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**Development and Characterization of Textron Continuous
Fiber Ceramic Composite Hot Gas Filter Materials**

**Final Report
September 30, 1994 - October 31, 1997**

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1.0 INTRODUCTION

1.1 Problem Statement

It is generally recognized that porous ceramic cross flow and candle filters represent an attractive technology for the required removal of high temperature particulate in advanced coal-based power generation systems. Porous-type ceramic hot gas filters in use today are generally made from clay bonded silicon carbide, alumina and mullite. Other classes of materials are also under consideration.

Existing monolithic ceramic cross flow and candle filters have demonstrated particulate removal efficiencies of greater than 99% under sub-pilot scale combustion and coal gasification process conditions.¹ When such filter systems are fielded for operational service, New Source Performance Standards will take effect which mandate that particulate outlet loadings not exceed 30 parts per million (ppm). In addition, the gas turbine requires that the particulate loading in the turbine inlet stream is less than 10 ppm. These performance standards in and of themselves will represent significant technical challenges for the existing generation of monolithic high temperature filter materials. However, perhaps even more difficult requirements to ultimately satisfy relate to the need for deploying ceramic filter element hardware that has adequate thermostructural stability and corrosion resistance at acceptable costs. Of particular concern for monolithic ceramics is their ability to withstand extended operational exposure (many thousands of hours) in a corrosive combustion environment which concurrently subject the filter elements to pulsed cleaning operations, system transients and structural loads from ash bridging.

Ceramic filter materials that are commercially available can generally meet particulate filtration requirements but do not currently possess sufficient mechanical durability and thermodynamic stability to survive for long periods in the anticipated pressurized fluidized bed combustor (PFBC) or integrated gasification combined cycle (IGCC) environments. Shortcomings in existing monolithic materials primarily relate to catastrophic crack propagation and thermal shock failures, events which are most often precipitated by thermostructural loads imposed during pulse cleaning or process upset conditions. Other materials-related deficiencies with monolithic ceramic filter elements pertain to thermodynamic instabilities under alkali corrosion conditions--especially for ceramics such as clay bonded silicon carbide. There is thus a need to improve phase purity or materials compositions so that the filter materials can withstand long-term exposure to corrosive conditions.

Uncertainties about the long-term ability of monolithic ceramics to survive in the IGCC or PFBC hot gas filter environment thus led DOE/METC to consider the merits of using continuous fiber reinforced ceramic composites (CFCCs) as potential next-generation high temperature filter elements. This seems to be a logical strategy to pursue in light of the fact that properly-engineered CFCC materials have shown much-improved damage tolerance and thermal shock behavior as compared to existing monolithic ceramic materials. Since the strength of CFCC materials are typically fiber-dominated, there may also be opportunities to fabricate filter elements with substantially better intrinsic strength and toughness than the highly porous monolithic

¹ Alvin, M.A. et al High Temperature Filter Materials; in *Proceedings of the Ninth Annual Coal Fueled Heat Engines, Advanced PFBC and Gas Stream Cleanup Systems Contractors Review Meeting*, DOE/METC, Oct 1992.

ceramic materials that are often employed in high temperature filter systems. This would offer the prospect of producing relatively thin-walled filters with good structural properties and gas flow permeabilities.

Another significant advantage to pursuing the use of CFCC filter materials relates to program timing. Initiation of the DOE/METC Advanced Hot Gas Filter Development Program fell within the Phase 1/Phase 2 time window for the DOE Office of Industrial Technologies CFCC Program, of which Textron is a participant. Selection of Textron as a participant in the Advanced Hot Gas Filter Development Program therefore presented METC with the chance to leverage and extend technology being developed on the CFCC Program, which is entirely directed at cost-effective manufacturing of ceramic composites for industrial applications, towards the development of next-generation higher performance CFCC filter materials.

1.2 Synopsis of Original Program Plan

Textron's Advanced Hot Gas Filter Development Program was intended to be a two year, two phase program which transitioned developmental materials R&D into prototype filter element fabrication. The first phase was to demonstrate the technical feasibility of fabricating CFCC hot gas filter elements which could meet the pressure drop specifications of less than ten inches of water (iwg) at a face velocity of ten feet per minute (fpm), while showing sufficient integrity to survive normal mechanical loads and adequate environmental resistance to steam/alkali corrosion conditions at a temperature of approximately 870°C (1600°F). The primary objective of the second phase of the program was to scale up fabrication methods developed in Phase 1 to produce full-scale CFCC candle filters for validation testing. Textron's principal subcontractor on this program was the Westinghouse Science and Technology Center (STC) who assumed responsibility for flow-through permeability measurements, corrosion testing and post-test microstructural characterization of materials developed during this effort.

The original program was structured as follows:

Task 1 - Textron prepared a draft and final report which provided processing and materials information required for the National Environmental Policy Act.

Task 2 - Textron and Westinghouse wrote a detailed test plan which described how filter materials and filter elements would be developed and qualified for use in PFBC and IGCC power generation systems.

Task 3 - Task 3 was concerned with the development and qualification of CFCC hot gas filter materials based upon Textron's already-demonstrated CFCC processing and manufacturing methods. This task was composed of three subtasks which were:

Subtask 3.1 - This activity represented the bulk of materials selection and processing efforts on the Phase 1 Program. It involved the preparation of subscale coupon-sized test samples for permeability, particulate filtration and corrosion testing at Westinghouse STC. This subtask was iterative with subtask 3.2.

Subtask 3.2 - This portion of the Phase 1 Program was concerned with permeability testing, corrosion testing, and post-test materials examination at Westinghouse STC. All testing was performed at the STC Flow-Through Test Facility

Subtask 3.3 - This was a Phase 2 portion of the program in which full-scale candle filters were to be fabricated and tested under simulated PFBC gas environment conditions in the Westinghouse High Temperature, High Pressure Test Facility.

Task 4 - Task 4 was to investigate issues relating to the manufacture of CFCC hot gas filters, including the development of QA/QC plans, manufacturing economics, and the application of state of the art nondestructive evaluation techniques.

Task 5 - This was an optional task which, after written approval from the Contracting Officer, was to produce 50 hot gas filters for pilot-scale testing.

As will be noted in the following report sections, Textron encountered significant process-related and technical difficulties in merely meeting the program permeability specifications, and much effort was expended in showing that this could indeed be achieved. Thus, by the time the Phase 1 program was completed, expenditure of program funds precluded continuing on with Phase 2, and Textron elected to terminate their program after Phase 1. This allowed Textron to be able to focus technical and commercialization efforts on their largely successful DOE CFCC Program.

