flow rate, which is the product of the face velocity and the surface area, is 12.5 cu ft/min. For the AiResearch filter configuration discussed in Section 3, the active face area is 2.03 sq ft. Thus, the required face velocity for a 12.5 cu ft/min flow is 6.2 ft./min. AiResearch has retained 10 ft/min as a design goal for material development, thus providing a substantial margin.

2.2 STARTUP/SHUTDOWN OPERATION

Typical startup conditions have been defined. These conditions, shown in Figure 2-1, relate specifically to the laboratory setup at Westinghouse. Note that the mass flow rate is assumed to be constant during the startup, at approximately 4 lb/min. There are four gas-temperature heatup rates during startup, the most severe at 26°F/min. For laboratory conditions, shutdown is relatively benign. Complete shutdown of the gas flow at the end of operation permits a gradual cooling of the filter element, which is enclosed in a well-insulated vessel.

2.3 CLEANING-PULSE OPERATION

Pulsing operation may result in conditions more severe than startup/shutdown. Typical pulsing conditions have been generated with the assistance of Westinghouse. For the Westinghouse laboratory conditions, the pulsing duration is 0.45 sec. Typical flow rate, temperature, and relative pressure of the cleaning pulse air at the inlet face of the filter element are shown as functions of time over this interval in Figures 2-2 through 2-4. The blowback tank is initially at 800 psia. Figure 2-3 presents pulsing air temperatures for an ambient temperature blowback tank and a blowback tank maintained at 400°F. The relative pressure, shown in Figure 2-4, is the pressure differential across the filter element during cleaning. The relative pressure and flow rates are similar for the two blowback tank temperature cases. The flow rate of cleaning gas varies during the

TABLE 2-1		
REFERENCE REQUIREMENTS FOR FILTER DESIGN – NORMAL OPERATION		
Parameter	Oxidizing Environment	Reducing Environment
Temperature, °F	1500 to 1650	1000 to 2000
Pressure, psia	70 to 250	150 to 1000
Particle loading, ppm	100 to 10,000	100 to 10,000
Particle removal efficiency, percent	99.99	99.99
Operating lifetime, hr	16,000	16,000
Maximum clean pressure drop* at 10 ft/min face velocity**, in. H ₂ O	5	5
Maximum actual face velocity, ft/min	10	10
Minimum surface area, sq ft	1.25	1.25
Maximum pressure drop prior to cleaning, psi	2	2
* For new filter element		
** At standard conditions		

pulsing interval, with a maximum value of 20 lb/min. The maximum pressure differential across the filter element is 11 psi. Due to the short residence time of the fluid in the filter plenum and lines during pulsing, the air temperature at the filter face rapidly approaches the supply tank temperature.

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Figure 2-1. Gas Temperature Profile for Heatup Transient

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Figure 2-2. Flow Rate of Cleaning Gas as a Function of Time Through Filter During Pulse Cleaning

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Figure 2-3. Temperature at Filter Clean Face During Pulse Cleaning

Figure 2-4. Profile of Relative Pressure Between the Filter's Active Surfaces and the Clean Face as a Reverse Pulse of Air is Applied to Clean Face for Cleaning

3. FILTER DESIGN

Ceramic crossflow filters produced to date have been constructed from alumina-based materials, which have marginal thermal shock and corrosion resistance. Silicon nitride offers the potential for improved filter performance because the material exhibits good mechanical strength and thermal shock resistance. As a result, silicon nitride is an excellent candidate material to meet DOE high-temperature, high-pressure gas stream particulate filtration goals.

The crossflow filter concept is illustrated in Figure 3-1 (taken from the RFP). The filter comprises a series of porous ceramic plates. The plates are arranged in layers so that alternating layers act as flow passages for dirty (unfiltered) and clean (filtered) gas streams. The flow passages are further defined by a series of ribs or fins attached to the plates. The ribs are configured to define a crossflow geometry, as shown in Figure 3-1. The alternating plate and rib layers are bonded together to form a monolithic filter structure. The ribs act as structural support for this monolithic filter.

In operation, hot unfiltered gas enters the dirty gas channels from both sides, as shown in the insert view of Figure 3-1. The gas flows through the thickness of the porous plate with particulate matter remaining on the surface. The filtered gas stream flows along the clean gas channels and is collected in the plenum before discharge from the system. The collected particulates are periodically removed from the dirty-side channels by applying a reverse pulse through the clean gas plenum section. This filter concept is attractive because it offers a large surface-area-to-volume ratio, operates with low pressure drop, provides nearly absolute filtration of ash, and can be operated at high face velocity.¹

The proposed AiResearch filter comprises a stackup of silicon nitride finned plates, bonded together in the green state and sintered as an integral unit. Clean-side and dirty-side fin passages are alternated in the stackup. The desired overall filter dimensions are shown in Figure 3-2.

The plates are formed in the green state with integral fins on one side. The fin geometry is different for the clean and dirty sides as shown on the plate drawings in Figure 3-3. The plates have identical plan form dimensions. The clean-side fins are 0.05 in. high, five per in., approximately 6 in. long, and an average thickness of 0.03 in. The actual fin root-to-tip thickness varies somewhat to aid in plate removal from the compression molding die. Each plate has eight fins and two 0.125-in.-thick header bars defining nine flow passages. The flow passage average dimension is 0.17 by 0.05 in.

The dirty-side fins are 0.20 in. high, three per in., approximately 2 in. long, and an average thickness of 0.03 in. Each plate has 15 fins and 2 header bars defining 16 flow passages. The flow passage average dimension is 0.303 by 0.20 in. The fin patterns and dimensions of each plate are shown in Figure 3-3.

¹Lippert, T. E., "Performance Evaluation of a Ceramic Cross-Flow Filter in a Bench-Scale Gasifier," *Proceedings of the Eighth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting*, DOE/METC-88/6092, May 1988.

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Figure 3-1. Generic Crossflow Filter Concept

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Figure 3-2. Overall Filter Dimensions

Figure 3-3. Filter Configuration

The finned plates are stacked in the filter length direction. The stack height or no-flow dimension is 6 in. There are 35 plates in the filter unit. Each plate is 0.05 in. thick. Seventeen of these plates have clean-side fins, another 17 have dirty-side fins, and one plate has no fins at all. This plate is one of the two sideplates (outer plates) on the filter. The other sideplate is a normal plate with either clean- or dirty-side fins. The plate stackup leaves 34 permeable plates available for particle filtering. Each plate has an active filter area of approximately 8.58 sq in. based on dirty-side available area. [This area is calculated by considering the 16 dirty-side flow passages, 0.303 in. wide and $2.02 - 2(0.125) = 1.77$ in. long. Active area = $(16) (0.303) (1.77) = 8.58$ sq in.] Note that due to different fin geometries on the clean and dirty sides, the permeation area on the clean side of the plate is somewhat less than the active filter area. For the 34 permeable plates, the total active filter area is approximately 2.03 sq ft. This area substantially exceeds the minimum required active filter area of 1.25 sq ft.

The two sideplates require external flanges in the dirty-flow direction (along the flange width). These flanges will be attached to the sideplates in the green state and sintered with the entire filter element. The purpose of the flange is to provide a surface to which the filter can be mechanically clamped and held in position in the gas circuit. The optimum green state fabrication method for the flange sections has yet to be determined. Pressed strips, injection molding, or extruding may be possible. Some thought will be given to possibly eliminating the flange and adopting some other attachment scheme, since this thick area increases thermal stress.

4. THERMAL/STRUCTURAL ANALYSIS

The thermal and structural analysis methodology was developed in parallel with the materials development effort (task 3). To aid in the analytical development, the known physical properties of heat exchanger grade RBSN were used for the initial investigation. This initial investigation encompassed a coarse-grid finite-element model of a filter plate. The coarse-grid analysis was used to identify the critical stress region in the filter. For the critical region, a more detailed fine-grid model was generated. The fine-grid model was analyzed using measured and estimated properties of porous RBSN.

The coarse-grid analysis performed with dense RBSN properties is discussed in para. 4.1. The model and the temperature maps resulting from the analysis are presented in Appendix A.

4.1 COARSE-GRID THERMAL MODEL

Based on the plate design shown in Figure 3-3, a thermal model was generated. The model comprises a coarse-grid finite-element model of a single filter plate and attached fins on both sides of the plate. The model includes the integral flange region in the stack height or no-flow direction (along the flange length). A single plate suffices for the analysis, since each plate sees essentially the same thermal and pressure loading. The thermal model is designed to run on the AiResearch thermal analyzer program (ATAP), an in-house code similar in function to commercially available thermal analysis codes. The model comprises over 400 elements.

The generated model is shown in Figure A-1 of Appendix A; each dot represents a node. The model consists of one-half of the plate with one-half of the clean-fin and dirty-fin heights on either side of the plate. Symmetry allows this simplification. Figure A-1b shows the nodes on the plate, and Figure A-1a and A-1c show the nodes on the dirty-side and clean-side fins, respectively. As indicated, some of the fins in the less critical region of the plate are combined to reduce the number of nodes. Gas flow streams, depending on the mode of operation, enter the filter from the dirty side or clean side of the fins. Each gas stream flows along the fin channel and branches off at each corresponding plate node. Each branching stream flows through the plate, merges with other gas streams along the other side of the fin channels, and then exits the filter.

The physical properties of the material used in the coarse-grid thermal analysis were those of well-characterized heat exchanger grade RBSN. This material has a porosity of about 18 percent. The relevant physical properties at operating temperatures are: thermal conductivity = 7.5 Btu/hr-ft-°F, density = 175 lb/cu ft, and specific heat = 0.15 Btu/lb-°F.

4.1.1 Cleaning-Pulse Operation Analysis

The initial analysis was performed for the cleaning pulse operation. The pulse duration is 0.45 sec. The flow rate through the filter and the gas temperature at the filter

face were presented in Figures 2-2 and 2-3. The more severe ambient temperature blowback tank conditions are used for gas temperature.

For pulsing operation, the filter plate was assumed to be at a uniform temperature of 1600°F initially. Heat transfer coefficients for flow along the clean- and dirty-side passages were generated using conventional relationships for flow through channels. The branching of the flow was accounted for, and the actual flow rate at each node along the plate (see Figure A-1b) was used for the heat-transfer coefficient prediction and the heat balance.

The heat transfer conductance through the thickness of the plate is very high. This is due to the very large surface area afforded by the small pores of the ceramic material. The heat transfer conductance through the thickness is difficult to predict; it is estimated to be around two orders of magnitude greater than the channel flow conductance. At this high level, the precise value used for the heat transfer conductance is not critical since the gas temperature closely approaches the plate temperature across the thickness of the plate. In fact, reducing the heat transfer conductance to one-fifth its nominal value had little effect on the predicted temperatures.

The thermal model was run on the ATAP with the inputs discussed above. The results are complete plate, fin, and fluid temperature maps as functions of time throughout the pulsing interval. Plate temperatures are presented as functions of time along two sectional views in Figures A-2 and A-3. The temperature curves are derived by drawing straight lines through the node temperatures; as such, the curves may not represent the precise temperature profile.

Figure A-2 presents the temperatures along section A-A in the direction of the clean-gas channels. Initially, the temperatures are uniform at 1600°F. As the gas temperature decreases with time, the plate is cooled. This heat transfer raises the temperature of the gas, thus reducing further plate cooling in the Y-direction. The effect of the clean-side fins can be seen in Figure A-2. The temperature reversals in the Y-direction represent higher plate temperatures in the plate nodes under the fins. This is due to the fact that the plate in these regions cannot be cooled directly by the gas flow, but only transfers heat by conduction with other plate regions and the fin.

Figure A-3 presents the temperatures along section B-B in the direction of the dirty-gas channels. Again, the plate is initially at 1600°F. The plate is cooled as the gas inlet temperature drops. The "sawtooth" temperature reversals represent increased plate temperatures in the plate region under the gas-side fins. The plate temperatures are relatively uniform along most of the plate in the X-direction. Near the edge of the plate, the temperatures rise rapidly. This is due to the large, uncooled thermal mass represented by the flange region.

The gas temperatures are also part of the thermal analysis output. The gas temperatures along section B-B (Figure A-3) are presented in Figures A-4 and A-5 for the upstream and downstream sides of the plate, respectively. The upstream temperatures are low, since the channel flow heat transfer conductance is relatively small. The only

exception is at 0.45 sec, when the flow rate is very low (see Figure 2-2). Comparison of Figures A-4 and A-5 shows the large heat absorption on passing through the plate.

The gas temperatures along section A-A (Figure A-2) are presented in Figures A-6 and A-7 for the upstream and downstream sides of the plate, respectively. Again, the effect of the flow through the plate is evident.

The coarse-grid analysis was used to identify the region on the filter plate expected to have the lightest stress level. No specific stress analysis was run for the coarse-grid model, since dense RBSN properties were used. The temperature maps indicate that the largest temperature gradient in the Y-direction occurred near the boundary between the flange and the remainder of the plate (see Figure A-2). In the X-direction, other than the header bar at the edge of the plate, the temperature variation is relatively uniform (see Figure A-3). The region of the greatest temperature gradient (Figure A-2) was used for the detailed fine-grid model.

4.1.2 Startup Analysis

Thermal analysis was performed for the imposed startup conditions discussed in para. 2.2. These conditions include a constant flow rate of 4 lb/min (52.3 scfm) and the gas temperature profile shown in Figure 2-1. The analysis concentrated on the most severe heatup period, commencing at 675 min after a long 750°F soak. The input temperature profile is shown in Figure A-8. The initial temperature was 750°F.

Figure A-9 presents the plate temperatures at various times along section A-A (in the direction of the clean-gas channels). The temperature gradients, which are quite small, are due to the effect of the massive flange and dirty-gas header bar. Figure A-10 presents the plate temperatures at various times along section B-B (in the direction of the dirty-gas channels). Very little temperature variation is noticeable. Figure A-11 shows the plate temperatures at various times along section C-C in the flange region. The effect of the flange can be seen, but the temperature gradients are quite small. The temperatures of the dirty-side and clean-side fins in the flange region are essentially identical to the plate temperatures.

Figures A-12 and A-13 are gas temperatures along section A-A (Figure A-9) for the upstream and downstream sides of the plate, respectively. Figures A-14 and A-15 are gas temperatures along section B-B (Figure A-10) for the upstream and downstream side of the plate, respectively. Because of the high heat transfer conductance for gas flowing through the plate, the plate temperatures and the downstream gas temperatures across the plate are essentially equal.

This analysis indicates that the temperature gradients in the plate caused by the assumed startup conditions are quite moderate. The change in gas inlet temperature with time is small (26°F per min). The relatively small thermal capacitance of the ceramic plate, combined with the extremely high heat transfer conductance through the thickness of the plate, results in relatively uniform plate temperatures, closely following the gas temperatures.

4.2 MODIFIED PHYSICAL PROPERTIES

The thermal analysis discussed in Appendix A utilized the physical properties of heat exchanger grade RBSN. This type of material has a porosity of about 18 percent. It became obvious during the initial material development activity that a much higher porosity would be required for filter-grade RBSN—probably in the 50 to 60 percent range. Some of the properties required for thermal and stress analysis have not been measured for the porous material. However, these properties, especially thermal conductivity, elastic modulus, and density, can have a significant effect on temperatures and stresses. As such, representative values of porous RBSN properties were estimated and used in subsequent thermal and stress analyses. The modified properties are discussed in the following paragraphs. Experiments are required to verify the estimated properties. The elastic modulus estimation is especially tenuous, since extrapolation of curve-fitted data is required.

4.2.1 Elastic Modulus

The elastic modulus for ceramic materials is strongly dependent on material porosity. Higher porosity results in lower elastic modulus. This relationship is extremely important to the filter stress analysis, since, for fixed boundary conditions (deformations), the stresses are essentially directly proportional to the elastic modulus.

A considerable body of data is available on the elastic modulus of silicon nitride as a function of porosity. The data can be correlated by the relationship.²

$$E = 295 (1 - \epsilon)^{2.89} \quad (1)$$

where E is the elastic modulus, GPa
 ϵ is the total porosity.

Assuming a total porosity of 60 percent, the elastic modulus based on Equation (1) is 20.88 GPa (3.0×10^6 psi). This value is about 12 percent of the elastic modulus for heat exchanger grade RBSN.

4.2.2 Thermal Conductivity

The thermal conductivity of ceramic materials is also a strong function of porosity. Higher porosity results in lower thermal conductivity. The effect of lower thermal conductivity on the filter thermal analysis is to increase thermally induced temperature gradients. This increases the deformation and partially offsets the stress reduction due to the lower elastic modulus.

²Datta, S. K., A. K. Mukhopadhyay, and D. Chakraborty, "Young's Modulus-Porosity Relationships for Si_3N_4 Ceramics—A Critical Evaluation," *Ceramic Bulletin*, Vol. 68, No. 12, 1989, pp. 2098-2102.

An approximate relationship between porosity and thermal conductivity in ceramics is:³

$$k/k_o = (1 - \epsilon)/(1 + \epsilon) \quad (2)$$

where k/k_o is the ratio of thermal conductivity of the porous material to that of the fully dense material.

Based on a nominal thermal conductivity of 7.5 Btu/hr-ft-°F for heat exchanger-grade RBSN (18 percent porosity), k_o can be calculated to be 10.79 Btu/hr-ft-°F from Equation (2). Further use of Equation (2) yields a thermal conductivity of 2.70 Btu/hr-ft-°F for filter-grade RBSN (60 percent porosity).

4.2.3 Density

The density of RBSN of 60 percent porosity is approximately 80 lb/cu ft, based on a fully dense Si_3N_4 density of 200 lb/cu ft.

4.3 FINE-GRID THERMAL MODEL

4.3.1 Model Preparation

Because the heat transfer conductance for gas flow through the thickness of the plate is much higher than the conductance for gas flow along the channels, the temperature gradient across the thickness of the plate may be significant. A more detailed thermal model has been created to address this issue.

The model concentrates on the region of the expected highest stress level in the filter plate, as indicated in Figure 4-1. The location of the detailed region was selected based on the results of the complete plate thermal analysis. As shown in Figures A-2 and A-3, the largest temperature gradient in the Y-direction occurred near the boundary between the flange and the remainder of the plate. In the X-direction, other than the header bar at the edge of the plate, the temperature variation is relatively uniform. The selected region exhibits the maximum temperature gradient due to the clean-side fins.

The model is shown in Figure 4-2. Also shown is a perspective view of the region modeled, with the actual dimensions included. The location of the X, Y, Z coordinate system is indicated. Because of symmetry, half of the fin height and thickness and half of the flow channel width was sufficient for the model.

The thermal model comprises 10 layers in the Z-direction. The grid in the X, Y plane is shown in Figure 4-3; each dot represents a node. Note the variation in node size. Not all the nodal points shown in Figure 4-3 appear in each of the 10 layers. Starting from $Z = 0$ (see Figure 4-2), the first three layers comprise the clean-gas fin and flange region. These layers are 0.023, 0.001, and 0.001 in. thick. The next six layers comprise the plate section, initially in the flange region and then in the porous

³Kingery, W. D., H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics*, 2nd edition, John Wiley and Sons, New York, 1976, p. 636.

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DETAILED THERMAL MODEL

Figure 4-1. Detailed Region of Ceramic Filter Plate
Shown on Model of Clean-Side Fins

Figure 4-2. Region Modeled for Fine-Grid Thermal Analysis

Figure 4-3. Thermal Grid in X, Y Plane

region (see Figure 4-2). The layers are 0.001, 0.001, 0.003, 0.005, 0.01, and 0.03 in. thick. The final layer is the dirty-side fin section, comprising the flange and dirty-side header bar. This layer is 0.1 in. thick.

4.3.2 Cleaning-Pulse Operation Analysis

The thermal model was run on the ATAP for the cleaning-pulse operation. The conditions were similar to those discussed in para. 4.1.1. Complete nodal temperature maps were generated at various times throughout the pulsing interval. Typical results are presented below. These maps are presented as examples only. The temperatures from the complete model are used in the stress analysis (see para. 4.4).

Figure 4-4 presents the temperatures of the layer at $Z = 0.0255$ in. (see Figure 4-2), along section A-A in the Y-direction. This is the first layer in the plate region (described in para. 4.3.1). As shown in Figure 4-4, the plate temperatures are relatively uniform along section A-A, with the plate cooling throughout most of the pulsing period. Towards the end of the pulsing period, the plates heat up slightly. This is due to the reduction in flow rate near the end of the pulsing interval, as shown in Figure 2-2.

Figure 4-5 presents the temperatures of the same layer ($Z = 0.0255$ in.) along section B-B in the X-direction. As shown in Figure 4-5, the region under the clean-side fin ($X < 0.015$ in.) exhibits larger temperature gradients compared to the porous plate region ($X > 0.015$ in.).

Figures 4-6 through 4-9 present the temperature through the thickness (in the Z-direction) at various locations (as indicated). At location C, in the porous plate region (Figure 4-6), a relatively large temperature gradient is observable. At location D, in the flange region (Figure 4-7), temperature gradients similar to those at location C are present. This is due to the effect of conduction from the porous plate, located only 0.0025 in. from location D. The conduction effects can also be seen at location E, in the flange region (Figure 4-8), and at location F, in the clean-fin region (Figure 4-9).

Figure 4-10 shows the gas temperatures through the plate thickness (in the Z-direction) at location C in the porous plate region. Comparison with Figure 4-6 shows that the gas and plate are at similar temperatures a short distance into the plate.

In general, the temperature gradients have increased, while the temperature level has decreased compared to the preliminary results based on heat exchanger grade material properties.⁴ These are due to the significant decrease in both thermal conductivity and density (thermal capacitance). The increase in thermal gradients would normally be expected to result in increased stress levels. However, the very large decrease in elastic modulus (see para. 4.2.1) will result in much lower stress levels.

⁴Strumpf, H., M. Coombs, T. Stillwagon, and J. Van Ackeren, "Membrane Filter Technology, RBSN Crossflow Filters," *Proceedings of the Advanced Research and Technology Development Direct Utilization, Instrumentation, and Diagnostics Contractors' Review Meeting*, DOE/METC-89/6108, October 1989.

Figure 4-4. Plate Temperatures Along Section A-A at $Z = 0.0255$ in.

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Figure 4-5. Plate Temperatures Along Section B-B at $Z = 0.0255$ in.

Figure 4-6. Plate Temperatures in Z-Direction at Location C

B-15887-A

Figure 4-7. Plate Temperatures in Z-Direction at Location D

Figure 4-8. Plate Temperatures in Z-Direction at Location E

B-15889-A

Figure 4-9. Plate Temperatures in Z-Direction at Location F

B-15888-A

Figure 4-10. Gas Temperatures in Z-Direction at Location C

4.4 FINE-GRID STRUCTURAL ANALYSIS

A structural model was prepared to evaluate the effects of thermal gradients. The model concentrates on the region of highest expected stress. The grid pattern is identical to that of the thermal model; this enables the predicted temperature distributions to be directly applied. The model runs on the ANSYS computer program, a commercial structural analysis code.

Since the model only covers a small region of the actual structure, the boundary conditions are not known precisely. Free structural boundary conditions are considered to be closest to the actual conditions, although the predicted stress might be somewhat optimistic.

The predicted temperatures and stresses at 0.45 sec (the end of the pulsing period) are shown in Figures 4-11 and 4-12, respectively. The maximum stress level is approximately 3.6 ksi. The highest stresses are at the fin-to-flange interface regions across the thickness of the filter.

The structural analysis results indicate that moderately high thermal stresses are generated during the cleaning-pulse period compared to the measured material strength (see Section 5). The stresses result from the application of ambient temperature cleaning air to the filter, which is at a uniform temperature of 1600°F. The thermal stresses generated during startup and shutdown will be much lower than the cleaning-pulse period thermal stresses, due to the much more gradual heating and cooling rates.

The pressure stresses generated during the cleaning-pulse interval are much lower than the thermal stresses. For the maximum pressure differential of 11 psi (see Figure 2-4), the plate bending stress is less than 100 psi. The maximum fin stress is of the same order of magnitude.

4.5 DISCUSSION

The thermal and stress analysis discussed in paras. 4.3 and 4.4 was performed using properties representative of the initial baseline filter material—60 percent porous RBSN. As discussed in Section 1, the recommended revised baseline material is porous SSN. The SSN filter-grade material has a porosity around 72 percent (see Section 5). Some of the physical properties required for thermal and stress analysis on the proposed material, specifically thermal conductivity and elastic modulus, are not known. The estimation procedures discussed in para. 4.2 become less valid at higher porosities. With the very high porosity of the proposed SSN, physical property measurements are believed to be required before a meaningful thermal or stress analysis can be performed.

Stress levels are expected to be lower for the more porous SSN, compared to the 60 percent porous RBSN. Both the thermal conductivity and the elastic modulus will be lower for the more porous material. The decreased thermal conductivity tends to result in increased thermal gradients, which might increase stress levels; however, the decreased elastic modulus decreases the stresses. The stress reduction due to the

ANSYS 4.4
 MAR 16 1990
 15:10:00
 PLOT NO. 2
 POST1 STRESS
 STEP=1
 ITER=1
 TEMP
 SMN =736.02
 SMX =1577

XV =1
 YV =1
 ZV =1
 DIST=0.386742
 XF =0.05
 YF =0.36185
 ZF =0.0875
 PRECISE HIDDEN
 A =782.719
 B =876.118
 C =969.517
 D =1063
 E =1156
 F =1250
 G =1343
 H =1437
 I =1530

B-21689

Figure 4-11. Finite-Element Model Temperature Input at 0.45 sec, °F

ANSYS 4.4
 MAR 16 1990
 15:12:43
 PLOT NO. 4
 POST1 STRESS
 STEP=1
 ITER=1
 SIGE (NOAVG)
 TOP
 DMX =0.001567
 SMN =126.041
 SMX =3590

 XV =1
 YV =1
 ZV =1
 DIST=0.386742
 XF =0.05
 YF =0.36185
 ZF =0.0875
 PRECISE HIDDEN
 A =318.506
 B =703.435
 C =1088
 E =1858
 F =2243
 G =2628
 I =3398

Figure 4-12. Stress Plots at 0.45 sec, psi

elastic modulus decrease is expected to be greater than the stress increase due to the thermal conductivity decrease.

It would appear to be desirable to reduce the pulse cleaning thermal stresses. This can be accomplished in a number of ways. First, the use of a heated blowback tank will reduce the temperature gradients caused by the cold cleaning air (see Figure 2-3), resulting in reduced stress levels. This approach would require the use of a valve able to operate reliably at the blowback tank temperature. A second approach is to provide an accumulator or plenum volume between the pulsing air valve and the filter element. The accumulator, which would be at essentially the same temperature as the filter, would contain sufficient air for the entire pulsing period (approximately 0.1 lb is required). Thus, the cleaning air charge would come entirely from the hot air stored in the accumulator.

Another approach involves using a regenerator between the pulsing air valve and the filter element. This regenerator, which could be fabricated from heat exchanger grade RBSN or SSN, would normally be at the operating temperature. During pulsing, the cold air would be heated by the energy stored in the regenerator. Since the total amount of air used for cleaning is small (approximately 0.1 lb), the regeneration requirement is low. For example, to heat the air to 1300°F, the total heat storage requirement is approximately 30 Btu.

5. OPTIMUM FILTER PROPERTIES (MATERIAL DEVELOPMENT)

The initial focus of work in this task (task 3) was on the formulation of a reaction-bonded silicon nitride (RBSN) material exhibiting sufficient permeability and strength for the filter application. Task 3 was divided into three subtasks: change porosity, flow measurement, and property measurement. More than 40 RBSN batch formulations were processed and evaluated as potential filter materials.

Reaction-bonded silicon nitride batches were prepared for this study using KemaNord Sicomill extra-refined grade IV, size C silicon powder. Typical impurity levels in this powder are 0.07% Fe, 0.06% Al, 0.01% Ca, and 0.08% C on a weight basis. An organic binder system, a plasticizer, and nitriding aids were used in all batches (see Figure 5-1). Also, organic pore formers were added to some batches.

Small batches of the experimental formulations (approximately 100 gm) were prepared using the mixing chamber of a Haake-Buchler torque rheometer (Figure 5-2). Particle-to-particle friction during the high-energy mixing heats the batch, yielding a plasticized mass with the consistency of clay (Figure 5-3). The lumps of mixed batch were then fed into a two-roll mill (Figure 5-4) to form plastic tape. Successive passes through the two-roll mill produced a smooth, flexible, tear-free tape (Figure 5-5). The final tape thickness (0.050 in.) was controlled by the spacing of the rolls. Small 1-in.-dia discs cut from these tapes were thermally processed, i.e., subjected to binder removal, nitriding, and/or sintering.

94831-6

Figure 5-1. Reaction-Bonded Silicon Nitride (RBSN) Batch Constituents

F-59290-A

Figure 5-2. Haake-Buchler Torque Rheometer Used for Mixing 100-g Batches F-59291-A

94831-4

Figure 5-3. Mixed RBSN Batch

Each experimental batch formulation was screened, after it was processed, by flow rate measurements. The flow-rate test apparatus is shown schematically in Figure 5-6. High-pressure nitrogen was regulated to achieve the desired pressure drop. A digital mass flow meter measured the amount of nitrogen flow through the filter sample. Flow rate could be measured as a function of pressure drop by varying the nitrogen pressure. Sample filter discs were mounted in the test fixture shown in Figure 5-7. Each sample was squeezed between two rubber O-rings which had been coated with vacuum grease to ensure a good seal. The diameter of the O-rings is 0.709 in., resulting in a test area of 0.395 sq in. for each sample. Flow rate measurements for this small active area were reported in ft/min for each pressure drop tested.

The design objective was to obtain a material which exhibited a pressure drop of 5 in. H_2O (ΔP) at a face velocity of 10 ft/min. Flow rate testing of batches was therefore an initial screening test. For those samples that met the approximate flow- ΔP criterion, the samples' densities and porosities were measured, and biaxial flexure strength tests were performed.

In parallel with the work performed to formulate an RBSN membrane filter, alternative materials and forming methods for producing a filter material having sufficient strength and permeability were considered. The alternatives considered include sintered silicon nitride (SSN), a mixture of RBSN and SSN, SSN or RBSN foam, and RBSN tape, which was laser drilled or mechanically punched with an array of small (i.e., < 100 micron) diameter holes.

F-62835

Figure 5-4. Two-Roll Mill

Figure 5-5. Flexible RBSN Tape

The subtasks performed on RBSN formulations are described in para. 5.1, and work conducted on the alternative RBSN approaches is described in para. 5.2. Sintered silicon nitride approaches are discussed in para. 5.3. Recommendations for the ceramic membrane filter material are presented in para. 5.4.

5.1 REACTION-BONDED SILICON NITRIDE

RBSN typically contains about 18 percent porosity. The flow measured through such an RBSN sample is zero at a pressure drop of 5.0 in. water. Thus, for the RBSN membrane filter, higher porosity is needed. The total porosity required depends on the porosity shape and size distribution, and the degree of interconnection between the pores. The bulk of the work performed in this task was therefore aimed at evaluating the effects of batch parameters on increasing the effective permeability in tapes formed of silicon.

The tape-forming parameters investigated include particle size, binder content, pore former amount, and pore former type. The porosity may be increased by adjusting these parameters as follows: (1) adding organic material which results in void space as the organics are removed during binder extraction; (2) lowering the packing density by using a coarser particle size with a narrower size range; and (3) decreasing the green density of the silicon tape by means of lower particle loading, i.e., increased binder or pore former content.

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B-14259

Figure 5-6. Flow-Rate Test Apparatus

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Figure 5-7. Aluminum Test Fixture for Flow-Rate Testing

5.1.1 Change Porosity in RBSN

The earliest RBSN batch formulations contained silicon powders with an average particle diameter of 7, 9, 11, or 12 μ ; binder additions of 18, 24, 30, or 35 percent; and pore former additions of 0, 10, 15, 20, 25, or 30 percent. The average particle size of the as-received silicon powder was 8.6 μ . This powder was air classified as a means of adjusting the particle packing density. Figure 5-8 is an example of particle size distribution curves. The curves shown in Figure 5-8 are for the as-received silicon powder (8.6 μ) and powder which was air classified to a mean diameter of 7.0 μ . Rice starch and milled rice (roughly spherical in shape), or polyester flock and nylon fibers (high length/diameter ratios) were added as fugitive pore formers. In the first twenty RBSN batches, varying amounts and combinations of binder, silicon particle sizes, and rice, polyester, or nylon pore formers were formulated.

The initial formulations containing rice starch showed that while the starch mixed uniformly within a batch, the resultant pores were very small (see Figure 5-9). This extremely small pore size resulted in low measured flow rates. In subsequent batches, the larger particle size milled rice was tried as a means of increasing the flow through the material. A sample which was prepared using milled rice (60 wt% coarse milled rice, 30 wt% fine milled rice, and 10 wt% rice starch) is shown in Figure 5-10. The average size of the RBSN grains appears to be in the range of 10 μ , with a matrix of interconnected pores in the 1- μ range. The larger pores formed by the milled rice are not visible in the view in Figure 5-10. While the flow rate through samples of this type was an improvement over previous samples, it was far below the requirement of 10 ft/min at a pressure drop of 5.0 in. water.

The other pore formers used in the initial batch formulations, polyester flock and nylon fibers, had a tendency to align parallel to the rolling direction of the tape. This preferential alignment of fibers, due to their high aspect ratio, results in porosity that is perpendicular to the desired direction of airflow in the filter. This effect is illustrated in Figure 5-11, in which a sample containing nylon fibers is shown. Based on the observation of preferential alignment, the decision was made to use larger, more equiaxed pore formers in subsequent batches.

Examination of data taken from early batch formulations revealed that the efficiency of binder/pore-former burnout decreased with an increase in pore former. This observation indicated that a carbon residue remained in the samples, due to the necessity of debinding the material in a nitrogen atmosphere. The samples require debinding in nitrogen because firing the samples in air would result in oxidation of the silicon powder. For that reason, organic pore formers which volatilize more completely in nitrogen atmospheres were obtained. The amount of residual ash left by such organics is negligible. In the next round of experiments, 21 batch formulations containing varying amounts and/or particle sizes of silicon powder, binder, and clean-burning pore formers were evaluated.