2.0 CFCC FILTER FABRICATION PROCESSING

2.1 Background and Process Overview for Textron CFCC Materials

Motivation for Selection SCS-™6 SiC Monofilament-Reinforced Nitride Bonded SiC or Nitride Bonded Silicon Nitride

From the onset of the METC/Textron Hot Gas Filter Program our intent was not to develop CFCC processing technology from the "ground up", but rather, to build upon processing experience gained during our Phase 1 and Phase 2 CFCC Program efforts and extend these basic fabrication approaches for producing continuous fiber reinforced hot gas filter materials. We felt that the needs of the Advanced Hot Gas Filter Development Program could best be addressed by drawing upon the prior experience Textron gained in the production of advanced metallic and ceramic composites, so that overall technical risks would be minimized and development costs and times would be significantly reduced. By using this evolutionary approach, it was felt that less time would be spent on matters relating to the actual fabrication of CFCC's and that more time and resources could be devoted to the issues of controlling the mechanical and thermodynamic characteristics of the fiber/matrix interface and optimizing performance characteristics of the CFCC hot gas filter constituent materials.

The ceramic matrices proposed for the Phase 1 program were based on employing gas phase nitridation techniques on mixtures of SiC and Si powders to produce a family of materials which are colloquially referred to as nitride bonded SiC (NBSiC) or nitride bonded silicon nitride (NBSN). NBSN is composed entirely of metallic Si powders prior to nitridation, while NBSiC is composed of variable mixtures of silicon and silicon carbide powders prior to nitridation. The technical considerations involved in the selection of this family of ceramic matrices for the Advanced Hot Gas Filter Development Program were as follows:

- Good elevated temperature strength retention and creep resistance to temperatures greater than 1200°C (2192°F);
- High constituent phase purity and resistance to oxidizing, reducing, combustion, etc. gas exposure;
- Modest cost of starting materials and manufacturing processes combined with rapid (few day turnaround) processing;
- Acceptable thermal conductivity and thermal shock resistance; and,
- Potential to fabricate complex bodies in net or near-net shape fashion with minimal dimensional changes from the "green state" to final firing, along with high degree of commonality for Textron's existing CFCC fabrication process route and baseline materials.

Selection of a continuous fiber reinforcement for the CFCC materials to be evaluated on this program was based on several factors, most of which related to the need to obtain adequate long term thermodynamic stability, good composite strength and toughness and the highest achievable

stresses for the onset of matrix microcracking. In this context, desirable fiber attributes were therefore believed to be as follows:

- Excellent elevated temperature strength retention, creep resistance and microstructural stability to temperatures exceeding 1200°C (2192°F) in oxidizing environments. (Stability in alkali corrosion conditions would also be implied);
- Coefficient of thermal expansion (α) and elastic modulus (E) characteristics appropriately matched to Si-based ceramic matrices (α_f greater than α_m ; E_f greater than E_m) made via gas phase reaction synthesis (where the subscripts "f" and "m" respectively refer to the fiber and matrix phases).
- Demonstrated thermodynamic compatibility and property retention with regard to Textron's CFCC nitridation processing methods as well as the ceramic matrix phase compositions themselves;
- Ability to tailor surface properties of the fiber for the anticipated operational environment and composite forming processes;
- Robust handleability (from the point of view of automated composite lay-up and fabrication methods); and,
- Commercial availability with reproducible technical properties at reasonable cost.

At the onset of the Phase 1 Advanced Hot Gas Filter Program, Textron's SCS-6TM chemically vapor deposited (CVD) SiC monofilament was the only continuous reinforcement which seemed capable of meeting most or all of the criteria mention above. SCS-6TM has excellent themomechanical properties to temperatures of 1400°C (2552°F) or higher, is technically mature, and is commercially available in reasonable quantity. Projections have also been made to the effect that SCS-6TM could be produced for approximately \$1330/kg (\$600/pound) at production rates of greater than 2700 kg (6000 pounds) per year.²

Textron's 143 μm (5.6×10^{-3} inch) diameter SCS-6TM monofilament is coated with a complex surface treatment that contains a thin layer of turbostratic carbon between two carbon plus SiC layers that are $\sim 1.5 \mu\text{m}$ (6×10^{-5} inch) thick.³ The presence of this partially graphitic carbon layer has been found to impart good interfacial debonding behavior to many types of SCS-6TM reinforced CFCC materials.⁴ The SCS-6TM monofilament can be consistently wrapped around radii of curvatures larger than 50 mm (2 inches) without fracture. Recently, Textron has also begun prototype production of a 75 μm (3×10^{-3} inch) diameter SiC monofilament that is called SCS-9ATM. This fiber has so far shown properties that compare very favorably with the SCS-6TM

² Grant, W.T., Excerpts from viewgraph presentation at 1995 Titanium Matrix Composites for Turbine Engine Components (TMCTECC) Meeting at Textron Systems Division.

³ Elridge, J.I., F.S. Honey, *J. Vacuum Science and Technology A*, 8(3)5-6/1990

⁴ Bhatt, R.T., *Properties of SiC Fiber-Reinforced Silicon Nitride Matrix Composites*, NASA TR No. 1b.88-C27.

fiber, and at half the radius of SCS-6™ this filament will be more amenable to wrapping around small radii of curvature. (See Figure 2-1 for an optical micrograph of Textron's SCS-6™ CVD SiC monofilament.)

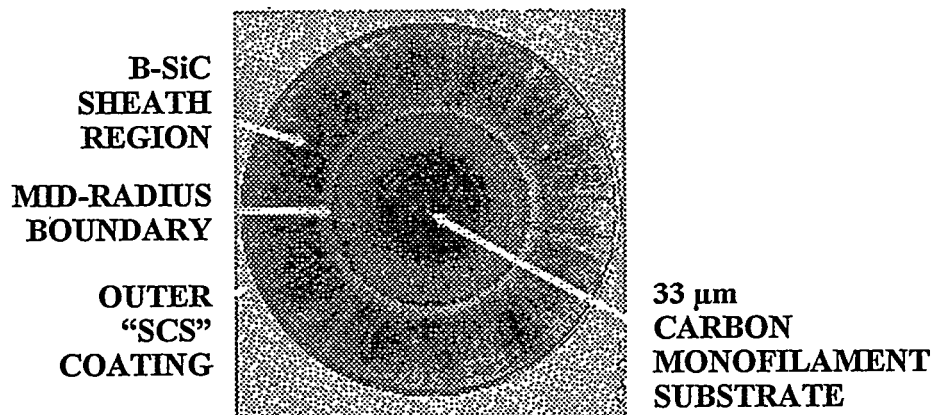


Figure 2-1: Optical Micrograph of Textron SCS-6™ CVD SiC Monofilament

Textron Hot Gas Filter Fabrication Process Overview

The major steps in Textron's hot gas filter fabrication process are described below. The filter fabrication processing sequence represents a straightforward extension of fabrication methods employed on Textron's CFCC Program, and can be used to prepare continuous fiber-reinforced as well as monolithic filter shapes.