Two pore former candidates that exhibit nearly complete decomposition in nitrogen were polymethyl methacrylate (PMMA) and polyalkylene carbonate (QPAC). A problem associated with these pore formers was the occurrence of straight-through

B-11087

Figure 5-8. Particle Size Distributions for As-Received and Air-Classified Silicon Powder

a) CROSS SECTION (MAGNIFICATION 100X)

(b) FACE (MAGNIFICATION 100X)

F-56822

Figure 5-9. Microstructure of RBSN Batch Having Average Silicon Particle Size of $7\ \mu$ (Before Nitriding), 30 wt% Binder Content, and 10 wt% Rice Starch Addition

Figure 5-10. Micrograph Showing RBSN Grains That Average 10 to 14 μ in Size with 5 to 20- μ Pores Connected by < 1- μ Channels. Milled Rice was Added as a Pore Former.

pinholes in the sample discs formed from the RBSN/PMMA and RBSN/QPAC batches. At first, this was attributed to the large particle size of the pore formers, but QPAC of smaller particle size was obtained and pinholes still developed in the RBSN/QPAC samples. Another difficulty encountered was the deformation of the PMMA and QPAC pore formers during mixing of the batches. The high temperature used to mix the RBSN batches softened these polymer pore formers. The lack of shape retention of the PMMA and QPAC sharply reduced their effectiveness in forming the desired systems of large, interconnected pores.

The third clean-decomposing pore former that was evaluated proved to be the best material. Polystyrene microspheres (size range of 20- to 180- μ dia) were incorporated in RBSN tape batches. Figure 5-12 shows the cross section of a 0.050-in.-thick, green (unfired) RBSN tape containing the polystyrene microsphere pore former. As shown, the polystyrene maintained its spherical shape throughout the batching, mixing, and tape-forming processes, due to the fact that its softening temperature is substantially higher than temperatures involved in these mixing processes.

After selecting polystyrene as the best pore forming material, batches were made containing various combinations of up to 35 percent binder, up to 30 percent pore former (polystyrene), and up to 12- μ -dia silicon powders. As with the earlier batch formulation studies, tests were performed on samples from those batches in order to determine the formulation which would yield the best combination of permeability and strength. It was found that a batch containing 45 wt% air classified coarse (11- μ -dia average) silicon powder, 25 wt% polystyrene, and 30 wt% binder gave the desired

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(a) CROSS SECTION (MAGNIFICATION 100X)

(b) FACE (MAGNIFICATION 100X)

Preferential alignment of the nylon-fiber pore former parallel with the direction of rolling is shown in the cross-section micrograph (a), while a lack of orientation is evident when viewing the face (b) of the sample.

Figure 5-11. Microstructure of RBSN Batch

Figure 5-12. Cross-Section of Green RBSN Tape Containing 12 wt% Polystyrene Microspheres

result. Duplicate batches of the 45 wt% silicon/25 wt% polystyrene/30 wt% binder formulation were made to evaluate repeatability.

5.1.1.1 Uniformity of Batches

Efforts were made to modify the processing of RBSN filter materials in order to achieve a homogeneous batch and minimize the problem of pinhole occurrence. Variations in processing included:

- (a) Sieving of binder to remove any agglomerates which would be incorporated in a batch
- (b) Jar-milling of dry ingredients prior to compounding in the high-intensity mixer
- (c) Increasing the mixing time in the high-intensity mixer
- (d) Changing the setting techniques in the binder extraction furnace

F-62447

The adoption of the first three processing variations resulted in more complete mixing of the material, thus producing a homogeneous batch with no large agglomerates of organic material in the green state. However, voids and pinholes in the samples, upon debinding, remained a persistent problem.

The fourth processing variation had the greatest effect on the quality of samples. Elimination of bubbles and voids was achieved by setting the sample discs on a porous medium such as graphite felt, woven graphite cloth, or a charcoal bed. The samples which had been set on dense alumina had all exhibited severe bubbling and voids on the face in contact with the setter. The voids appeared to have been caused by volatilization of the organics which could not escape through the dense alumina setter and, therefore, were trapped in the sample. The samples set on any of the porous media exhibited no bubbling or voids on their surfaces. However, when the samples were packed in a charcoal bed or placed on graphite felt, the powder or felt adhered to their surfaces and a cleaning step was required. The samples set on woven fabric did not stick to it and did not require cleaning after binder removal. Woven graphite felt was therefore chosen as setter material for future batches.

5.1.1.2 Preventing Deformation During Debinding

Two problems inherent in ceramic bodies with low levels of solids loading are a low green strength and a tendency to deform during binder removal. Several batch formulations having promising flow rates displayed severe deformation following debinding. A novel pretreatment process, developed with internal funding, virtually eliminated the deformation problem. The process entails dipping the green part into a solution which chemically cross-links the organic binder, yielding a hardened part. The cross-linked parts retain their shape throughout the debinding process.

The debinding deformation of uncross-linked cylinders formed from green tape was evaluated. Green tape, 0.050 in. thick, was rolled to form cylinders of approximately 1-in.-dia by 1-in.-tall. The cylinders were set on end and processed in a debinding run. All of the uncross-linked cylinders showed signs of slumping and deformation.

Cross-linked cylinders were also evaluated after debinding and showed no signs of deformation. Following the cross-linking, these cylinders were processed using the same debinding cycle as that used for the uncross-linked cylinders. After debinding, these cylinders showed no signs of slumping and retained their shape.

Also included in the cross-linking evaluation was a T-shaped sample formed by bonding two pieces of green tape together, similar to the fin-to-plate orientation in the filter module. This T-shaped sample enabled the cross-linking technique and the green tape bonding process to be evaluated simultaneously. The sample was set in the furnace with the top of the T facing down. Following debinding, this sample retained its shape and the bond between the tapes appeared strong.

5.1.2 Flow Rate Measurement

The measured flow on samples from all RBSN formulations was negligible after the nitriding process. Examination of batch specimens with an optical microscope before and after nitriding revealed that, even in samples with a high degree of open porosity, all passages became filled with α -silicon nitride fibers during processing (see Figure 5-13). Therefore, methods of eliminating the fibrous α -silicon nitride phase from the interconnected porosity were addressed.

Three RBSN batches containing polystyrene microspheres were formulated with various levels of silicon nitride powder additions. It was thought that the growth of α -silicon nitride would be retarded by substituting fine-grained silicon nitride for some of the silicon powder. However, the pores were filled completely with α -silicon nitride (similar to the sample shown in Figure 5-13) and the measured flow rate was zero for these samples.

Another method employed to inhibit the formation of α -silicon nitride was to alter the heating schedule that had typically been used in RBSN nitriding runs. It is known that the growth of α -silicon nitride is favored over the formation of β -silicon nitride at lower temperatures within the nitriding temperature range ($< 1400^{\circ}\text{C}$). A nitriding run containing samples of silicon, silicon plus silicon nitride (as an α -silicon nitride inhibitor), and silicon plus polystyrene microspheres was performed in which the temperature was ramped quickly to 1400°C , followed by a typical schedule of temperatures for the remainder of the run. The increase in ramping rate proved ineffective, however, as the

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Figure 5-13. Cross Section of a Nitrided RBSN Sample (RBSN-09299-3) Showing an Abundance of α -Silicon Nitride Filling the Pores (White Areas) (32X Magnification)

percentage of conversion from silicon to silicon nitride was much lower than the conversion obtained with the conventional nitriding schedule. Also, the flow rate in the samples was far below the required flow rate due to blockage of the pores.

The focus of effort shifted from preventing the formation of α -silicon nitride to removing it from the pores of the samples. Discs of RBSN were placed in an ultrasonic bath in deionized water, but no change in the flow rate through the material resulted. Those samples were soaked in a 100 percent solution of hydrofluoric acid (for 72 hr), and again were treated in the ultrasonic bath (for 4 hr), but the flow rate through the material remained near zero.

Another possibility of clearing the pores was to heat-treat the samples in air (static atmosphere) as a means of removing or consolidating the fibrous, high-surface-area, α -silicon nitride. The heat treatment schedules that were evaluated are summarized in Table 5-1. The first heat treatment of RBSN/25% polystyrene spheres was a soak for 2 hr at 1600°C (ramp rate to 1600°C was 400°C/hr). The flow measured on those samples was 28.8 ft/min, or nearly three times the required 10 ft/min. The next heat treatment, at 1400°C for 2 hr, resulted in a flow rate of up to 28.5 ft/min. The heat treatments which followed were run to determine the lowest soak temperature which would consistently produce a flow greater than the minimum required. The third and fourth treatments at 1000° and 1200°C (for 2 hr) produced inadequate change in the samples' permeability. The soak temperature was increased to 1300°C with a soak time of 4 hr, which resulted in an average flow rate of $\approx$ 10 ft/min. The flow rates of a group of 25 specimens from another batch soaked at 1400°C for 3 hr are listed in Table 5-2.

TABLE 5-1			
HEAT TREATMENT OF RBSN + 25% POLYSTYRENE MATERIALS (50% weight gain from nitriding)			
Ramping Rate, °C/hr (RT to Temperature)	Soak Temperature, °C	Soak Time, hr	Average Resulting Flow, ft/min
400	1000	2	0.3
400	1200	2	9.2
400	1300	4	10.3
400	1400	3	20.7
400	1600	2	28.8

A sample of the heat-treated material was submitted for X-ray diffraction analysis to determine the molecular species present. The results of this analysis are shown in Figure 5-14. The data indicate that a large proportion of the material is SiO_2 (cristobalite). To a first order, the height of the peaks is proportional to the mole percentage of the constituent species, which would indicate that the material is approximately 40 percent cristobalite (SiO_2). The oxidation of silicon nitride comprises the following reaction:

TABLE 5-2	
FLOW RATE MEASUREMENTS ON RBSN/25 WT% POLYSTYRENE SAMPLES (60% weight gain from nitriding)	
Sample No.	Flow Rate, ft/min
1	9.6
2	6.2
3	6.6
4	8.5
5	12.3
6	6.6
7	11.1
8	11.4
9	9.8
10	11.0
11	7.4
12	4.8
13	10.3
14	5.9
15	4.6
16	4.9
17	6.5
18	12.4
19	11.2
20	11.6
21	6.1
22	9.2
23	14.6
24	9.4
25	6.7
Average flow rate:	8.7 ft/min
Standard deviation:	2.7 ft/min

Figure 5-14. X-Ray Diffraction Pattern on Filter Sample with 25 Percent Polystyrene, Heat Treated in Air to 1300°C for 3 hr

This result was confirmed by correlating the weight gains of the material during various processing steps to the chemical species present. Also, dissolving the SiO_2 using hydrofluoric acid confirmed the high quantity of SiO_2 present in the material.

Several experiments were undertaken to mitigate this conversion of Si_3N_4 to SiO_2 . A batch of filter material containing a greater percentage (37.5 percent) of pore former was processed for use in a variety of heat-treatment experiments. The greater amount of pore former and shorter exposure to air at the high temperatures was expected to result in a sufficient amount of interconnected porosity to allow the prescribed flow rate, but with a minimum of conversion to SiO_2 .

Discs of the material were treated in air at 1000°, 1100°, 1200°, 1300°, 1400°, and 1500°C with no hold (soak time) at temperature. Flow testing was performed for each heat treatment, and no increase in flow resulted from the heat treatments below 1400°C. The flow rates resulting from the 1400° and 1500°C heat treatments were 2.5 and 3.1 ft/min, respectively. The disc that had been treated at 1500°C was soaked in hydrofluoric acid overnight. The flow in the sample increased to 4.1 ft/min, and the weight loss in the sample was about 48 percent.

Concurrently with these experiments, other filter discs, which had not been heat treated in air, were heat treated in a vacuum. Samples were heated in a vacuum to 1470° and to 1600°C. The objective of these experiments was to selectively remove the high-surface-area α -phase blocking the pores, while eliminating conversion of the silicon nitride to silica.

The treated samples appeared to have an open, porous structure when examined on an optical microscope (Figure 5-15). The treatment resulted in weight loss in the samples of about 40 percent, accompanied by a small increase in flow rate. The flow was about 2.5 ft/min for samples containing 20 percent polystyrene and about 3.6 ft/min in samples containing 37.5 percent polystyrene after heat treatment in a vacuum.

Several methods of removing and/or inhibiting the growth of α - Si_3N_4 in the pores of the material were investigated. These were:

- (a) Less severe oxidation and acid etch to remove any SiO_2 : No oxidation schedule that provided even minimum flow was found unaccompanied by significant, i.e. > 30 percent, weight loss.
- (b) Vacuum sublimation of the α - Si_3N_4 : High-temperature (1470° to 1600°C) vacuum sublimation provided moderate increases in flow (3.6 ft/min), but weight loss in samples was very high (up to 36 percent).
- (c) Postnitriding sintering of RBSN: Infiltration of sintering aids and subsequent sintering of the material yielded no change in flow rate or material weight.
- (d) High-pressure nitriding: High-pressure nitriding offers the potential for a reduced α/β silicon nitride ratio. However, no significant air flow was apparent with discs nitrided under high pressure.

Figure 5-15. SEM Micrograph Showing Structure of Filter Sample after Heat Treatment in Vacuum (1470°C for 3 hr)

All efforts to produce a permeable form of RBSN without seriously degrading the matrix material itself were unsuccessful. Consequently the program focus shifted to efforts on alternative materials.

5.1.3 Properties

The initial batch compositions of RBSN, which contained rice starch, milled rice, polyester flock, nylon fibers, PMMA, or QPAC, had measured porosities of up to 50 percent. The pores were very small, as shown in Figure 5-9, or were aligned perpendicular to the direction of flow, as shown in Figure 5-11. In all cases, pores in the samples containing the above-mentioned pore formers were not sufficiently interconnected to allow gas to pass through at a pressure drop of 5 in. water. As these samples did not pass the initial screening test (flow rate measurement), the formulations were rejected as filter material candidates, and no additional property measurements were taken.

The batch compositions containing polystyrene microspheres as a pore former failed the initial screening (flow rate) test as well, but unlike the earlier compositions, the RBSN/polystyrene samples were improved by the static air heat treatments. The effect of heat treatments may be observed by comparing Figure 5-16, showing the unpolished cross section of a heat-treated RBSN sample (which contained 25 wt% polystyrene, 35 wt% binder) with Figure 5-13 (a sample of the same composition prior to heat treatment). The densities and porosities of this material were measured before and after heat treatment by the Archimedes principle. The bulk density of the material

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Figure 5-16. Unpolished Cross Section of Heat-Treated RBSN/ Polystyrene Specimen Showing Open Porosity

decreased upon heat treatment from 1.24 g/cc to 1.16 g/cc (average). The open porosity increased upon heat treatment from 48.2 to 56.3 percent.

Two types of strength measurements were used to characterize the material: (1) biaxial flexure tests conducted on the thin circular discs also used for flow measurements, and (2) four-point bend tests conducted on standard bar, having dimensions of 1/8 by 1/4 by 2 in. Examples of these are shown in Figure 5-17.

The biaxial flexure test has become popular as a method of measuring the strength of glass and ceramics.⁵ Three loading schemes that produce biaxial tension in flat-plate specimens (i.e., ball-on-ring, piston-on-ball, and ring-on-ring tests) have been evaluated using finite-element methods.^{5,6} The piston-on-ball test (adopted as an ASTM standard) has a unique advantage in that specimens that are slightly warped can be accommodated by three-point support.⁵ This loading configuration eliminates premature fracture from an edge defect or anomaly.⁷

⁵Ritter, J.E., K. Jakus, A. Batakis, and N. Bandyopadhyay, "Appraisal of Biaxial Strength Testing," *Journal of Non-Crystalline Solids*, Vols. 38 & 39, 1980, pp. 419-424.

⁶Shetty, D., A. Rosenfield, P. McGuire, G. Bansal, and W. Duckworth, "Biaxial Flexure Tests for Ceramics," *Ceramic Bulletin*, Vol. 59, No. 12, 1980, pp. 1193-1197.

⁷ASTM Designation: F394-78, "Standard Test Method for Biaxial Flexure Strength (Modulus of Rupture) of Ceramic Substrates," 1984.

Figure 5-17. Disc Used for Flow Test and Biaxial Flexure Test and Bar Used for Four-Point Bend Test

Determining the strength of brittle materials by three- or four-point uniaxial bending is a long-established technique, but these tests have two major deficiencies: (1) edge effects resulting from specimen preparation techniques contribute to the measured strength, and (2) since strength is strongly influenced by the flaws created during surface grinding or polishing, the effect of grinding striations (latitudinal or longitudinal) cannot be fully analyzed except by testing two sets of specimens.⁸ According to Radford and Lange, the biaxial flexure test overcomes all the deficiencies of the three- or four-point bend test.⁸ The test is independent of edge conditions, accounts for all flaws regardless of direction, is simple and low in cost, and does not require rigorous preparation of samples.

Biaxial strength measurement tests were performed on heat-treated RBSN discs to which polystyrene had been added as a pore former. A modification of the ASTM "Standard Test Method for Biaxial Flexure Strength (Modulus of Rupture) of Ceramic Substrates" (American Society for Testing and Materials Designation: F 394-78) was used.⁷ The calculated biaxial flexure modulus of rupture (MOR) characteristic strength and Weibull modulus for these specimens are shown in Table 5-3. The characteristic strength and Weibull modulus measured in the test indicate that this material is a good membrane filter material candidate.

⁸Radford, K.C., and F.F. Lange, "Loading (L) Factors for the Biaxial Flexure Test," *Journal of the American Ceramic Society*, Vol. 61, No. 5-6, 1977, pp. 211-213.

TABLE 5-3		
BIAXIAL FLEXURE TEST RESULTS FROM RBSN/25 WT% POLYSTYRENE/ HEAT-TREATED DISC SPECIMENS		
MOR Rank	Breaking Load, lb	Stress MOR, ksi
1	12	3.5
2	12	3.5
3	12	3.5
4	13	3.7
5	13	3.7
6	13	3.7
7	13	3.7
8	13	3.7
9	14	4.0
10	14	4.0
11	14	4.0
12	15	4.3
13	15	4.3
14	15	4.3
15	15	4.3
16	15	4.3
17	15	4.3
18	15	4.3
19	15	4.3
20	15	4.3
21	16	4.6
22	16	4.6
23	16	4.6
24	17	4.9
25	17	4.9
Characteristic strength, ksi: 4.3		
Weibull modulus: 10.3		

Four-point bend strength measurements were conducted on machined bar specimens. The test data for 25 such bars are presented in Table 5-4. These data indicate a characteristic strength of 2.4 ksi and a Weibull modulus of 8.1.

The seeming disparity between the characteristic strengths derived from the biaxial (disc) and four-point (bar) measurements can be reconciled. While the characteristic tensile strength of samples is required for reliability analysis, experimental data are usually acquired using the more convenient four-point bend strength test or biaxial flexure strength test. The calculations performed to obtain the volume and surface characteristic tensile strength are discussed below.

TABLE 5-4		
FOUR-POINT BEND TEST RESULTS FROM RBSN/25 WT% POLYSTYRENE/ HEAT-TREATED BAR SPECIMENS		
MOR Rank	Breaking Load, lb	Stress MOR, ksi
1	5	1.5
2	7	2.0
3	7	2.0
4	7	2.0
5	7	2.0
6	7	2.0
7	7	2.0
8	7	2.0
9	7	2.1
10	7	2.1
11	7	2.2
12	8	2.3
13	8	2.3
14	8	2.3
15	8	2.3
16	8	2.3
17	8	2.3
18	8	2.3
19	8	2.3
20	8	2.3
21	8	2.3
22	8	2.4
23	8	2.4
24	7	2.4
25	7	2.4
26	7	2.5
27	9	2.6
28	9	3.0
Characteristic strength, ksi: 2.4		
Weibull modulus: 8.1		

The relationship between characteristic test strength and characteristic tensile strength is:⁹

$$\sigma_t/\sigma_o = L^{1/m}$$

where:

L = Loading factor

m = Weibull modulus

σ_o = Characteristic test strength

σ_t = Characteristic tensile strength

The characteristic tensile strength from volume failure is calculated using the disc biaxial flexure characteristic test strength as follows:⁸

a = 0.4 in. = Support ring inner radius

b = 0.252 in. = Piston radius

c = 0.5 in. = Plate radius

The volume loading factor, L_v , is taken from Figure 2 of Reference 8 after making the following calculations:

$$Q = b/c = 0.0252/0.5 = 0.050$$

$$T = a/c = 0.4/0.5 = 0.8$$

Then, from Figure 2 of Reference 8:

$$L_v = 0.00017$$

and

$$\sigma_t/\sigma_o = (0.00017)^{1/10.3} = 0.431$$

$$\sigma_t = (0.431)(4.3) = 1.85 \text{ ksi}$$

The characteristic tensile strength from surface failures is calculated using the disc biaxial flexure characteristic test strength as follows (L_A is the surface loading factor):⁸

$$L_A = L_v(m + 1)$$

$$L_A = (0.00017)(10.3 + 1) = 0.00192$$

$$\sigma_t/\sigma_o = (0.00192)^{1/10.3} = 0.545$$

$$\sigma_t = (0.545)(4.3) = 2.34 \text{ ksi}$$

⁹Strumpf, H.J., D.M. Kotchick, and M.G. Coombs, "Development of a Ceramic Recuperator for Army Gas Turbine Applications," U.S. Army TACOM Report 12887, December 1983, p. 81.

The characteristic tensile strength from volume failures is calculated using the four-point bend bar test strength as follows:⁹

$$\begin{aligned}
 L_v &= (2 + m)[4(m + 1)^2] = (2 + 8.1)/[4(8.1 + 1)^2] \\
 &= 0.0305 \\
 \sigma_t/\sigma_o &= (0.0305)^{1/8.1} = 0.650 \\
 \sigma_t &= (0.650)(2.4) = 1.56 \text{ ksi}
 \end{aligned}$$

The characteristic tensile strength from surface failures is calculated using the four-point bend test strength as follows:⁹

$$L_A = [(2 + m)/4(m + 1)^2] [\{mw/(w + h)\} + 1]$$

where:

$$\begin{aligned}
 w &= \text{Specimen width} = 0.25 \text{ in} \\
 h &= \text{Specimen height} = 0.125 \text{ in.} \\
 L_A &= [0.0305] [\{(8.1)(0.25)/(0.25 + 0.125)\} + 1] \\
 &= 0.1952 \\
 \sigma_t/\sigma_o &= (0.1952)^{1/8.1} = 0.817 \\
 \sigma_t &= (0.817)(2.4) = 1.96 \text{ ksi}
 \end{aligned}$$

The characteristic test strengths and the two types of characteristic tensile strengths are presented in Table 5-5. While a large difference in characteristic test strengths exists between the four-point bend and biaxial flexure tests, the difference between the test types is not large for the characteristic tensile strengths. As previously mentioned, the characteristic tensile strength is required for reliability analysis. Therefore, it may be concluded that no discrepancy exists in the pertinent data between the strength measurements acquired by biaxial flexure tests and four-point bend tests.

TABLE 5-5		
RECONCILIATION OF BIAXIAL AND FOUR-POINT BEND TESTS— COMPARISON OF CHARACTERISTIC TEST STRENGTHS AND CHARACTERISTIC TENSILE STRENGTHS		
	Four-Point Bend, ksi	Biaxial Flexure, ksi
σ_o	2.40	4.30
σ_t (volume)	1.56	1.85
σ_t (surface)	1.96	2.34

5.2 ALTERNATIVE RBSN APPROACHES

When difficulties developed with the baseline RBSN, several alternative RBSN approaches were undertaken, as presented in the following paragraphs. Sintered silicon nitride approaches are discussed in para. 5.3.

5.2.1 Foaming Agents

Silicon powder (11- μ average particle size) was combined with components of polyurethane mixtures having densities of 10, 30, and 60 lb/cu ft. The mixtures were poured into cylindrical molds and allowed to foam and cure without constraint. The typical microstructure of the foamed material is shown in Figure 5-18. Subsequent conversion to silicon nitride yielded a material that provided a flow of about 10 ft/min at the prescribed pressure drop. While the flow rate was adequate, the strength was very low, and consequently the approach was not considered further.

Figure 5-18. Silicon in Polyurethane Foam Prior to Binder Extraction (Foam Density of 60 lb/cu ft)

5.2.2 Drilled Holes

Another approach investigated was the drilling of holes in green RBSN tape, using a laser. An array of 625 holes per sq in. was drilled in a 0.050-in.-thick green silicon tape using a pulsed CO₂ laser (Figure 5-19). The holes are somewhat irregular, which is due to the high-energy beam volatilizing some of the surrounding binder. In addition, the hole diameters were not uniform, due to sagging of the material, which allowed the tape to move away from the optimum laser focal length. The hole diameters vary from

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less than 50 μ to approximately 300 μ . At a pressure drop of 5 in. H_2O , the measured flow was 45 ft/min before nitriding and 42 ft/min after nitriding.

Figure 5-19. RBSN Tape Containing 625 Laser-Drilled Holes/sq in.

An alternative method of obtaining a tape with a discrete array of very small holes was to use a mechanical, numerically controlled punch machine to obtain the desired hole size and pattern. This technique is illustrated in Figure 5-20, which shows a 70-mil-thick tape that was punched with 4-mil-dia holes at 625 holes/sq in. This tape yielded a flow rate of 15.6 ft/min in the green state at 5 in. H_2O . However, following nitriding, the holes were effectively plugged with α - Si_3N_4 and required significant heat treatment to obtain the required flow.

5.3 SINTERED SILICON NITRIDE

The effort to develop a filter made of SSN began in parallel with the work on the RBSN filter. Some of the initial batches, using coarse Si_3N_4 powder, showed promise as a potential filter material; flow rates through the material exceeded the required 10 ft/min at a pressure drop of 5 in. water. However, the strength of the material was very low. Efforts to improve the strength resulted in moderate improvement at best. This work is discussed in para. 5.3.1.

Subsequent work focused on the use of fine Si_3N_4 powder plus pore formers and sintering aids. A formulation of this type which displays adequate strength and greater than adequate flow rates while maintaining its shape during processing was developed. This effort is discussed in para. 5.3.2.

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Figure 5-20. Green, Silicon Tape Sheet Mechanically Punched with an Array of 4-mil-dia Holes (625 holes/sq in.)

5.3.1 Coarse Silicon Nitride Powder

All sintered silicon nitride (SSN) batches contained the same binder system used in the RBSN formulations. Commercial-grade, coarse silicon nitride powders were used in the initial batches. The SSN batch parameters that were investigated include: particle size of silicon nitride powder, amount of binder in the system, addition of silicon powder, addition of pore former, addition of sintering aids, and the pressure and temperature used in the sintering schedule.

The flow rate measured on the initial samples of sintered coarse silicon nitride was zero. Figure 5-21 is a micrograph of sintered silicon nitride, and it shows an unexpectedly high number of small ($1\text{-}\mu$) size silicon nitride grains. Silicon nitride, which had been screened to between 150 and $250\text{ }\mu$, and 25 wt% binder comprised the batch formulation. The presence of small size grains might have been due to grinding together of the large grains during mixing, or they may have adhered to the surface of the large grains during sieving and batching. Permeability of the samples from this batch may have been greatly reduced by the tight compaction of these fine particles between the large silicon nitride grains. Also, the low permeability was partly attributed to the low binder content in the batch. Removal of the finer constituent from the silicon nitride powder and an increase in binder content was expected to result in more open porosity.

The silicon nitride powder was washed to remove any fine particulates clinging to the coarse grains. An SSN batch was made which contained 35 wt% binder. The sample in Figure 5-22 can be compared with the sample in Figure 5-21, showing that the washed silicon nitride powder and increased amount of binder resulted in a more

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Figure 5-21. SEM Micrograph of SSN Sample Showing Lack of Porosity Due to Fine Particulates Filling the Spaces Between the Large Silicon Nitride Grains

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Figure 5-22. Washed Silicon Nitride Powder Yields an Open Porous Structure with High Permeability

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open, porous structure. The flow rate through this material exceeded the flow requirements by 50 percent. While the desired flow had been achieved, the strength of the material was very low. Thus the next batches, in which silicon powder was added and silicon nitride particle sizes were combined, were formulated to increase the strength of the SSN.

Silicon powder was added to some SSN batches as a means of forming reaction-bonds between the silicon nitride particles. It was expected that the coarse, poorly packed silicon nitride powder, in combination with a small amount of reaction-bonded silicon nitride, would result in a porous body containing strongly bonded silicon nitride grains. The addition of finer (60/80 mesh) silicon nitride powder to the coarse (40/60 mesh) powder was also expected to contribute to the strength. A series of batches was produced in which 5 wt% silicon powder was added to coarse (40/60 mesh) silicon nitride plus 15, 30, 35, or 40 wt% binder. Another series of batches contained 1, 5, 10, 15, or 20 wt% silicon, a 50/50 mixture of 40/60 mesh and 60/80 mesh silicon nitride powders, and 35 wt% binder. It was found that α -silicon nitride formation was significant in all samples containing silicon powder. As expected, the amount of α -silicon nitride decreased with the amount of silicon, but the handling strength also decreased rapidly with a decrease in the amount of silicon in the batch. This approach was rejected, as the measured flow rate was close to zero in all samples.

Another approach for increasing the strength while maintaining permeability was to add sintering aids to the batch. Figures 5-23 and 5-24 are typical micrographs of specimens with and without sintering aids. The microstructure in Figure 5-23, of a batch containing no sintering aids, shows an open crystalline matrix. Figure 5-24 shows a similar formulation but contains 12 wt% sintering aids. This microstructure displays an amorphous bond matrix linking the large silicon nitride grains. The handling strength of SSN samples increased when sintering aids were added, and, while the flow rate was reduced, it remained above the acceptable level.

The most effective means for increasing the strength of SSN was to change the sintering schedule to a higher temperature, high-pressure sintering process. Samples from batches containing coarse silicon nitride powder, fine silicon nitride powder plus polystyrene microspheres (as a pore former), and duplicates of those batches plus sintering aids were sintered at 1800°C and 1500 psi. Previous samples had typically been sintered at 1700°C and 20 psi; the higher temperature allowed more complete sintering, and the high pressure prevented degradation of the silicon nitride.

There was some concern about the viability of the joints with the SSN approach. To investigate this aspect, small finned plate samples were fabricated (Figure 5-25) and the resulting joints examined. The joints appeared to be excellent, giving some indication that a complete crossflow filter could be fabricated using the SSN approach.

The samples containing coarse silicon nitride plus sintering aids exhibited the greatest permeability and the highest apparent strength of those included in the high-temperature, high-pressure sintering process. A cross section of this material is shown in Figure 5-26. The light grey and very dark grey areas of the photograph are SSN, and the medium grey areas are interconnected pores (that have been filled with mounting

Figure 5-23. Cross Section of SSN-09289-1. Sintering Without the Use of Sintering Aids Yields an Open, Crystalline Structure

Figure 5-24. Cross Section of SSN-09289-2. The Use of Sintering Aids Yields a Structure Having an Amorphous Bond Phase

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Figure 5-25. Two-Layer Crossflow Module of Green SSN Finned Tapes

Figure 5-26. Cross Section of an SSN Disc Formed from Coarse (40/60 Mesh) Si_3N_4 Powder Plus Sintering Aids

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epoxy). The average flow measured at a pressure drop of 5 in. water for these samples was 19.8 ft/min. The characteristic strength of these samples, measured with a four-point bend strength apparatus, was 4.2 ksi, as shown in Table 5-6. The Weibull modulus of 2.4 is quite poor and indicates the wide variation in the data.

TABLE 5-6		
FOUR-POINT BEND TEST RESULTS FROM COARSE SSN (PLUS SINTERING AIDS) TEST BAR SPECIMENS		
MOR Rank	Breaking Load, lb	Stress MOR, ksi
1	2	1.5
2	5	1.8
3	5	2.2
4	4	2.4
5	6	2.5
6	5	2.6
7	4	2.9
8	7	3.9
9	5	4.0
10	8	4.0
11	8	4.4
12	5	4.4
13	7	5.0
14	8	6.8
Characteristic strength, ksi: 4.2		
Weibull modulus: 2.4		

5.3.2 Fine Silicon Nitride Powder

Work on SSN as a filter material to this point centered on the use of coarse silicon nitride powders and a high binder content to obtain the necessary flow. While high flow rates were achieved in these samples, the material lacked the necessary strength.

In an attempt to increase the strength, a fine silicon nitride powder with nitriding aids (designated GN-10), was employed with a number of potential pore formers. Batches were made using 47.5 wt% GN-10, 27.5 wt% binder, and 25 wt% of the following pore formers:

- (a) Duke polystyrene
- (b) Huntsman polystyrene

- (c) Composition Materials wood flour
- (d) Composition Materials ground rubber
- (e) CMA rubber
- (f) Atlos rubber
- (g) RRI rubber
- (h) HMU rubber
- (i) Sparton rubber
- (j) Polypropylene

Samples of these batches were debindered using the standard schedule in a nitrogen atmosphere. Other samples of these batches were debindered in air in order to allow a more complete burnout of the pore formers. A complete burnout in the following batches would result in about 52 percent weight loss, except in the Huntsman polystyrene, which if complete, would have a 56 percent weight loss. The percent weight loss for samples debindered in nitrogen and in air are listed in Table 5-7.

Samples which had retained their shape through binder removal were sintered at 1800°C and 1500 psi. The flow was measured in those samples which retained their shape through the sintering step, and those flow rates are also listed in Table 5-7.