Step 1: NBSiC or NBSN Matrix Precursor Synthesis

Appropriate starting powders are first prepared. As mentioned before, for nitride bonded SiC CFCC materials, the starting constituents are mixtures of SiC + Si powders that have been specially chosen for their particle size and surface chemistry characteristics. This facilitates achievement of optimized slurry density (particle packing behavior) and dispersion stability. For NBSN matrices, carefully chosen Si powders with multimodal particle size distributions are used.

Though aqueous and nonaqueous vehicles can be used to create NBSiC or NBSN dispersions, water-based vehicles are preferred for environmental reasons and for the superior ability of water to efficiently disperse SiC and Si particulate at high solids loadings.

Binders or resins such as polyvinyl alcohol (PVA) or polyethylene glycol (PEG) can be added to the water-based dispersions in order to modify drying and rheological behavior of the particulate dispersions and also to increase green body physical strength. This can be advantageous during filament winding processes, which require that the dispersions remain wet and be sedimentation-resistant over a period of hours as the CFCC green body is being wound.

Step 2: Addition of Pore Forming Species to the Dispersion

For this program, Textron investigated two methods for creating highly porous ceramic matrices for CFCC hot gas filters. They were respectively based on the use of (1) "fugitive" or "reactive" pore forming agents such as latex, carbon or ceramic microballoons; and, (2) *in-situ* methods using emulsion or "soap bubble analog" pore-forming species, based on the use of emulsification agents or bubble-formers.

This second step in the CFCC filter fabrication process involves mixing of either microballoons or *in-situ* pore formers after the NBSiC or NBSN dispersions stabilize with regard to their surface chemistries, a process which can take from two days to one week depending on the size and surface condition of the starting powders. At this point, the water-based dispersions were loaded with the pore-forming species to varying levels--generally at two to twenty weight percent loading levels as a fraction of the total solids concentration. After two or three days of additional mixing, dispersions were then ready for filament winding (in the case of CFCC preforms) or conventional slip casting (in the case of monolithic, test coupon-type, bodies).

Step 3: Green Body Formation by Filament Winding or Conventional Slip Casting

Monolithic or CFCC filter green bodies can be (and were) prepared by conventional slip casting onto plaster molds and by filament winding onto plaster of paris mandrels fitted to the filament winder spindle assembly. Conventional slip casting of monolithic porous NBSiC and NBSN bodies was performed as an expedient way to make microballoon-loaded 38 mm (1.5 inch) diameter disks for permeability testing. Slip casting of monolithic bodies thus served as a first-level screening methodology to quantitatively assess the effects of varying levels of pore former addition on sample permeability and corrosion behavior.

Filament winding of closed-ended and open-ended CFCC tubular shapes was chosen as the baseline composite forming method on this program. Winding of tubular candle filter-type shapes first involved fabrication of a mandrel assembly which formed the inner diameter of the tubular preform. NBSiC or NBSN slurries were then simultaneously introduced onto the mandrel as one or more filaments were being wound, as seen in Figure 2-2. When the desired fiber construction was completed, the CFCC green body was allowed to dry for a period of one-half to one day. At this point, the green body was ready for extraction from the mandrel assembly and insertion into the nitridation furnace.

Step 4: Gas Phase Reaction Synthesis (Nitridation)

Gas phase reaction synthesis of continuous fiber ceramic composite materials is an attractive route for matrix densification since the process causes essentially no (less than 0.1%) shape change to the overall preform dimensions and requires no mechanical fixturing or restraint tooling during nitridation. Burnout (or pyrolysis) of the pore-forming species also takes place in the same furnace in which nitridation is performed. This aspect of the processing sequence simplifies

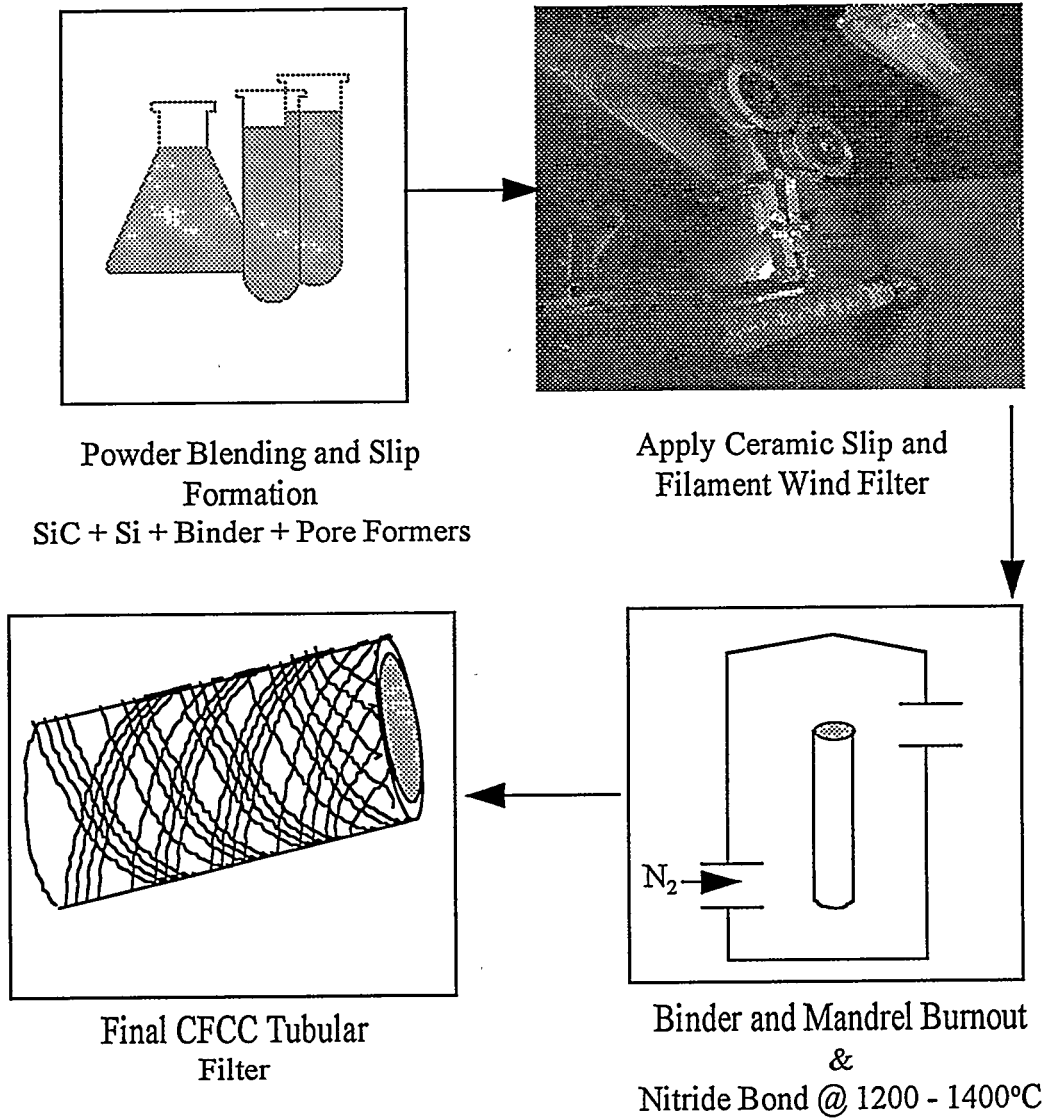


Figure 2-2: Schematic of CFCC Filter Fabrication Process

practical considerations related to intermediate handling of the preforms and lowers overall manufacturing expenses significantly.

Conversion of silicon metal to silicon nitride can be carried out in a vacuum furnace or gas-tight box furnace wherein nitrogen is flowed over the green bodies as the load is heated in controlled fashion to peak temperatures in the vicinity of 1400°C (2552°F). (Further discussion of details on nitridation methods employed during this program can be found in Section 2.2.2.)

Though typical grades of commercially-produced monolithic NBSiC or NBSN can involve nitridation exposures from a few hours up to hundreds of hours at temperatures in the 1200-1450°C (2282-2642°F) range, Textron has arrived at nitridation cycles which produce acceptable nitridation conversion levels (greater than 93-99%) at temperatures in the vicinity of 1350-1400°C (2462-2552°F). Transient exposures of this sort will only result in slight strength loss in the SCS-6™ monofilament, but existing ceramic yarns such as Tyranno™ or Nicalon™ would be severely degraded. This motivated the choice of SCS-6™ as the primary reinforcement on this Phase 1 Program.

2.2 Microballoon Additions

2.2.1 Monolithic NBSiC and NBSN - Preform Fabrication Trials

Subtask Objectives

The principal objectives of this subtask were to arrive at a methodology for creating a high-solids content, homogeneous mixture of powder particles, the dispersion vehicle (water) and microballoon-type pore formers, and to discover the volume loading at which microballoon additions allowed NBSiC and NBSN matrix materials to meet the program-imposed permeability specifications. The latter was essentially the point at which a sufficiently low flow resistance, open-cell foam could be formed in the matrix of interest. Though a large number of microballoon products were considered as potential candidates for forming porosity in NBSiC and NBSN ceramic matrices, the following selection criteria were used to limit the number of microballoon materials that could actually be evaluated as viable candidates from a processing and manufacturing perspective.

1. The microballoons chosen as pore formers had to be commercially available and of reasonable cost;
2. Any microballoon-type addition had to be compatible with water-based NBSiC and NBSN dispersions. In other words, the microballoons had to be stable with regard to wettability, surface chemistry, rheological characteristics and flocculation behavior when added to aqueous dispersions;
3. Microballoons which yielded essentially no (or purely carbonaceous) pyrolysis decomposition products were the most desirable from a materials standpoint. This minimized concerns with regard to "poisoning" of nitridation reactions and reduction of matrix phase purity; and,

4. The microballoon additions had to be available with size distributions which could effectively act to increase NBSiC and NBSN matrix permeability to the desired level of less than 10 iwg/10 fpm while not trapping excessive amounts of fine particulate, resulting in segregated SiC distribution in the matrix. It was believed that microballoons with diameters of fifty microns or less could fulfill this requirement.

A process-related objective of this subtask was to demonstrate the feasibility of utilizing microballoon-loaded slurries with our existing infrastructure and facilities for filament winding of CFCC tubular shapes. A very important long-range goal of the Phase 1 development program was therefore to have the NBSiC and NBSN slurry formulations behave like Textron's "standard" slurry compositions employed on their CFCC Program, which behave rather like resin systems used in the manufacture of organic matrix composites.

Technical Approach

Development efforts for creating workable NBSiC and NBSN dispersions focused on formulation of high-solids content matrix precursors (slips) that could be used for subsequent formation of NBSiC or NBSN ceramic matrices into which microballoon-type pore-formers would be introduced. Technical efforts emphasized synthesis of slips that could easily be modified with water-soluble resins and binders, principally for economic and environmental reasons. Parametric limits on particle sizes and slip viscosities which were consistent with the needs of slip casting and filament winding procedures were defined in this subtask. Slurry formulations investigated on the Phase 1 CFCC Program contained from 60-85 weight percent alpha silicon carbide powder and 15-40 weight percent silicon powder, where, as mentioned previously, silicon metal was the "active species" that formed silicon nitride when exposed to nitrogen gas at high temperatures. An approach was chosen for this effort that concentrated heavily on control of interparticle surface chemistry and particle size distribution so as to produce high quality, compositionally-tailorable and sedimentation-resistant NBSiC suspensions.

Particle surface chemistry is a dominant factor when creating ceramic dispersions, especially for slip casting, because it regulates interparticle attractive and repulsive forces, which in turn have significant effects on slip rheology, casting rate, and the subsequent microstructural evolution of green and nitrided CFCC bodies. Traditional ceramic slip casting requires low viscosity suspensions that are highly loaded with solids. Tight control over particulate surface chemistry is required for such suspensions. Low viscosities are needed for pourability (which incidentally makes such dispersion well-suited for composite forming) and high solids contents are needed to maximize casting rates and green body densities. Typically, methods for obtaining low-viscosity, concentrated suspensions entail the use of polydisperse particle size distributions and mutually repulsive interparticle forces that can arise from surface-adsorbed ions or polymers. However, more recently, it has also been demonstrated that low-viscosity, highly-concentrated suspensions in aqueous and non-aqueous vehicles can also be formed by the use of attractive forces between particles that are coated with lubricating polymers.⁵

⁵ Aksay, I.A., Principles of Ceramic Shape Forming with Powder System, *Ceramic Transactions*, Vol 1., Ceramic Powder Science II, ACS, 1988, 663-673).