TABLE 5-7				
WEIGHT LOSS AND FLOW THROUGH SSN FILTER SAMPLES FOLLOWING DEBINDERING IN A NITROGEN ATMOSPHERE OR IN AIR				
Pore Former	Weight Loss, percent (N ₂)	Flow, ft/min	Weight Loss, percent (air)	Flow, ft/min
Duke polystyrene	48.4	4.6	50.7	9.8
Huntsman polystyrene	54.6	2.4	55.1	1.4
CM wood flour	44.1	(Blistered)	---	(Cracked)
CM rubber	41.5	0.1	49.9	(Distorted)
CMA rubber	43.2	0.3	49.7	(Cracked)
Atlos rubber	42.3	0.7	49.5	2.2
RRI rubber	42.4	0.1	50.8	0.9
HMU rubber	30.4	(Blistered)	---	(Cracked)
Sparton rubber	44.2	(Distorted)	---	(Distorted)
Polypropylene	50.0	---	---	---

Most of the pore formers tested proved unsuitable. While Huntsman polystyrene leaves a relatively small amount of ash following binder removal, the flow rate through the material is low, and the shape of the material is distorted. The wood flour leaves a high amount of ash, and the samples become blistered during the binder removal. All rubber samples left a high ash content following binder removal, and had low flow rates or were too distorted or cracked to measure the flow.

Based on these results, the Duke polystyrene approach provided the best performance. However the flow rate with nitrogen burnout was about half that required. Consequently, new formulations of the Duke polystyrene and GN-10 Si_3N_4 powder were prepared, changing the amount of polystyrene and some other batch variables. Flow rate and biaxial flexure strength measurements were performed. The results are summarized in Table 5-8. (Note that average, not characteristic, strengths are reported in Table 5-8.)

TABLE 5-8					
AVERAGE FLOW RATES AND BIAXIAL FLEXURE STRENGTHS					
Batch	Wt % Polystyrene	Zinc Stearate	Binder: Plasticizer Ratio	Flow Rate, ft/min	Average Biaxial Flexure Strength, ksi
1	35.0	Yes	1:1	14.2	4.6
2	33.3	Yes	1:1	9.9	4.4
3	30.0	Yes	1:1	5.6	5.1
4	30.0	No	1:1	4.2	4.9
5	27.0	Yes	2:1	4.8	5.0
6	27.4	Yes	2:1	3.0	4.6

Based on these results, batch 1 (Table 5-8) was adopted as the new baseline formulation.

Batches of the new baseline SSN filter material were processed (mixed, rolled into tape, pressed, debindered, and sintered) for flow, density, and strength measurements. Additional batches were prepared to make plates for corrosion testing, bars for strength testing, and pressings for the bonding and shrinkage study of the filter material. Micrographs of the material were taken, and a sample was prepared and used in X-ray diffraction analysis.

The average face velocity at a pressure drop of 5 in. water for the baseline SSN material in the original screening test was 14.2 ft/min, with a standard deviation of 2.6 ft/min (Table 5-8). The flow data for this sample group are shown in Table 5-9. More discs of this same batch were sintered in another sintering run, and the average face velocity was measured at 11.5 ft/min with a standard deviation of 1.0 ft/min. The data from this sample group are shown in Table 5-10.

TABLE 5-9	
FACE VELOCITY AT A PRESSURE DROP OF 5 IN. WATER FOR BASELINE SSN FILTER SAMPLES (SINTERING RUN 1)	
Sample	Flow rate, ft/min.
1	13.7
2	13.6
3	15.4
4	13.7
5	13.6
6	11.0
7	17.7
8	20.3
9	16.5
10	13.0
11	11.2
12	13.3
13	11.2
Average flow rate	14.2 ft/min
Standard deviation	2.6 ft/min

TABLE 5-10	
FACE VELOCITY AT A PRESSURE DROP OF 5 IN. WATER FOR BASELINE SSN FILTER SAMPLES (SINTERING RUN 2)	
Sample	Flow rate, ft/min.
1	12.1
2	12.4
3	13.6
4	12.4
5	11.9
6	10.2
7	11.7
8	11.9
9	11.4
10	12.4
11	9.9
12	10.7
13	11.2
14	9.9
15	10.3
Average flow rate	11.5 ft/min
Standard deviation	1.0 ft/min

These results indicate that flow through the material is consistent (within a standard deviation) in the two sintering runs. The repeatability of the face velocity will continue to be monitored as additional batches of the baseline formulation are processed.

The second screening test performed on the baseline material was the biaxial strength test. The data showed the average strength to be 4.6 ksi (see Table 5-8), the characteristic strength to be 5.0 ksi, and the Weibull modulus to be 5.5. the biaxial strength measurement data for this group are shown in Table 5-11.

The biaxial flexure strength was also measured on the group of samples sintered in the second run, and the data are shown in Table 5-12. The results of biaxial flexure strength measurements and calculations on those samples indicated a characteristic strength of 5.6 ksi and a Weibull modulus of 8.6.

These results also indicate consistency in the two groups of data. The strength of additional duplicate batches will be monitored as they are processed.

The bulk density and total porosity of the samples from the two groups were measured by the Archimedes principle. As shown in Table 5-13, the average bulk density of the first group of samples was 0.87 g/cc, with a standard deviation of 0.03 g/cc. The average bulk density of the second group of samples was 0.90 g/cc with a standard deviation of 0.02 g/cc, as shown in Table 5-14. The total porosities of the first and second groups, respectively, were 73.5 percent (standard deviation of 1.3 percent) and 72.9 percent (standard deviation of 0.7 percent).

The results of the flow, strength, and density measurements are summarized in Table 5-15. These data show that there is no significant statistical difference between the two groups (within one standard deviation for each property).

TABLE 5-11		
BIAXIAL FLEXURE TEST RESULTS FROM BASELINE SSN FILTER SAMPLES (SINTERING RUN 1)		
MOR Rank	Breaking Load, lb	Stress MOR, ksi
1	11	3.2
2	12	3.5
3	13	3.7
4	14	4.0
5	15	4.3
6	16	4.6
7	17	4.9
8	17	4.9
9	17	4.9
10	17	4.9
11	17	4.9
12	18	5.2
13	22	6.3
Characteristic strength, ksi: 5.0		
Weibull modulus: 5.5		

TABLE 5-12		
BIAXIAL FLEXURE TEST RESULTS FROM BASELINE SSN FILTER SAMPLES (SINTERING RUN 2)		
MOR Rank	Breaking Load, lb	Stress MOR, ksi
1	16	4.6
2	16	4.6
3	17	4.9
4	17	4.9
5	17	4.9
6	17	4.9
7	18	5.2
8	18	5.2
9	18	5.2
10	19	5.5
11	19	5.5
12	20	5.8
13	20	5.8
14	24	6.9
Characteristic strength, ksi: 5.6		
Weibull modulus: 8.6		

TABLE 5-13		
DENSITY AND TOTAL POROSITY MEASURED BY ARCHIMEDES PRINCIPLE ON BASELINE SSN FILTER SAMPLES (SINTERING RUN 1)		
Sample	Density, g/cc	Total Porosity, percent
1	0.84	74.7
2	0.85	74.4
3	0.89	73.0
4	0.86	74.1
5	0.81	75.6
6	0.85	74.3
7	0.88	73.3
8	0.91	72.5
9	0.88	73.3
10	0.83	74.9
11	0.90	71.8
12	0.91	71.4
13	0.91	71.7
Average	0.87	73.5
Standard deviation	0.03	1.3

TABLE 5-14		
DENSITY AND TOTAL POROSITY MEASURED BY ARCHIMEDES PRINCIPLE ON BASELINE SSN FILTER SAMPLES (SINTERING RUN 2)		
Sample	Density, g/cc	Total Porosity, percent
1	0.92	72.2
2	0.93	71.9
3	0.90	72.7
4	0.92	72.2
5	0.90	72.9
6	0.90	72.8
7	0.90	72.7
8	0.89	73.3
9	0.85	74.3
10	0.86	74.0
11	0.89	73.1
Average	0.90	72.9
Standard deviation	0.02	0.7

TABLE 5-15								
COMPARISON OF BASELINE SSN SAMPLES PROCESSED IN TWO SINTERING RUNS								
Sintering Run Number	Average Flow, ft/min	Standard Deviation, ft/min	Charac- teristic Biaxial Flexure Strength, ksi	Weibull Modulus	Average Bulk Density, g/cc	Standard Deviation, g/cc	Average Total Porosity, percent	Standard Deviation, percent
1	14.2	2.6	5.0	5.5	0.87	0.03	73.5	1.3
2	11.5	1.0	5.6	8.6	0.90	0.02	72.9	0.7

Initial linear shrinkage measurements have been taken on the discs tested for flow and biaxial flexure strength. One such disc is shown in Figure 5-27. Discs are cut in the green state from tape with a 1.125-in.-dia punch. The diameter of the discs typically shrinks by about 11.5 percent during processing. It may be seen that the disc has remained approximately circular throughout processing, i.e., the shrinkage is fairly uniform.

Figure 5-27. Top View of SSN Filter Disc Which Has Shrunk By About 11.5 Percent During Processing with a Minimum of Distortion

Successful pressing and good bonding of the SSN filter material are apparent in Figure 5-28, which shows that the pressed and bonded finned disc has retained its circular shape. No apparent distortion is seen in the side view of the bonded stack, shown (along with the top view) in Figure 5-29.

F-62446

Figure 5-28. Top View of Pressed and Bonded Finned Disc Stack Which Has Shrunk By About 11.5 Percent During Processing with Little Distortion

Figure 5-29. Uniform Shrinkage from Processing Is Displayed in Pressed and Bonded Finned Disc Stacks

F-62445

The bonding strength of stacks, as shown in Figure 5-29, is relatively high. Attempts to break the bonds between layers resulted in a broken finned disc (with one half of the disc still bonded to the fins of the disc below it), which indicates that the bond may be as strong as the parent material.

The optically magnified fracture surface of a baseline SSN filter disc is shown in Figure 5-30. The high degree of interconnected porosity is evident in the micrograph. A higher magnification was achieved on the scanning electron microscope (SEM), and it may be seen in Figure 5-31 that small needles of α - Si_3N_4 have grown in the pores during the sintering process. Figure 5-32 shows a SEM micrograph closeup of the needles in the pores.

Figure 5-30. A High Degree of Interconnected Porosity Is Seen Through the Cross-Section of a Baseline SSN Filter Disc

These micrographs illustrate the importance of controlling the sintering temperature ramp rates. A slow ramp rate through the temperature range where α - Si_3N_4 growth is favored will result in a greater abundance of the fibers in the pore system. The flow through the material would therefore be increased if the heating and cooling portions of the sintering cycle were as rapid as possible within the limits of the furnace control.

A qualitative X-ray diffraction (XRD) analysis has been performed on the baseline SSN filter material. The XRD pattern of the SSN filter material is shown in Figure 5-33. β - Si_3N_4 is identified as the major phase. The remaining phase is $\text{Y}_2\text{Si}_3\text{N}_4\text{O}_3$ (15 percent) which results from the addition of the sintering aid.

F-62420

Figure 5-31. An Abundance of α - Si_3N_4 Fibers Is Observed in the Pore System of a Baseline SSN Filter Disc (Fracture Surface) on a SEM Micrograph

Figure 5-32. SEM Micrograph Shows α - Si_3N_4 Fibers Which Have Grown in the Pores of Baseline SSN Filter Material During Sintering

F-62444

Figure 5-33. XRD Pattern from Scan of SSN Filter Material

5.4 RECOMMENDATIONS

In view of the data presented in paras. 5.1 through 5.3, it was recommended that the sintered silicon nitride (SSN) formulation be adopted as the baseline material for the ensuing filter element fabrication and demonstration phase of the program. The material exhibited the required permeability, and its strength, while lower than expected, appeared to be adequate for the filter application. The bond studies indicated that the filter could be fully assembled in the green state, debindered, and sintered to produce monolithic structure where no further assembly would be required.

6. FILTER MANUFACTURE

6.1 FINAL DESIGN

The design of the half-scale filter element presented in Section 3 was used as shown for the final design. A possible modification to the design was the elimination of flanges along the width (2-in. dimension) of the module. The initial construction of modules did not include flanges on the ends; it was expected at first that pressure along the side flanges would form an adequate seal. Further discussions with Westinghouse led to the addition of the end flanges, as described in para. 6.3.1. The resulting module matched the design shown in Figure 3-2 of Section 3.

6.2 TOOLING

Compression molding tools were designed and procured in this subtask. Two sets of dies were required, one to form plates with clean-gas channels, and the other to form plates with dirty-gas channels. Each set of dies comprised a finned die and a backing plate. The finned die forms the desired pattern on a molded SSN tape. The backing plate contains water channels to provide heating and cooling capability to the finned die. They were procured through an outside machine shop.

6.3 MODULE CONSTRUCTION

The fabrication method selected for manufacturing the ceramic filter utilizes a plastic-forming process that has been used in the development of compact silicon nitride recuperators. The overall fabrication process is shown schematically in Figure 6-1. A detailed flow sheet for the manufacturing process is shown in Figure 6-2.

6.3.1 Material Forming, Stacking, and Assembly

Silicon nitride batches are formulated from the following raw materials: silicon nitride powder, binder, plasticizer, pore former, and sintering aid. The batch constituents are preblended, and then fed into a high-energy mixer. The friction resulting from the mixing action heats the batch, resulting in a rubbery mixed mass. The mixed batch is then fed through a two-roll mill and sheeted into tape. Tape thickness is controlled by successively passing the tape through the rolls while reducing the roll spacing until the desired thickness is attained.

Tape stock of the desired thickness is then formed into the filter plate configurations using a compression molding technique. Molding is performed using a 150-ton hydraulic press. A four-post die set on the press contains the filter plate dies. Two sets of dies are required, one to form plates with clean-gas channels, the other to form plates with dirty-gas channels. The filter plate designs are discussed and illustrated in Section 3. The SSN batch is a thermoplastic material. Therefore, to facilitate molding, the dies have the capability to be heated and cooled. The tape and dies are heated prior to molding to increase the flexibility of the tape. Following compaction, the dies are cooled to give the molded tape increased tear strength to facilitate removal from the dies.

Figure 6-1. Ceramic Filter Element Fabrication

IG-06202

Figure 6-2. Process Flow Sheet for SSN Filter Elements

The compression molding operation consists of two facets: (1) the ability to form a well-molded plate, and (2) the ability to remove it undamaged from the die. To obtain a well-molded piece, uniform pressing pressure and good material flow are necessary. Die temperature, tape thickness, pressing pressure, and pressing time are all important parameters in the molding operation. A proper combination of these parameters will result in a completely filled molded part that can be removed intact from the die.

Individual clean-gas and dirty-gas plates are alternately stacked and bonded in the green (unfired) state using a bonding agent. A group of alternating clean-gas and dirty-gas plates are shown in Figure 6-3 to illustrate the construction of half-scale filter modules. A flat sheet of tape is bonded to the last finned plate in the assembly to complete the filter element.

The first filter module, in the "green state" (not yet processed at high temperature), is shown in Figure 6-4. The filter module contains 20 clean-gas plates, 19 dirty-gas plates, and a flat cover plate (on which the module rests in Figure 6-4). The large dirty-gas passages of the filter stand out as the module's most prominent feature in Figure 6-4. The flange runs vertically to the right of the dirty-gas passages. The clean-gas channel ends as shown to the right of the flange.

In Figure 6-5, the module rests on its flanges and clean-gas passage ends. A view through the dirty-gas passages is shown. A view of the clean-gas channels and the bottom of the flanges is displayed in Figure 6-6.

After some discussion with Westinghouse about installing filter modules in their test unit, a slight change in the modules was implemented. While on test, a filter is clamped into the holding fixture, with a compressible ceramic blanket material placed between the filter and the fixture, by applying pressure to the tops of the flanges. The pressure of the clamp provides a tight seal between the clean face, the ceramic blanket material, and the test fixture. In the module shown (Figure 6-6), sufficient sealing area exists along the longer sides of the clean face, but the sealing area is minimal along the shorter sides.

To provide additional sealing area, two dirty-gas side plates were bonded to each end of the module. The filter base, after adding the four plates, is shown in Figure 6-7. These plates did not increase the filter active surface area; their only function was to increase the clean face area, which ensures a tight seal all around the module base in the test fixture. A side view of a filter module, including added dirty-gas side plates, is shown in Figure 6-8.

6.3.2 Module Processing

A processing procedure was developed for the modules before and during the compression molding tool fabrication. The dimensions of processed filter modules are (approximately) 6 by 6 by 2 in., with a 0.5 by 0.5 in. flange running along the length of the bottom of the filter. The high organic content in the filter material batch caused concern that a half-scale module would slump under its own weight during processing.

Figure 6-3. Clean-Gas Side and Dirty-Gas Side Plates Are Alternately Stacked, Aligned, and Bonded to Form a Filter Module

100391-2

100562 - 3

Figure 6-4. Dirty-Gas Passages of the First Green Filter Module Are Shown to the Left of the Flange, While the Ends of the Clean-Gas Passages Are Shown to the Right

100562 - 1

Figure 6-5. Dirty-Gas Channels are Formed through the Width of the Filter Module
When Plates Are Alternately Stacked and Bonded

100562-5

Figure 6-6. Clean-Gas Channels Run the Height of the Module, with the Channel's Open Ends in the Base. The Base of the Module and Channel Openings Are Shown

Figure 6-7. The Addition of Plates on the Ends of the Filter Yields Sufficient Sealing Area on the Clean Face

Figure 6-8. The Plates Added to the Ends of the Filter do not Increase the Filtering Capability; Their Only Function is to Provide a Good Sealing Area

F-63891

To observe processing behavior, a tall stack of pressed SSN filter material was prepared. The material was compression molded on an existing ceramic heat exchanger finned plate tool. The tool had a fin height of 0.125 in. The pressings were trimmed into rectangular plates of approximately 2 by 2.5 in., then were stacked and bonded.