Regulating interparticle surface forces by altering slip chemistry is also of paramount importance for elimination of casting or winding related layer heterogeneities such as gross porosity variations, sedimentation of larger particles, and local variations in particulate packing density. Each of these defects can act as a site for crack initiation in the ceramic matrix. Cracks can form during green body drying due to nonuniform shrinkage stresses, especially for CFCC green bodies. In this subtask, Textron utilized both electrostatic and polymeric stabilization techniques in aqueous suspensions to regulate interparticle surface forces.

For work conducted during the Phase 1 Program, we generally selected SiC and Si powders that could be commercially procured with the desired particle size distribution. Suspensions were deflocculated through the combined use of low speed mixing and appropriate dispersants in the suspending liquid. Fortunately, there are a good number of producers of both silicon and silicon carbide powders who collectively offer an extremely wide range of powder products, which made it possible to purchase what was needed for processing trials in "off-the-shelf" fashion. This materials selection strategy had the additional benefit of minimizing processing costs and process complexity, as typical large-scale manufacturers of silicon carbide and silicon powders exercise good control over technical characteristics of the powders they offer. In the NBSN and NBSiC dispersions used on our CFCC Program we tended to use particle distributions which ranged from sizes greater than 100 micron (4×10^{-5} inch) down to the submicron realm.

Dispersion efficiency and slip solids loading were maximized through selection of appropriate dispersion aids and by exercising careful control over initial particle size distribution and chemistry. Our general philosophy regarding particle size selection was to avoid ball milling of powders whenever possible, as milling (obviously) alters particle size distributions and often changes powder surface chemistry in unpredictable ways. This is especially the case for silicon metal powders, which can be quite reactive when fresh surfaces are exposed. An additional disadvantage of ball milling in this program would have been the tendency to damage microballoon-type additives in the dispersions. The principal function of the dispersion aids was to modify the electrical double layer around each powder particle, building up mutually repulsive charges at the surfaces of the particles; thereby producing sedimentation-resistant dispersions.

Three types of microballoon additions were investigated for this effort.

Dualite[®] is an expanded polyvinylidene copolymer microballoon with very low bulk density (less than 0.13 g/cc (8 pcf)) and is available in commercial quantities for a price of approximately \$1.80/kg (\$4/lb). Dualite[®] is manufactured with fairly broad, essentially Gaussian, size distributions over the 25 to 100 micron (1×10^{-3} - 4×10^{-3} inches) range. It was the only polymeric microballoon product we investigated which was adequately wet by water and could be dispersed in NBSiC or NBSN dispersions. Dualite microballoons are produced with a calcium carbonate sizing to facilitate dry pouring. Though this sizing was water-soluble, it may have had a slightly deleterious effect on nitridation kinetics, as is discussed in the next section. Dualite is manufactured by Pierce and Stevens; Buffalo, New York; phone (716) 856-4910.

Carbospheres is a pure carbon hollow microsphere with bulk tap densities from less than 0.13 to 0.4 g/cc (8-24 pcf). Carbospheres are available with diameters between 5 and 150 microns

(0.2×10^{-3} - 4×10^{-3} inches) and wall thicknesses typically less than one to two microns. They are produced in a few thousand pound per year quantities at prices in the range of \$50-100/kg (\$110-220/lb). Textron's concept for the use of Carbospheres called for quantitative removal of carbon via the conversion to SiC during pyrolysis processing just prior to nitridation. This would occur as a result of the presence of free carbon and Si metal in the porous green body. Carbospheres are manufactured by Carbospheres, Inc.; Fredericksburg, Virginia; phone (703) 898-4058.

Hastings Plastics MJO 0930 is a phenolic microballoon product with bulk tap densities from 0.05 to 0.13 g/cc (~3-8 pcf). MJO 0930 size distributions are typically Gaussian, centered in the 50 to 100 micron (2×10^{-3} - 4×10^{-3} inches) range. The product is commercially produced in few thousand pound per year quantities and is available for a cost of approximately \$1.80/kg (\$4/lb). Phenolic polymers can be directly converted to carbon via controlled heating profiles under pyrolysis conditions. Upon conversion of the phenolic to carbon, conversion of carbon to SiC can take place prior to nitridation. MJO 0930 is manufactured by Hasting Plastics; Santa Monica, California, phone (310) 839-3449.

About twenty distinct slurry, microballoon and binder formulations were tested in both NBSiC and NBSN aqueous dispersions. Dualite[®] microballoons were found to be the only pore-forming additives which were rheologically stable, sedimentation-resistant and capable of making dispersions with reasonably high (greater than 60%) solids loadings. Carbospheres and the MJO 0930 phenolic microballoons could be mixed into water-based dispersions, but they tended to float during slip casting and form bodies with unacceptable density gradients. In addition, both these latter additives caused NBSN and NBSiC dispersions to dry much too rapidly for slip casting or filament winding purposes.

Upon choosing Dualite[®] microballoons as the pore-forming species, we began systematically varying microballoon size selection and loadings, measured in weight percent, in order to study the effects of these variables on permeability behavior. A summary of the materials combinations examined are summarized in Table 2-1.

In some cases, water-soluble resins such as polyvinyl alcohol and polyethylene glycol were added to the NBSiC and NBSN/microballoon dispersions in order to control drying characteristics and facilitate subsequent composite lay-up operations. Such additives were generally mixed into suspensions which had already mixed for some period of time, thus allowing particulate surface chemistry to equilibrate.

Results

The outcome of this effort showed mixed successes, and a great number of semi-empirical trials were required to obtain high solids loading suspensions that exhibited temporally-stable behavior. Out of a total of over twenty distinct Si + SiC dispersion formulations that were investigated, we found seven that were worthy of further development (see Table 2-1, Dispersion Types).

Table 2-1
Representative Compositional Variations Examined for NBSiC and NBSN Hot Gas Filter
Matrix Phases: Slip Cast Monolithic Samples Only

<i>Microballoon Weight Percent Added to Dispersions</i>					
Dispersion Type	M6017AE ¹	M6033AE ²	M6036AE ³	M6001 ⁴	Lattice NT050 ⁵
20/80 Si/SiC NBSiC blend	8 weight percent	-	-	-	-
20/80 Si/SiC NBSiC blend	14 weight percent	4 weight percent	-	-	-
20/80 Si/SiC NBSiC blend	9 weight percent		4 weight percent	2 weight percent	1 weight percent
100% Si metal NBSN blend	8 weight percent	-	-	-	-
100% Si metal NBSN blend	10 weight percent		-	-	-
100% Si metal NBSN blend	12 weight percent	-	-	-	-
100% Si metal NBSN blend	20 weight percent	-	-	-	-

1. M6017AE - Mean diameter less than 70 microns
2. M6033AE - Mean diameter less than 25 microns
3. M6036AE - Mean diameter less than 30 microns
4. M6001AE - Mean diameter less than 40 microns
5. Lattice NT050 - Microcrystalline starch additive with mean diameter less than 3 microns

Furthermore, as will be seen in the next major section of this report, only two of these seven appeared to have shown some promise for meeting the Hot Gas Filter program permeability specifications. All NBSiC suspensions described here did not crack upon drying, at least as monolithic bodies. As mentioned in the previous section, Dualite[®] microballoons were found to be the only pore-forming species that performed satisfactorily in our water-based NBSiC and NBSN dispersions.

Dualite[®], being a very low density product, occupies a large volume in dispersions per unit weight added. This made it rather difficult to engineer high solids loading particulate dispersions, which are required to form strong green bodies. Much of the total green body volume is free space even at relatively low microballoon loadings.

Dualite[®]-loaded NBSiC and NBSN dispersions with less than about ten to twelve weight percent microballoons showed handling characteristics rather similar to dispersions without microballoon loading. The forming of fairly robust, crack-free, disk-shaped green bodies was possible using conventional slip casting methods. Drying times could be altered over about two orders of magnitude by varying initial particle size distributions and binder additions. Microballoon loadings of over twelve to fourteen weight percent could successfully be slip cast, but the as-cast 38 mm (1.5 inch) diameter, 3 to 8 mm (0.118 to 0.325 inch) thickness disk specimens exhibited low strength and were susceptible to handling damage. NBSiC and NBSN dispersions which contained twenty weight percent microballoon loadings were very fragile and tended to shrink

considerably during green body drying. Pure silicon metal (NBSN) dispersions were especially problematic at the higher Dualite[®] loadings, as the mean particle size in NBSN dispersions was much smaller than in NBSiC dispersions due to the requirement for having silicon powder with sufficient surface area to minimize nitridation cycle duration.

Stable Dualite[®] loaded NBSiC and NBSN suspensions could be made with aqueous dispersion vehicles employing many different types of particle size distributions, ranging from sharply bimodal (i.e., greater than 100 microns (4×10^{-3} inch) and less than 20 microns (8×10^{-4} inch) particulate) to somewhat monomodal (sizes centered about a mean in the 2 microns ($\sim 8 \times 10^{-5}$ inch) to 5 microns ($\sim 2 \times 10^{-4}$ inch) realm). The addition of resins and binders complicated the behavior of the aqueous suspensions, but did not present intractable problems. In some instances, the addition of binders actually enhanced suspension stability (possibly due to polymeric stabilization in nonaqueous systems) while in other cases suspension stability was degraded. In virtually every instance, as would be expected, drying rates of green bodies were substantially slowed by the addition of binders or resins to the suspensions. Preferential segregation of binders to free surfaces (or "skinning over") during drying was frequently observed, though this effect could be minimized by selecting alternate dispersants or surfactants.

In the particular case of polyethylene oxide (PEO) and polyvinyl alcohol (PVA) we noted substantial increases in strength of green bodies compared to bodies prepared from suspensions which did not contain binders. This becomes an even more important consideration when constructing very large and/or complex-shaped CFCC components.

Within the range explored here, there was not a substantial effect of Dualite[®] diameter on the drying behavior of the dispersions, or the physical strength of green bodies. The main intent of varying microballoon diameter was therefore to assess whether or not permeability characteristics of the matrix changed significantly as the mean pore size was varied. Some trials were also conducted with mixed size distributions of microballoons. The intent here was to maximize matrix permeability at the lowest possible microballoon loading by optimizing microballoon packing behavior. Results of the permeability testing of these monolithic coupons are summarized in Section 3.0.

Conclusions

Rheologically stable NBSiC and NBSN suspensions which are loaded with microballoon-type pore formers can be made using aqueous dispersion vehicles. Careful selection of starting powder chemistry and particle size distribution eliminates the need for costly and time-consuming ball milling and permits use of conventional powder mixing techniques. Additionally, elimination of ball milling enhances suspension stability over time, as it is more likely that stable hydroxyl and/or oxide surface layers formed on the surfaces on the Si, SiC powders and microballoons. Once equilibrated, both types of Dualite[®]-loaded dispersions exhibited very predictable rheological behavior as a function of mixing time. This simplifies downstream processing considerations during CFCC preform handling and construction.

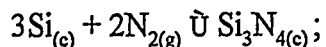
Sedimentation-resistant and stable NBSiC and NBSN suspensions can be made over a wide range of particle sizes and relative fractions of Si powder, SiC powders and microballoons, as long as particulate surface chemistry is understood and controlled. Classical electrostatic and possibly polymeric stabilization techniques both appear to be effective at promoting the buildup of mutually-repulsive interparticle forces in NBSiC and NBSN suspensions.

For cases involving dispersions which contain significant fractions of large (greater than 100 microns (4×10^{-3} inch)) alpha SiC particulate and moderate (less than 10 weight percent) Dualite[®] loadings, we observed that shrinkage of the drying green body was less than a few percent, and also that the amount of binder that was required in order to make a robust preform was lessened. Relatively small additions of binders in aqueous NBSiC suspensions have also been seen to have a potent beneficial effect on green body strength. The same beneficial effects, however, were not seen for NBSiC and NBSN dispersions which were loaded with over 12 to 14 weight percent Dualite[®]. In these latter cases, it was quite difficult to prepare physically robust monolithic green bodies with any combination of starting materials. At microballoon loadings of 18 to 20 weight percent and higher, the as-cast matrix material was so weak that it could not reasonably be expected to successfully withstand routine composite making operations like filament winding of candle filters.