The first step in the processing of filter material is binder extraction. The bonded stack was placed on a porous ceramic setter plate. A slow heatup schedule was used, with nitrogen sweeping through the furnace to remove the vaporized organic materials. The stack was oriented as shown in Figure 6-9 in the binder extraction furnace. Binder extraction was completed with good results. As shown in Figure 6-10, the shrinkage was uniform, and no slumping occurred as the organics were extracted from the material.

The same stack orientation as in the binder furnace was used in the sintering run. The stack was sintered using a HIP furnace at high pressure and temperature in a one-day cycle. The sintering results were also encouraging in that no distortion or warpage was evident. The sintered stack is shown in Figure 6-11.

It appeared from this work that for successful processing, the half-scale filter modules should be similarly oriented in the furnaces. The first filter module was thus processed with the plates lying horizontal to the furnace floor, as shown in Figure 6-4. It was thought that bond strength would be enhanced by the pressure on the bonds from the weight. However, this placement of the module proved unsatisfactory, as shown in Figure 6-12. Distortion of the module is evident; the middle area of the module appears to have slumped, while the base/flange area (along the left side) became slightly curved. Also, the dirty-gas side plates (added for sealing purposes) at the top of the module separated from each other during the binder run.

Better results were achieved with the second filter module, which is shown after binder extraction in Figure 6-13. The module was debindered while resting on its base, as it appears in the photograph. The module base remained flat, and in general, the shrinkage appears to be more uniform than it was in the first module. However, the outermost dirty-gas side plates separated just as they did in the first module.

The recurring problem was that the two dirty-gas side plates at each end, bonded directly to each other, separated from the rest of the module. This result suggested a difference in shrinkage behavior between dirty-gas side plates bonded directly to each other and dirty-gas side plates bonded to clean-gas side plates; non-uniform shrinkage seemed a likely cause of separation. Thus, the third filter module was constructed entirely from alternating clean-gas side and dirty-gas side plates, as shown in Figure 6-14. The clean-gas channels were sealed off at the base of the filter to provide a good seal between the module and the test fixture.

Module 3 was processed while resting on its base. The end plates of the third module also delaminated during processing, but in this case it was primarily due to bloating of the sealed-off clean gas channels. As potential bloating problems had been anticipated, sealed-off clean-gas plates were processed in an experiment prior to the

9 9 8 6 4 - 1

Figure 6-9. Stack of Finned SSN Filter Material in the Green State

Figure 6-10. No Evidence of Slumping Is Seen in the Stack of Finned SSN Filter Material Following Binder Extraction

99926-3

Figure 6-11. Original Shape Is Retained in the Stack of Finned SSN Filter Material Following Sintering

F-63892

Figure 6-12. Distortion of the First Filter Module Occurred During Binder Extraction When Oriented in the Furnace as Shown

F-63893 -A

Figure 6-13. Except for the End Plates, the Proportions of the Second Module Were Better Retained During Binder Extraction when Oriented in the Furnace as Shown

Figure 6-14. The Third Filter Module was Constructed Entirely of Alternating Clean-Gas Side and Dirty-Gas Side Plates

binder extraction of module 3, and the bonded plates appeared flat. However, the bloating did occur in module 3, which caused some separation between the adjacent dirty-gas plates.

The fourth module is shown in Figure 6-15. Since the shrinkage mismatch that caused separation in the first two modules was not apparent in module 3, the same stacking arrangement was used to construct the fourth module. None of the clean-gas channels were sealed. However, separation occurred as it did in the end plates of the first three modules.

The plates that separated on each module during the binder extraction step were not functional filter membranes. As described earlier, they provide additional sealing area on the clean face. They were cut off above the flange, therefore, with no effect on module filtering capabilities or on the clean face sealing areas. After removing the end plates above the flange, the module shape matched the original design shown in Figure 1-2 of para. 1.2.2.

Module 1 was the first to be sintered. Figure 6-16 is a side view of the first module, taken after the high-pressure, high-temperature sintering run. The module was oriented in the HIP furnace as shown; it rested on its clean face. The general shape of the module did not become further distorted as a result of sintering. However, many of the bonded plates separated to a greater extent during sintering. This separation is most easily observed in the flange area in Figure 6-16, and on the clean face

F-63895 -A

Figure 6-15. Module Four (Shown in Green State) Was Constructed Entirely of Alternating Plates

F-63889 -B

Figure 6-16. Further Separation of the Bonded Plates Occurred During Sintering of the First Filter Module

shown in Figure 6-17. This first module would have required extensive patching with a refractory cement in order to test its filtering capability.

Figure 6-17. Separation Between Plates Is Clearly Shown on the Clean Face of the First Filter Module After Sintering

Better results were observed with the other sintered modules, each processed in separate furnace runs under the same conditions. The second, third, and fourth SSN modules are shown in the sintered state in Figure 6-18. The fourth module is in the center, the second module is on the left, and the third module is on the right. Separation between the plates is minimal in the top, flange, and clean face areas of these modules. In some of the finned areas, however, separation between the fins and the adjacent plate occurred. The filtering capability should not be affected by these fin/plate separations, but module strength could be affected.

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F-64860

Figure 6-18. Three SSN Filter Modules Are Shown Prior to Qualification and Testing

7. FILTER EVALUATION

7.1 FILTER QUALIFICATION

Preliminary inspection of the modules was performed at AiResearch prior to delivery to Westinghouse. Westinghouse subcontracted to AiResearch to conduct qualification tests on three filter elements and performance tests on two filter elements. The qualification and performance tests were performed at the Westinghouse Science and Technology Center High Temperature, High Pressure Test Facility.

7.1.1 Dimensional Tolerance

Westinghouse built a test fixture to accommodate the AiResearch filter dimensions, which are (approximately) 6 by 6 by 2 in., with a 1/2 by 1/2-in. flange all around the filter base. A 6- by 2-in. (inner dimensions) rectangular metal ring was made to be slipped over the filter and, by resting on the flange, to act as a clamp when bolted to the test mount. A 1/2- to 3/4-in. compressible ceramic blanket material was cut to form the seal between the filter clean face and the test fixture. A sketch of such a mounting arrangement is shown in Figure 3-1 of Section 3.

7.1.2 Flaws or Cracks

Separation between some of the module plates occurred during processing, as discussed in para. 6.3.2, which should not affect the filtering capability, except in module 1, but could lower module strength. By visual inspection, modules 2, 3, and 4 were judged to be the best candidates for qualification and testing. A bubble test was performed at AiResearch to locate leak paths not visible to the eye.

Along with checking for leak paths, flow uniformity through each module was observed via submersion/bubble tests. A boot was clamped to the module base, and pressurized air entered the clean gas channels through the boot (similar to the reverse-pulse cleaning of a module during a filtering operation) while the assembly was submerged in water.

The first bubble test of module 2 revealed two leak paths in the dirty-gas channels. A commercial grade alumino-silicate refractory cement was applied to those areas, and was effective in sealing the leaks. Uniform bubbling during the second bubble test of module 2 (after sealing the leaks) is displayed in Figure 7-1. Modules 3 and 4 were leak-free; their bubble tests resembled that of Figure 7-1. While no leak paths required sealing on modules 3 and 4, small amounts of the cement were applied to separations between plates in the flange and top surface areas of modules 2, 3, and 4.

The modules, when delivered to Westinghouse, were also inspected there (favorably) as a first step in the qualification procedure. The next step of the qualification procedure, the flow test, is discussed in para. 7.1.3.

100895 - 3

F-64859

Figure 7-1. Uniform Bubbling of Air Through the Submerged Module Indicates Uniform Flow

7.1.3 Filter Permeability

Prior to delivering modules 2, 3, and 4 to Westinghouse for qualification and testing, the pressure drop and flow were measured at AiResearch. An existing flow/ ΔP room temperature test stand was used, which was limited to a maximum flow rate of 100,000 sccm. As in the submersion/bubble tests, air entered through the clean air channels, passed through the filter material, and exited through the dirty gas channels. The three modules exhibited similar flow rates; as shown in Figure 7-2, as the pressure drop (ΔP) across the filter increased, the flow increased linearly. Pressure drops across each of the filters were less than 6 in. H₂O at the maximum flow of 100,000 sccm (3.53 scfm).

The flow tests at Westinghouse covered a wider range of flow and pressure drop. The tests ranged from 6 in. H₂O ΔP (flow of 3.22 scfm) to 44 or 48 in. H₂O ΔP (19.29 scfm). Again, the flow curves for the three modules are fairly consistent with one another, as shown in Figure 7-3. While the pressure drop is somewhat higher than expected at a given flow, Westinghouse qualified the three modules for filter testing.

7.1.4 Filter Element Strength

The strength of the filter elements was measured by testing bars which had been cut from flat plates of SSN filter material. The plates were processed along with the modules from start to finish (i.e., batching, mixing, molding, binder extraction, and sintering), and therefore are representative of the modules.

The SSN filter material strength tests were performed at Westinghouse. The strength of as-fabricated material was measured at room temperature and at elevated temperatures. Also, test bars which had been rubbed with ash or char fines and held at high temperatures were strength-tested at elevated temperatures. The four-point-bend strength test method was used, and the strengths were reported as an average (i.e., not characteristic strength as determined by Weibull analysis). The SSN filter material strength measurements are presented in Table 7-1, and are discussed in the following paragraphs.

7.1.4.1 Room Temperature Measurements

The average strength of the as-fabricated SSN material (2.6 ksi), measured by the four-point-bend method at Westinghouse, is lower than the average strength of the SSN material (4.7 ksi) measured by the biaxial-flexure test method at AiResearch. The corresponding characteristic biaxial flexure strength of the material is 5.3 ksi.

This apparent discrepancy in the material strength numbers from the two types of tests is discussed in para. 5.1.3 of Section 5 of this report for the RBSN filter material, and correlates exactly with the SSN strength data. As stated in Section 5, the characteristic tensile strength of a material is used for reliability analysis. The characteristic tensile strength of RBSN filter material was calculated from biaxial flexure strength data and from four-point-bend strength data. These characteristic tensile strengths calculated from the two sets of strength data were in close agreement. It was therefore concluded that no pertinent discrepancy existed between the two sets of data.

100K MFM, 20 in. H2O Gauge

Figure 7-2 The Three Candidate Modules for Testing Display Linear Increases in Flow with an Increase in Pressure Drop

Flow vs. Pressure Drop

Westinghouse Qualification

Figure 7-3. The Curves of the Three Modules Were Consistent With One Another

TABLE 7-1

AVERAGE STRENGTH (PSI) OF SSN FILTER MATERIAL TESTED AT
WESTINGHOUSE BY FOUR-POINT-BEND METHOD
TEST TEMPERATURE SAME AS TREATMENT TEMPERATURE

Conditions	As Fabricated	Ash	Char
Room Temperature	2598 $\pm$ 526	—	—
870°C, No hold	1749 $\pm$ 267	—	—
870°C, 400 hr	1780 $\pm$ 237	1943 $\pm$ 80	2044 $\pm$ 138
980°C, 400 hr	1547 $\pm$ 177	1380 $\pm$ 106	1293 $\pm$ 38
870°C, 1500 hr	1542 $\pm$ 53	1498 $\pm$ 70	1393 $\pm$ 118

The differences between the biaxial flexure strength and the four-point-bend strength of SSN filter material is parallel to those differences for RBSN material (overall, the SSN strength data are slightly higher). The characteristic strength and Weibull modulus of the SSN material were not included in the four-point-bend data. The characteristic tensile strengths therefore cannot be calculated for the four-point and compared with the biaxial. However, the average strength relation between the RBSN four-point and biaxial data sets is parallel to the average strength relation between the SSN four-point and biaxial data sets. The two sets of strength data can thus be correlated.

7.1.4.2 Elevated Temperature Testing of Treated, Heat-Soaked SSN Filter Material Test Bars

Test bars of SSN filter material were broken at Westinghouse by the four-point-bend method at 870°C or 980°C. To examine corrosion effects on the material, bars that were as-fabricated or were rubbed with pressurized fluidized-bed combustor ash or fluidized-bed gasifier char fines were heated at 870°C for 400 or 1500 hr, or at 980°C for 400 hr.

In general, the strength of the material decreases when it is tested at elevated temperatures, and/or when it has been heat-treated. The strength loss increases due to either a longer soak time at the same temperature (870°C), or a higher temperature treatment for the same soak time (400 hr).

The effects of the ash or char fines on the material strength are not as clear, but it appears that exposure to ash at elevated temperature degrades the SSN filter material strength, and that it is degraded to a slightly higher degree when exposed to char fines. Further testing was recommended to confirm these trends.

7.2 FILTER EVALUATION

7.2.1 Facility Selection

The high-temperature, high-pressure (HTHP) test facility located at the Westinghouse R&D site has been operated over the past 8 years to evaluate the performance and operating characteristics of high-temperature gas-cleaning systems. The facility has more than 5000 hr of test operation over a wide variety of filter systems and test conditions.

Figure 7-4 shows a schematic of the flow loop and identifies the major equipment items. In this system, fuel is combusted with excess air, and reentrained ash is injected to produce a high-temperature, particle-laden gas flow. The facility is capable of operating at temperatures greater than 2000°F and pressures to 200 psig. The installed compressor capacity is capable of providing air flow rates from 0 to 285 scfm with an available single compressor, and 415 scfm if a second installed unit is used in parallel. At these flows, the dust metering and injecting system is capable of accurately delivering a full range of dust concentrations, ranging from a few ppm to greater than 30,000 ppm of ash.

The piping and test unit pressure housings are refractory lined pipe sections so that the pressure boundaries operate at a relatively low temperature. The inlet pipe section is provided in a length that minimizes heat loss while enabling a proper particulate/gas sample to be taken from the gas entering the filter housing proper. The system can be configured to accommodate several different test vessel configurations.

The high-pressure air supply is a 75-hp, two-stage reciprocating compressor that is capable of continuously providing up to 285 scfm of air at 200 psig. Since Westinghouse installed this unit over 10 years ago, it has proven to be a reliable workhorse that requires minimal maintenance. A second, 250-psig, 130-scfm unit is connected parallel to the air supply and can be operated to extend the range of flow conditions. The flow, temperature, and pressure control systems ensure accurate and constant test conditions. The flow control system consists of conventional orifice plates with pressure, differential pressure, and temperature transmitters reporting to a standard utility-type or recording mass flow controller. Temperature is controlled by sensing the passage temperature and subsequently automatically adjusting the fuel flow control valve. Passage pressure is maintained by a system backpressure control valve and controller. All passage operating parameters are controlled, displayed digitally, and stripchart recorded at the main passage control panel.

The combustion system has been fired on propane, natural gas, and methanol, and is presently running on the natural gas system, which consists simply of a small oil-free natural gas compressor to boost house-supplied natural gas from 15 to 200 psig for use in the passage. The high-pressure natural gas is piped through the temperature control valve directly to the combustor section. In this refractory-lined spool piece, a small aerodynamically shaped flame holder stabilizes the flame as the bulk of the flow is mixed and heated.

The dust metering and injection system is capable of providing on-line readout of the powder and transport gas mass flow rates. This is of great value in the analysis of the performance of a test device. This highly accurate powder feed system consists of a gravimetric powder feeder with a twin-screw feed barrel for uniform powder feeding. The device is enclosed in a large pressure vessel that can house the feeder and its hopper. A small amount of transport air is metered to the system through a small mass flow controller; this is used to entrain the metered powder and carry it to the pressurized system.

The data-acquisition systems available for the unit consist of the computer hardware and software required to accept typical thermocouple and pressure transducer signals and record them directly onto a microcomputer disc for storage. Subsequent data reduction and reporting are thus facilitated to a great degree. Traditionally, short-term testing of filter units has been adequately monitored through the existing control panel's array of stripchart records; however, for extended testing or cases in which many signals must be monitored, the microcomputer data-acquisition system has been used.

The particulate and gaseous species sampling systems used at the test facility have varied widely in sophistication and ease of use. Particulates are routinely sampled using a simple isokinetic extractive probe that takes a total grab sample suitable for gravimetric analysis and Coulter counter analysis if required. Facilities are available for the use of high-pressure and elevated-temperature sampling, along with cascade impactors if indicated. State-of-the-art laser light-scattering devices are available for particle concentration and size distribution measurements.

7.2.2 Filter Tests

The existing Westinghouse HTHP gas cleaning test facility will be used in this task. The tests will be conducted under the following nominal conditions:

- (a) Temperature, 1600°F
- (b) System pressure, 150 psi
- (c) Dust (reentrained ash), 1000 to 10,000 ppm
- (d) Gas flow, up to 100 acfm
- (e) Typical gas composition (percent by volume):
 - Nitrogen, 73
 - Water vapor, 14
 - Carbon dioxide, 7
 - Oxygen, 6

A preliminary test matrix is shown in Table 7-2. As shown the preliminary plan called for cumulative 100-hr tests to be performed on each module. Westinghouse typically runs extended shifts to complete 10 hr of testing per day, so the plan shown in Table 7-2 calls for ten start/stop cycles per module. Also in the preliminary test plan, one filter would be tested to destruction by application of excessive stress; likely methods of applying excessive stress would be to increase the operating temperature and/or the blowback pressure. The preliminary test plan was revised after discussing the plan with the Westinghouse Science and Technology Center.