2.2.2 Monolithic NBSiC and NBSN - Nitridation Trials

Technical Approach

The reaction between silicon and nitrogen to form silicon nitride (equation 1) is thermodynamically spontaneous under normal nitrogen partial pressures (~ 0.1 Mpa (15 psi)). The reaction becomes kinetically significant only at temperatures above 1100°C (2012°F). At temperatures of practical interest (1200-1400°C (2192-2552 °F)) useful bulk production rates are only possible with high surface area silicon powders (typically less than 10 microns) because the reaction becomes solid state diffusion-limited.⁶



$$\Delta G_{1370} \approx -205 \text{ kJ/mol} \quad (1)$$

Reaction (1) is strongly exothermic with $\Delta H \sim 730$ kJ/mol. The highly exothermic nature of the silicon nitride conversion reaction therefore needs to be accounted for during reaction synthesis processing, either by "active" or "passive" means.

Uncontrolled exotherms can cause localized melting of unconverted silicon metal during the nitriding process, which, at a minimum, will cause formation of gross porosity (due to liquid Si wicking out through pore spaces) in the ceramic matrix. Though this would mainly represent an inconvenience in instances where relatively small amounts of silicon are being nitrided,

⁶ Riley, F.L., "Silicon Nitridation", in *Progress in Nitrogen Ceramics*, NATO AISI Series, Nihoff Publishers, 1981

uncontrolled exotherms can have much more severe safety-related consequences when large CFCC bodies are being nitrided.

In situations where relatively small nitriding loads were in the furnace, we approached the exotherm problem in a rather simple way; by adding appreciable amounts of SiC powder to the CFCC green body to serve as a passive buffering agent for the conversion reaction. This technical approach appears to have been quite successful. For other processing scenarios where we expected to be nitriding fairly large CFCC components, both passive and active control capabilities were built into the furnace, as well as the process itself. During the Phase 1 development program, we have already addressed operational concerns about exotherms through an active control approach involving incorporation of a demand cycle controller on the furnace design, in which it was possible to "sweep" controlled amounts of high thermal conductivity gases (i.e., hydrogen or helium) into the nitriding atmosphere in order to attenuate or completely quench reaction exotherms.

The density of silicon is 2.33 g/cc (0.086 lbs/in³) and that of silicon nitride is 3.21 g/cc (0.12 lbs/in³), thus the conversion process leads to a volumetric expansion of 21.7% which occurs during silicon nitride formation. On the basis of the Pillings-Bedworth relationship, one cannot therefore expect coherent silicon nitride films to form on silicon surfaces by normal diffusional processes. Furthermore, at typical gas phase nitridation temperatures, silicon does not show appreciable plasticity, and as the overall volume change in a Si-containing green body is essentially zero, it is apparent that considerable rearrangement of the internal structure must take place in the internal pore spaces of the compact. Volumetric rearrangements in the green body must be accounted for by properly engineering the pore structure of the CFCC part to be nitrided.⁷ One is hence faced with the somewhat contradictory requirements of creating an NBSiC matrix pore structure that is interconnected enough and large enough in scale to allow reactant transport in and out of the body, while at the same time producing a nitrided body that is sufficiently dense to show useful mechanical and oxidation characteristics. As might be expected, this was not a serious concern with the hot gas filter formulations investigated for this work, as the matrix materials were inherently quite porous.

During the Phase 1 effort, Textron investigated the use of nitriding time/temperature cycles of about 3-5 hours of exposure at temperatures in the vicinity of 1350-1380°C (2462-2516°F), conducting runs in both vacuum-assisted and non-vacuum nitriding furnaces. Pyrolysis of the Dualite[®] microballoons was accomplished during a slow ramp (less than 200 °C/hr (less than 392°F/hr)) heating schedule at temperatures below 1000°C (1832°F). DTA/TGA analysis of Dualite[®] microballoons prior to nitridation trials indicated that this pyrolysis procedure would decompose the polymer with much less than 1 weight percent remaining carbonaceous char. Initial nitriding studies were conducted using a prototype scale furnace equipped with nitrogen demand cycle control and a hot zone size of approximately 0.6 m (~2 ft.) in diameter by 1 m (3.28 ft.) in height. Other furnaces capable of nitridation processing, in sizes up to ~2 m (6.56 ft.) in diameter and ~3 m (9.84 ft.) in height, are also available at Textron.

⁷ Ziegler, G, Heinrich, *Journal of Materials Science*, 22 (1987) 3041-3086

For all of the gas phase nitridation trials, the planar or cylindrical CFCC specimens were merely rested on setter plates, inserted in the nitridation furnace and then exposed to a computer-controlled ramp/soak cycle ending at a peak temperatures in the vicinity of 1350-1380°C (2462-2516°F). Bottled or purified house nitrogen gas was flowed by the specimens at small rates, generally in the few liter per minute range. Experiments were also performed in which the CFCC green bodies were given vacuum "pre-treatment" at temperatures below 1000°C (1832°F). This was intended to remove volatile oxides such as SiO from the powder particle surfaces and so make them more able to form silicon nitride nuclei at lower temperatures than might normally be the case. Sample temperatures were measured directly during nitridation via physical contact with a Type "C" sheathed thermocouple.

As-nitrided monolithic NBSiC and NBSN porous 38 mm (1.5 inch) disks were first weighed to determine nitridation conversion efficiencies, and were then typically characterized with scanning electron microscopy (SEM), optical microscopy and other relevant physical measurement (i.e., geometrical density) techniques. These methods were used to characterize matrix microstructures and track density variations as a function of microballoon loading.

After performing the routine examinations described above, monolithic NBSiC and NBSN filter materials in the form of 38 mm (1.5 inch) disks with 3-8 mm (0.118-0.315 inch) thicknesses were shipped to Westinghouse STC for permeability and alkali corrosion testing in their flow-through apparatus at a temperature of 870°C (1600°F) for 100 hours.

Results

Visual and metallographic examinations showed no signs of silicon "melt-out" or other evidence of uncontrolled exotherms such as gross inhomogeneities in any of the nitrided NBSiC or NBSN disk-shaped test specimens made in this subtask. Additionally, we saw that the pore spaces left over after the microballoons were pyrolyzed were not plugged with alpha silicon carbide whiskers, which nucleate from the gas phase. This was an issue which was raised as a matter of concern by the METC program monitor early in the Phase 1 effort, as such a phenomenon had been previously observed for a reaction bonded silicon nitride hot gas filter development effort that was unsuccessful.⁸ Nitridation in this case caused pore spaces to be plugged with whiskers and thus the filter material never met the permeability requirement.