TABLE 7-2					
PRELIMINARY TEST MATRIX FOR SSN 100-HR HTHP FILTER TESTING					
Test Series	Time at Condition, hr	Filter Face Velocity, ft/min	Startup Thermal Gradient, °F/min	Pulse Intensity	Comment
1	10	5	< 10	As required for effective cleaning	Filter conditioning period
2	50	10	< 10	As required for cleaning	Baseline
3	10	10	10 to 20	As required for cleaning	Increased thermal shock
4	10	10	10 to 20	2X	Increased cleaning intensity
5	20	> 10	> 30	> 2X	High stressing

Modifications of the plan were made to enhance the program or conserve resources. The two tentative test plans that were developed, one for each module, are shown in Tables 7-3 and 7-4.

The test period for one of the modules was extended to 150 hr, assuming the filter element is testing successfully, as shown in Table 7-3. The filter would only be exposed to the minimum pressure pulse needed to provide cleaning. This plan was designed to demonstrate filter 'life' and obtain increased insight into long term performance of the material. The second filter element would be exposed to increasingly severe conditions during the presumed 50 hr of testing. As shown in Table 7-4, high stressing would be imposed on the module as the test progresses; the final conditions are to be determined based on the life of the element.

7.2.2.1 Testing of Module 2

Module 2 was selected for the first filter test. The test was conducted according to Table 7-3, with the exception of the face velocity parameters. Instead of setting a face velocity value of combustion gas through the filter, a nominal actual flow of 12.5 cu ft/min was set for the test. This actual flow was based on the nominal conditions

TABLE 7-3					
TEST MATRIX FOR SSN 150-HR HTHP FILTER TESTING					
Test Series	Time at Condition	Face Velocity, ft per min	Startup Thermal Gradient, °F per min	Pulse Intensity	Comment
1	10	5	< 10	As required for effective cleaning	Filter conditioning period
2	70	10	< 10	As required for effective cleaning	Baseline
3	70	10	10 to 20	As required for effective cleaning	Increased thermal shock

TABLE 7-4					
TEST MATRIX FOR SSN 50-HR HTHP FILTER TESTING					
Test Series	Time at Condition	Face Velocity, ft per min	Startup Thermal Gradient, °F per min	Pulse Intensity	Comment
1	10	5	< 10	As required for effective cleaning	Filter conditioning period
2	20	10	< 10	As required for effective cleaning	Baseline
3	20	10	10 to 20	As required for effective cleaning	Increased thermal shock
4	TBD	TBD	TBD	TBD	High-stressing conditions

discussed in Section 2. Given a target of 10 ft/min through a filter with an area of 1.25 sq ft, the required actual volumetric flow rate is 12.5 cu ft/min. The actual test conditions for module 2 are summarized in Table 7-5.

The first test series, the filter conditioning period, was conducted with no problems. The conditions, for a total of 10 hr, were:

- (a) Temperature: 1275°F
- (b) System pressure: 150 psi
- (c) Flow: 9.5 actual cu ft/min

TABLE 7-5
TEST CONDITIONS FOR
MODULE 2 HTHP FILTER TESTING

Test Series	Time at Condition, hr	Actual Flow, ft ³ /min	Startup Thermal Gradient, °F/min	Pulse Intensity/Duration	Temperature, °F	Comment
1	10	9.5	< 10	0.25 psi/0.2 sec	1275	Filter conditioning period
2	30	13.5	< 10	0.25 psi/0.2 sec	1440	Baseline

The module and test chamber were heated by the hot gas (product of natural gas combustion) flowing through it. Dust was added to the gas stream at 2200 parts per million after establishing a baseline ΔP (42 in. H₂O) across the module at temperature.

The module displayed good filtering and cleaning capability during the conditioning period. When the ΔP had increased by 10 in. H₂O (to 52 in. H₂O), the accumulated dust was blown off by a reverse-pulse of air. The pulse, which measured about 0.25 psi across the filter for a 0.2-sec duration, was sufficient to restore the ΔP to its baseline of 42 in. H₂O. The consistent return to the baseline ΔP indicated that the reverse-pulse cleaning was effective.

An isokinetic sample, placed in the exhaust line, was periodically removed, examined, and weighed to monitor the amount of dust passing through the filter into the exhaust. The sample appeared clean and gained weight at a slow rate (typically 1 mg/6 hr) during the filter conditioning period. The clean sample from the exhaust line indicated that the filter was effectively removing particulates from the hot gas stream.

The conditions for series 2, the baseline test series, were:

- (a) Temperature: 1440°F
- (b) System pressure: 150 psi
- (c) Flow: 13.5 actual cu ft/min

The filter module blowback, of the same intensity and duration as in the conditioning period, was also effective during the baseline test series. The pressure drop across the filter consistently fell to the baseline ΔP , 46 in. H₂O at 1440°F, after each blowback pulse.

A slight increase in the rate of dust collection on the isokinetic sample was noted during the first day of baseline testing; the sample appeared darker and gained weight at 4 mg/6 hr. A greater increase in the dust collection rate was apparent on the second day of testing; the isokinetic sample was darker still, and gained weight at 10 mg/2.5 hr. The testing continued through the third day with continued dirty exhaust, so the test was ended in order to inspect the module. The increase in exhaust dust was due to

leaks that developed as the filter was exposed to the higher temperature in the baseline test series.

The module was shipped to AiResearch for inspection. The cause of dust leakage shown in Figure 7-5, which is a view of the filter module, with the clamping ring resting on the ceramic blanket material and the module flange, as it was received from Westinghouse. The filter module had expanded during the test, but was constrained near the filter base by the clamping ring. Cracks developed in the endplates, as shown in Figure 7-6, after the module increasing length exceeded the length of the clamping ring inner dimension. The dust in the exhaust gas stream increased as the cracks developed.

An attempt was made to patch the module with the intention of resuming the test. The cracked end plates were cut off of the module, and the ring and the fiberfrax gasket were removed. A section of the module base then separated from the rest of the module. The base of the filter is shown intact in Figure 7-7; the base separated at the second row of clean gas channels from the left. A hairline crack is shown extending from that row of clean gas channels to the outer edge of the filter flange. The section apparently had been held in place by the fiberfrax gasket and/or by the cracked end plate.

The cracked end plate was examined on a SEM and compared with as-processed material for changes in microstructure. A fracture surface from one of the cracked endplates of module 2 is shown in Figure 7-8 (a). Figure 7-8 (b) shows the fracture surface of a disc that was processed along with module 2 in the same binder extraction and sintering runs. Higher magnification SEM micrographs, focused on a pore of the module 2 material and on a pore of the discs material, are shown in Figure 7-9. There are no apparent differences in the microstructures of tested material and untested material. The alpha-silicon nitride whiskers, shown clearly in Figure 7-9 a and b, have the same range of lengths and diameters before and after exposure to the test conditions.

X-ray diffraction analysis indicated that the major phase in the SSN filter material, both before and after exposure to test conditions, is beta-silicon nitride. The other prominent phase in the filter material is a yttrium-silicon-oxide-nitride ($Y_2Si_3N_4O_3$) compound. The XRD patterns for the tested and as-processed materials are shown, with accompanying phase diffraction patterns below them, in Figures 7-10 and 7-11.

The major peaks of $Y_2Si_3N_4O_3$, at around 30 and 32 deg 2-theta, appear at a lower relative intensity on the pattern for tested material (Figure 7-10) than for as-processed material (Figure 7-11). These qualitative observations indicate that the $Y_2Si_3N_4O_3$ has undergone a phase change. The instability of the $Y_2Si_3N_4O_3$ phase at elevated temperatures was first observed by Lange.¹⁰ A volume increase of about 30 percent occurs when $Y_2Si_3N_4O_3$ is exposed to air at high temperature.

The expansion, in and of itself, did not appear to affect the performance of the SSN filter module. The filtering capability was diminished because cracks developed as

¹⁰Lange, F. F., "Silicon Nitride Polyphase Systems: Fabrication, Microstructure, and Properties," *International Metals Review*, Vol. 25, No. 1, 1980, pp. 1-18.

101075-8

Figure 7-5. SSN Filter Module 2 Shown with Clamping Ring in Place

101075-11

F-64007

Figure 7-6. Cracks Developed in the End Plates as the Module Expanded into the Clamping Ring

101075-9

F-6400t

Figure 7-7. The Base of the Filter Separated at the Second Row, Along the Left, of the Clean Gas Channels

(a) MODULE 2 AFTER TESTING

(b) AS-PROCESSED MATERIAL

F-64009

Figure 7-8. Fracture Surfaces of SSN Filter Material

(a) TESTED MATERIAL

(b) AS-PROCESSED MATERIAL

F-64010

Figure 7-9. The α -Si₃N₄ Fibers in a Pore of Tested Material and in a Pore of As-Processed Material Have Similar Size Distributions

B-24759

Figure 7-10. Phases in Tested SSN Filter Material Are Identical as α - Si_3N_4 and $\text{Y}_2\text{Si}_3\text{N}_4\text{O}_3$

B-24760

Figure 7-11. Major Peaks of $Y_2Si_3N_4O_3$ (at About 30° and 32° 2θ) Have Greater Relative Intensity in the As-Processed Material

the module expanded into the clamping ring. It followed that the other qualified modules would expand in volume by the same amount as module 2 during a filter test. The clamping ring for module 4, the next module to go on test, was therefore constructed with ample tolerance to prevent any damage that would occur from swelling.

7.2.2.2 Module 4 Testing (150-hr Test)

Module 4 was placed on test according to the same filter test plan matrix that was started for module 2. The test was conducted according to Table 7-3, again with the exception of the face velocity parameters. Instead of targeting a face velocity value, the actual flow through the filter was set. The actual test conditions for module 4 are shown in Table 7-6.

TABLE 7-6 TEST CONDITIONS FOR MODULE 4 HTHP FILTER TESTING						
Test Series	Time at Condition, hr	Actual Flow, ft ³ /min	Startup Thermal Gradient, °F/min	Pulse Intensity/Duration	Temperature, °F	Comment
1	10	9.5	< 10	0.25 psi/0.2 sec	1290	Filter conditioning period
2	140	13.5	< 10	0.25 psi/0.2 sec	1440	Baseline
3	20	27	10	0.25 psi/0.2 sec	1520	High stressing conditions

Test series 1, the filter conditioning period, was conducted as it was on module 2. The conditions, for a total of 10 hr, were:

Temperature: 1290°F

System pressure: 150 psi

Flow: about 9.5 actual cu ft/min

Dust was added to the gas stream at 2200 parts per million after establishing a baseline ΔP (approximately 40 to 50 in. H₂O) across the module at temperature.

Module 4 performed well through the conditioning period. When the ΔP had increased by 10 in. H₂O (to about 60 in. H₂O), the accumulated dust was blown off by a reverse-pulse of air at 0.25 psi for a 0.2-sec duration. The pressure drop across the filter returned consistently to the baseline ΔP , and the isokinetic sample in the exhaust line appeared clean each time it was checked throughout the conditioning test series.

The conditions for the test series 2, the baseline series, were:

Temperature: 1440°F

System pressure: 150 psi

Flow: about 13.5 actual cu ft/min

The blowback pulse was of the same intensity and duration as in the conditioning period, and the ΔP consistently returned to the baseline ΔP (about 55 in. H₂O).

The performance of module 4 is illustrated in Figure 7-12. The plot in Figure 7-12 shows the change in ΔP (pressure drop, in. H₂O) across the module as it filtered dust from the combustion gas stream. The plot shown is typical of the daily filter performance plots. Each peak on the plot shows that the pressure drop across the filter rose steadily as dust collected on the surface of the module. When the ΔP increased by about 10 in. H₂O, the blowback pulse was applied, which resulted in a sharp drop to the baseline ΔP .

The regular intervals between pulse cleaning in the performance plots is one indication of effective particulate filtration; other evidence of good filtration during the test series was the lack of dust particles on the isokinetic samples placed downstream of the filter. Westinghouse reported clean exhaust throughout the test by inspecting and weighing the isokinetic samples. Also confirming effective filtration is the clean exhaust flange shown in Figure 7-13. The mounting flange and gasket, onto which module 4 was clamped during the test, and the clean interior through which filtered gas passed are shown in the photograph. In contrast, a dirty exhaust flange is shown in Figure 7-14. The flange shown had held module 2, which developed cracks during its test, allowing dust to pass through the module and into the exhaust flange.

The consistent return to the baseline ΔP in the performance plots (see Figure 7-12) indicates thorough cleaning by reverse-pulse. Effective pulse cleaning was confirmed when the module was removed from the test apparatus. Module 4, attached to the mounting exhaust flange, is shown in Figure 7-15 as it was removed from the test chamber. Since few of the dirty gas channels are blocked, it is clear that the blowback pulse was sufficient.

Westinghouse observed that the filter had displayed excellent performance during the first 150 hr of test conditions. The dirty gas channels were cleaned much more completely than expected by the blowback pulse. The module was easily vacuumed clean after it was removed from the test chamber. Since there was no evidence of degradation, the filter appeared suitable for further testing.

7.2.2.3 Higher Stress Testing of Module 4 (50-hr Test)

Module 4 was reinstalled in the test chamber for the test series shown in Table 7-4. The filter conditioning series was performed in the 150-hr test, so test series 1 was omitted from the plan. To increase the stress on module 4, the flow of combustion gas was twice the flow used in the 150-hr test. The increased flow through the filter allowed a higher startup thermal gradient (ramp rate) and a higher temperature of operation. These actual conditions are summarized in test series 3 of Table 7-6.

A high level of stress was expected from the faster ramp rate and higher operating temperature during test series 3 of Table 7-6. An increase in the cold pulse pressure could have been applied to provide additional stress, but the thermal stress increase provided by the higher operating temperature was already significant. Also, the

Figure 7-12. Performance Curve, Typical of a Test Day Cycle, Shows Consistent Filtration and Pulse Cleaning at Regular Intervals

F-65366

Figure 7-13. Effective Filtration by Module 4 Is Apparent in the Clean Exhaust Flange

Figure 7-14. Evidence of Filter Leakage Is Shown in the Dirty Exhaust Flange After the Module 2 Test

Figure 7-15. Open, Dirty Gas Channels in Module 4 Indicate Effective Pulse Cleaning of the Filter

pulse parameters used in the first 150 hr were more than adequate for complete cleaning of the module.

Dust leakage through the module became apparent within 20 hr of operation at high stress conditions. The cause of dust leakage is discussed in para. 7.3 on the posttest analysis.

7.3 POSTTEST ANALYSIS

The cause of dust leakage during the high-stress testing was that module 4 had fractured along the flange and between some of the rib-to-plate seams. The fractured sections were cleaned and pieced together as shown in Figure 7-16; the failure apparently occurred in the third and fourth rows (right side of module) of dirty gas channels. The module was sectioned for strength evaluation, morphology characterization (including measurement of depth-of-fines-penetration), and X-ray diffraction analysis.

7.3.1 Strength and Morphology Characterization

The bulk of the module 4 post-test analysis was performed at the Westinghouse Science and Technology Center. Westinghouse measured the baseline strength of as-processed material by machining four-point bend bars out of the endplates which had separated from module 4 during processing. For comparison, the strength of bend bars machined out of the tested material was measured by the same method. Westinghouse also characterized the morphology and the depth of dust fines penetration in the tested material. The Westinghouse report on the tested material's characterization is presented in Appendix B.

7.3.2 X-ray Diffraction Analysis

After a section of the tested module was removed for analysis at Westinghouse, the remainder of the module was shipped to AiResearch for X-ray diffraction analysis. The diffraction pattern and phase identification patterns are shown in Figure 7-17. The major phase in the exposed filter was beta-silicon nitride, as it was in module 2 after exposure and in as-processed material. The minor phase, $Y_2Si_3N_4O_3$, forms from the added sintering aids during module processing. The instability of this phase at elevated temperatures was described in para. 7.2.2.1. The major peaks for the $Y_2Si_3N_4O_3$ phase (at around 30 and 32 deg 2-theta) in module 4 appear at a lower relative intensity in the tested material in Figure 7-17 than in the as-processed material shown in Figure 7-11. This result indicates that the expected phase change and accompanying volume-expansion occurred, as it did in module 2.

Figure 7-16. Module 4 Fractured in the Third and Fourth Rows (From the Right) of Dirty-Gas Channels During the First 20 hr of High-Stress Test Conditions

Figure 7-17. The Major Phase in Module 4, Posttest, is Beta-Silicon Nitride as Identified by X-ray Diffraction Analysis

8. CONCLUSIONS AND RECOMMENDATIONS

A fabrication technique of calendering, compression molding, solvent bonding, and sintering has proven successful in developing a porous sintered silicon nitride (SSN) filter. Calendering is used to form thin sheets of the SSN filter material which are compression molded to form finned clean gas and dirty gas-side filter plates. Solvent or slurry bonding techniques are used to alternately stack and bond the plates together to form a module. The module is sintered at high temperature in a high-pressure inert atmosphere. Three half-scale modules (approximately 6 in. by 6 in. by 2 in.) were constructed which qualified for high-temperature, high-pressure pressurized fluidized bed combustion testing.

Two of the qualified modules were tested on the Westinghouse Science and Technology Center's High-Temperature-High-Pressure Filter Test Unit. The first module failed when, at high temperature, the module expanded into the clamping device. Cracks developed, allowing dust to pass into the exhaust gas stream. The second module effectively filtered the simulated pressurized fluidized bed combustion gas stream, up to 1440°F with 13.5 cu ft/min gas flow through the filter, for a cumulative 150-hr period. The module showed signs of failure after the flow was doubled and the operating temperature raised to 1520°F. The module had fractured along the flange and rib-to-plate seams.

The filter's performance was described as effective by the Westinghouse test team, with filter efficiency measurements of up to 99.99 percent (see table showing filter efficiencies in Appendix C). The SSN filter's excellent cleanability was noted after the test. The filter material's strength was reduced by 75 percent during the less than 200 hr of testing. X-ray analysis indicated that a phase change had occurred in the filter material at high temperature during testing, which resulted in a volumetric expansion. The phase change may be directly related to the filter material's reduction in room-temperature strength following its exposure to high temperature.

A change in the relative amounts of sintering aids and/or the processing parameters is recommended, to avoid the formation of the unstable $Y_2Si_3N_4O_3$ phase during sintering. The same compounds can still be effective sintering aids when added in different proportions, but minor phases other than the unstable $Y_2Si_3N_4O_3$ tend to form. Also, pressure and temperature schedules can be altered to produce a strong SSN filter material while promoting the formation of more stable secondary phases.

APPENDIX A

COARSE-GRID THERMAL ANALYSIS WITH DENSE RBSN PROPERTIES

Figure A-1. Thermal Grid of Ceramic Filter Model

Figure A-2. Plate Temperatures Along Section A-A

Figure A-3. Plate Temperatures Along Section B-B

Figure A-4. Upstream-Side Gas Temperatures Along Section B-B

Figure A-5. Downstream-Side Gas Temperatures Along Section B-B

Figure A-6. Upstream-Side Gas Temperatures Along Section A-A

Figure A-7. Downstream-Side Gas Temperatures Along Section A-A

B-16158

Figure A-8. Inlet Gas Temperature for Ceramic Filter Startup Condition

Figure A-9. Plate Temperatures Along Section A-A During Startup

Figure A-10. Plate Temperatures Along Section B-B During Startup

Figure A-11. Plate Temperatures Along Section C-C During Startup

Figure A-12. Upstream-Side Gas Temperatures Along Section A-A During Startup

Figure A-13. Downstream-Side Gas Temperatures Along Section A-A During Startup

Figure A-14. Upstream-Side Gas Temperatures Along Section B-B During Startup

Figure A-15. Downstream-Side Gas Temperatures Along Section B-B During Startup

APPENDIX B

CHARACTERIZATION OF A SINTERED SILICON NITRIDE CROSS FLOW FILTER AFTER HIGH-TEMPERATURE, HIGH-PRESSURE PRESSURIZED FLUIDIZED BED COMBUSTION TESTING

92-9TBO-XFAIR-R1

Characterization of a
Sintered Silicon Nitride
Cross Flow Filter After
High Temperature High
Pressure Pressurized
Fluidized Bed Combustion
Testing

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CHARACTERIZATION OF A SINTERED SILICON NITRIDE CROSS FLOW FILTER AFTER HIGH TEMPERATURE HIGH PRESSURE PRESSURIZED FLUIDIZED BED COMBUSTION TESTING

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Gas Cleaning Systems

ABSTRACT

Development during the past four years has lead to the fabrication of 6 x 6 x 2 inch sintered silicon nitride (SSN) cross flow filters. The durability of both the material, as well as the cross flow structure has been evaluated through ~200 hours of high temperature, high pressure (HTHP) simulated pressurized fluidized-bed combustion (PFBC) testing at 1080-1500°F and 150 psig at the Westinghouse Science and Technology Center.¹ This report provides the results from the material characterization efforts that were performed at Westinghouse on both an as-fabricated SSN filter endplate, as well as the actual SSN cross flow filter that experienced ~200 hours of HTHP testing. Specifically we focused on attempting to determine whether the strength of the SSN matrix was retained after ~200 hours of HTHP simulated PFBC testing. In addition scanning electron microscopy/energy dispersive x-ray analyses (SEM/EDAX) were performed to determine whether morphological changes occurred within the SSN microstructure after HTHP testing. Lastly we attempted to demonstrate whether fines were retained along the dirty gas channels and filtration surfaces, or if fines penetrated into the SSN cross flow filter walls.

1. 187 hours with dust feed; 202 hours at temperature. Operating temperature of 1082-1460°F was maintained for 176 hours of testing, and 1400-1500°F was maintained for 26 hours of test.

1. INTRODUCTION

Prior to high temperature, high pressure, simulated pressurized fluidized bed combustion testing, the initial 8 x 8 x 2 inch cross flow filter structure and endplate were characterized in terms of their physical appearance. The light weight cross flow filter appeared to be virtually intact, without separation along the rib-to-wall seams (Figure 1). Separation along the rib-to-wall seams of the endplates was evident, as well as curvature along the length and/or width of the actual walls (Figure 2). After ~200 hours of HTHP simulated PFBC testing the filter suffered failure along both the flange and several rib-to-plate seams.

In order to preserve the areas where failure occurred for fracture analysis, the cross flow was sectioned within the intact portion of the filter body (Areas A and B, Figure 3). The removed section of the filter was used for strength testing along the rib-to-plate areas; for morphology characterization; and for depth of fines penetration characterization. The results of these analyses follow.

Strength Testing

Attempts were made to characterize the filter endplate material strength. Due to the curvature and thin wall thickness of the SSN endplate, only seven bend bars could be prepared for 4-point bend, 1/4-point flexure testing. The length of the bend bars was taken as the length of the dirty gas channel passage. As a result of the limited number of bend bars, we decided to perform only room temperature strength measurements. As shown in Table 1, the as-fabricated SSN material has at a maximum a strength of 2759±534 psi.

The section of the filter that was removed from the HTHP simulated PFBC-tested cross flow filter was similarly subjected to strength characterization. Difficulty was again experienced in removing bend bars from the channel areas of the filter, and as a result, only

four acceptable bend bars were obtained. The direction of the bend bars, as with the endplate, was taken along the dirty gas channels. Based on 4-point bend strength measurements, the room temperature strength of the tested filter material is at a maximum 740 ± 130 psi, indicating that an ~75% loss of the initial, as-fabricated, room temperature material strength occurred after ~200 hours of HTHP PFBC testing (Table 2).

An alternate attempt was made to remove bend bars from the flange region of the cross flow filter (i.e., along the tab of the flange that extended out from the filter body). Room temperature strength characterization of this area was comparable with that along the channel area (i.e., maximum 748 ± 319 psi). The resulting strength measurements based on the limited number of bend bars used in these analyses is questioned in terms of statistical validity. We do, however know that from our disc measurements (DOE Contract No. DE-AC21-88MC25034), that an as-fabricated room temperature strength of 2733 ± 273 psi is acceptable for the SSN material. Further effort would be needed to produce significantly more data in terms of statistical acceptability, as well as identifying the actual strength of the filter matrix at process operating temperatures.

Scanning Electron Microscopy Analysis

A section of the HTHP PFBC tested SSN filter was removed, exposing a fresh fractured cross-sectioned area through the filter channel wall. As shown in Figure 4a, two parallel walls are separated by a clean gas channel. The outer surfaces along both sides of the parallel walls were originally part of the dirty gas channels.

As shown in the bottom micrograph of Figure 4a, an ~50 μm layer of PFBC fines remains along the dirty gas channel walls. The presence of the $\alpha\text{-Si}_3\text{N}_4$ whiskers is readily evident throughout the entire SSN matrix. In comparison to the original SSN matrix, elongation of the $\alpha\text{-Si}_3\text{N}_4$ whiskers which extend into the pore cavities, appears to have occurred. Figure 4b shows the SSN matrix/fines interface, as well as high magnification micrographs of the particles present in the dust cake layer.

Figure 4c shows the morphology of the matrix/dust cake interface at an alternate location. Fines are present in the dust cake, and are seen to adhere to the α -Si₃N₄ whiskers. Near the SSN matrix/dust cake interface, fines are relatively evident within the pores. These fines appear to be lodged or creviced between the α -Si₃N₄ whiskers (i.e., particularly evident in the bottom micrograph).

Isolated fine particles are also evident near the center of the SSN cross flow filter rib (Figure 4d). The presence of isolated fines within the HTHP-tested SSN matrix appears to be a general trend throughout the entire cross flow filter wall thickness.

During filter use, the cross flow had delaminated and cracked along the flange, causing particulate laden gas to flow into the clean gas channels during pulse cleaning. As shown in Figure 4e, fines are evident along the α -Si₃N₄ whiskers of the SSN clean gas channel surface. The bottom right micrograph illustrates both a pore (Area A) and ligament area (Area B) near the clean gas channel surface. Note fines are evident particularly along the pore cavity wall, and appear to be absent within the ligament section of this material.

Microprobe Analyses

To further discern the depth of fines penetration through the HTHP PFBC tested filter, elemental microprobe analyses were used to map the presence of calcium, aluminum, iron, and oxygen through the cross-sectioned filter wall. Areas 1 and 2 in Figure 5a illustrate the presence of these elements along or near the dirty gas channel surface. Calcium and iron are associated with the PFBC dust fines. Aluminum is expected to also be associated with the dust fines, but based on our x-ray analyses generated as part of DOE Contract No. DE-AC21-88MC25034, aluminum may be associated with remnants of the sintering aid that was used during the manufacture of the filter body. Oxygen is associated with fines along the dirty gas channel dust cake layer, and fines that have penetrated into the filter wall. Based on these analyses, oxidation of the sintered silicon nitride microstructure at HTHP PFBC test conditions appears to be minimal.

Figure 5b indicates the microprobe analyses that were obtained at approximately the mid-section of the filter wall thickness. A relatively heavy deposit of fines is indicated in this region as shown by the relatively high intensity areas of calcium. Fines are clearly evident along the clean gas channel surface (Figure 5c) of the HTHP PFBC tested filter.

2. SUMMARY

Strength testing of the SSN material from an actual cross flow filter is rather difficult based on the initially thin gas channel walls. As a result of very limited testing, data seem to indicate that the SSN material loses ~75% of its original room temperature strength after ~200 hours of operation under HTHP PFBC conditions.

Ash fines appear to permeate through the porous walls of the SSN cross flow filter, not filling the pores, but lodging within and being held by the α - Si_3N_4 whisker phase. From the standpoint of particulate fines carry-through the filter, the whisker-like α - Si_3N_4 phase may play a significant role in preventing fines from penetrating completely through the wall to the clean gas channel. Application of a thin smaller pore diameter membrane coating along the dirty gas channel surface is recommended to prevent fines penetration into the SSN microstructure.

Elemental microprobe analysis indicates that oxidation of the SSN microstructure after ~200 hours of exposure to HTHP PFBC test conditions is minimal.

TABLE 1
ROOM TEMPERATURE BEND STRENGTH DATA

- Sintered Silicon Nitride -
As-Fabricated Filter Endplates
Dirty Gas Channels

Test Sample No.	Temp., °C	Cross Head Speed, cm/min	Width, in.	Height, in.	Loads, lbs.	Strength, psi
1	RT	0.02	0.244	0.046	1.52	3467
2	RT	0.02	0.246	0.047	0.84	1820
3	RT	0.02	0.244	0.045	1.13	2693
4	RT	0.02	0.244	0.041	1.10	3158
5	RT	0.02	0.245	0.033	0.58	2560
6	RT	0.02	0.245	0.030	0.48	2563
7	RT	0.02	0.245	0.031	0.61	3051

As-Fabricated Average Strength: 2759±534 (7)

Chart Speed: 5 cm/min.

Upper Span: 20 mm

Lower Span: 40 mm

4 Pt; 1/4 Flexure

TABLE 2
ROOM TEMPERATURE BEND STRENGTH DATA
- Sintered Silicon Nitride -
High Temperature, High Pressure Tested Filter

Test Sample No.	Temp., °C	Cross Head Speed, cm/min	Width, in.	Height, in.	Loads, lbs.	Strength, psi
Dirty Gas Channels						
1	RT	0.02	0.246	0.039	0.23	714
2	RT	0.02	0.243	0.021	0.08	857
3	RT	0.02	0.244	0.022	0.06	568
4	RT	0.02	0.245	0.031	0.16	820
Flange						
1	RT	0.02	0.176	0.085	0.60	558
2	RT	0.02	0.176	0.084	0.55	519
3	RT	0.02	0.176	0.085	0.51	474
4	RT	0.02	0.175	0.083	1.15	1121
5	RT	0.02	0.176	0.087	1.21	1070

Average Channel Strength: 740±130 (4)

Average Flange Strength: 748±319 (5)

Chart Speed: 5 cm/min.

Upper Span: 20 mm

Lower Span: 40 mm

4 Pt; 1/4 Flexure

Figure 1 - Sintered Silicon Nitride Cross Flow Filter

Figure 2 - Sintered Silicon Nitride Cross Flow Filter Endplate

Figure 3 - Areas Indicating Section Removed From The HTHP PFBC-Tested SSN Cross Flow Filter That Was Used For Strength Analysis And Morphology Characterization

Figure 4a - SEM Characterization Of The HTHP PBBC Tested SSN Cross Flow Filter (Dirty Gas Channel Area)

Figure 4b - SEMs Illustrating The Dust Cake/SSN Matrix Interface
And High Magnification Micrographs Of The Dust Cake Fines

Figure 4c - SEMs Illustrating The Dust Cake/SSN Matrix Interface At An Alternate Location

Figure 4d - SEMs Illustrating The Presence Of Fines Near The Center Of The SSN Cross Flow Filter Wall

Figure 4d (Cont'd) - SEMs Illustrating The Presence Of Fines Near The Center Of The SSN Cross Flow Filter Wall

Figure 4e - SEMs Illustrating The Presence Of Fines Along The Clean Gas Channel Wall Of The HTHP PFBC Tested Cross Flow Filter

Figure 4e - SEMs Illustrating The Presence Of Fines Along The Clean Gas Channel Wall Of The HTHP PFBC Tested Cross Flow Filter

SEM + BSE

Area 2

2a

Al

Fe

O

SEM + BSE

Area 1

Ca

Al

Fe

O

Figure 5a - Elemental Microprobe Analysis Of The SSN Cross Flow Filter Along The Dirty Gas Channel Surface

Figure 5b - Elemental Microprobe Analysis Of The SSN Cross Flow Filter At Approximately The Mid-Section Of The Filter Wall Thickness

Figure 5c - Elemental Microprobe Analysis Of The SSN Cross Flow Filter Along The Clean Gas Channel Surface

APPENDIX C
FILTER EFFICIENCIES

TABLE C-1

FILTER EFFICIENCY (PERCENT) CALCULATED DAILY DURING HTHP SIMULATED PFBC TESTING OF MODULES 2 AND 4

FROM ADU ELECTROMECH SYS			12. 9.1992 13:14		P. 2	
NUMBER	WT (mg)		(min.)	CUMUL. (hr)	ppm	
IN#-2 Dust feed rate in - 2200 ppm						
PR 2 92	1	3.90	4.40	30	26.0325	98.82
	2	2.03	4.30	77	13.8654	99.37
	3	1.00	11.60	75	2.5319	99.88
R 3 92	5	2.23	29.60	114	2.2127	99.9
R 6 92	6	6.32	39.60	245	4.8357	99.78
R 7 92	7	4.15	34.10	340	3.5744	99.84
R 8 92	8	10.01	55.30	265	5.3163	99.76
R 9 92	9	4.16	29.50	158	4.1417	99.81
IN#-4 Dust feed rate in - 2200ppm						
Y 5 92	1	2.26	13.00	60	5.1059	99.77
	2	6.33	44.20	235	4.2062	99.81
Y 6 92	3	9.17	8.60	65	31.3166	98.57
	4	2.43	12.50	120	5.7095	99.74
	5	8.43	20.30	60	12.1965	99.45
Y 7 92	6	5.71	10.10	83	16.6042	99.25
	7	2.17	24.80	98	2.5699	99.88
Y 8 92	8	3.06	9.30	141	9.6637	99.56
	9	8.79	19.20	120	13.4460	99.39
	10	2.52	14.50	120	5.1043	99.77
Y 12 92	12	10.37	28.50	90	10.6866	99.51
	13	3.26	8.10	90	11.8205	99.46
Y 13 92	14	2.66	20.70	170	3.7741	99.83
Y 14 92	15	0.24	12.50	120	0.5639	99.97
	16	1.91	10.60	30	5.2921	99.76
Y 18 92	18	2.55	33.10	180	2.1337	99.9
Y 19 92	19	1.82	55.40	120	0.9649	99.96
Y 20 92	20	7.47	26.20	120	8.3738	99.62
Y 26 92	22	31.06	45.90	120	19.8743	99.1
Y 27 92	23	0.27	14.10	135	0.5624	99.97
Y 28 92	24	0.47	64.00	120	0.2157	99.99

END

**DATE
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