We generally observed uniform matrix material and pore microstructures for all microballoon plus powder combinations nitrided for this effort, and also noted that the bond between the silicon nitride grown by gas phase nitridation and surrounding particles appeared to be strong. This was at least the case for formulations containing less than approximately 12-14 weight percent Duralite[®] additions. Particle packing efficiency was evidently better in NBSN dispersions than in NBSiC dispersions, as the bulk density of as-nitrided NBSN samples was consistently higher than for NBSiC samples, at equivalent microballoon loadings. This is likely due to the fact that the relatively large alpha SiC particulate that was used in NBSiC dispersions did not, in the presence of the microballoon additions, optimally redistribute during the casting process.

Bulk density measurements on slip cast and nitrided disk samples in the 0.6-0.8 g/cc (0.02-0.03 pounds/in³) range were typically obtained for NBSiC and NBSN which contained 14-20 weight percent Dualite[®], while those which contained 8-10 weight percent microballoons were generally in the 1.3-1.4 g/cc (0.05-0.52 pounds/in³) range (See Table 2-2). For the lowest density materials, nitridation weight gains were also below 90-95% of theoretical, whereas dispersions with lower microballoon loadings often nitrided to 98% of theoretical. (Note that Textron normally finds 97-99% weight gains upon nitriding "fully dense" NBSiC or NBSN CFCC matrix materials with the same nitridation schedules.) At the same time, however, optical metallographic and SEM examination of as-nitrided NBSiC and NBSN coupons did not reveal the presence of free silicon. It is therefore conceivable that excessive microballoon additions may have had a poisoning effect on silicon nitridation reactions, likely due to the calcium carbonate sizing on the surface of Dualite[®] microballoons forming calcium silicate phases. In addition, silicon carbide would form from the Si + C reaction. Both reactions would quantitatively remove silicon from the matrix and would lower the expected theoretical weight gain. There was insufficient time on the Phase 1 program to address these issues in adequate detail.

Table 2-2
Summary of Nitridation Data on Monolithic Hot Gas Filter Materials

Fabrication Process	Materials Systems	Bulk Density Range (gm/cm ³)	Si to Si ₃ N ₄ Conversion (% theor.)	Nitridation Results
<i>Modified Slip Casting</i>	• Monolithic NBSiC w/ 8-20 weight percent Dualite	• ~0.50-1.3	• 93-98%	• very friable at ρ less than 0.7 gm/cm ³
	• Monolithic NBSN w/ 8-20 weight percent Dualite	• ~0.80-1.4	• 88-92%	• Not as permeable as NBSiC matrix

Physical strengths of as-nitrided NBSiC and NBSN monolithic compositions were fairly good for dispersions containing less than 12-14 weight percent microballoons, while it became clear during these process trials that the skeletal strength of the matrix dropped quite rapidly at loadings above this level. Samples with 20 weight percent microballoon additions were barely handleable and tended to chip or crack very easily; bulk densities of the matrix materials at 20 weight percent loadings went as low as 0.5 g/cc (0.02 pounds/in³), which is only 15-20% of typical densities for "standard" NBSiC and NBSN matrices after slip casting and nitridation. The postulated poisoning effect of the calcium carbonate sizing on Dualite[®] may also have contributed to the loss in matrix strength, since appreciable amounts of silicon (and therefore silicon nitride) may have been removed from the green bodies prior to nitridation via the mechanisms mentioned earlier.

X-ray diffraction (XRD) characterization of sectioned and polished NBSiC and NBSN monolithic filter materials provided more quantitative indications of crystalline phase content in the as-nitrided condition. We were especially interested in detecting the presence of residual

silicon and other unintentionally-introduced or undesirable species. The NBSiC specimens examined contained a phase mixture of 6H alpha SiC, minor amounts of β SiC (likely from SiC formation due to solid state reaction of Si and C), alpha silicon nitride and beta silicon nitride. Alpha to beta ratios varied from about 1.5:1 to 2:1, generally consistent with earlier findings on monolithic and CFCC NBSiC materials.

The NBSN filter specimens examined contained a phase mixture of alpha silicon nitride, and beta silicon nitride, and sometimes silicon oxynitride (at less than 1% levels). Alpha to beta ratios varied from about 4:1 to 2:1, also consistent with earlier findings on monolithic and NBSN matrix CFCC materials. Occasionally, trace amounts of iron silicate were seen (due to the presence of iron in the starting Si powder), but no free silicon was ever found within the sensitivity limits of the X-ray instrument.

Conclusions

Workable nitriding schedules which avoid uncontrolled exotherms have been demonstrated for NBSiC and NBSN. Microstructural and microchemical examinations of fully-nitrided NBSN and NBSiC monolithic filter materials are typified by multimodal distributions of large and small grained, well-bonded, crystalline SiC and Si₃N₄ phases, at least for matrix materials which contain less than 12-14 weight percent microballoons. Trace element and impurity phase content of both the NBSiC and NBSN monolithic filter materials was seen to be rather low, which normally would indicate that the skeletal matrix phase materials would show good thermochemical stability at elevated temperatures in oxidizing environments. However, as will be seen in Section 3.0 on corrosion test results, phase purity of the matrix materials for porous NBSiC and NBSN did not appear to be a viable predictor of performance in the alkali corrosion environment.

Porous NBSiC and NBSN filter compositions with 14-20 weight percent microballoon loadings can be quite fragile even after nitriding. Though the density of the pure silicon nitride matrix material is higher than the silicon nitride/silicon carbide phase mixtures for the same Dualite[®] loading, it is doubtful whether either class of materials could show useful matrix microcracking strengths when reinforced with SCS-6[™] monofilaments. This would raise attendant concerns about the mechanical integrity of such CFCC materials under cyclic exposure and ash bridging conditions in the hot gas filter environments.

NBSiC and NBSN-based ceramics with less than 14 weight percent microballoon loadings can have good mechanical strength, but it is doubtful as to whether materials with this level of induced porosity could meet the Phase 1 Program permeability specifications. (See test results in Section 3.0.)

The calcium carbonate sizing used to enhance the dry pouring characteristics of Dualite microballoons may have a deleterious effect on the nitridation behavior of NBSiC and NBSN matrices at high loading levels. Further analytical and materials processing work would be required to determine whether or no silicon is being removed from the starting powder mixes either via formation of volatile calcium silicate phases or beta silicon carbide formation.

2.2.3 SCS-6™/NBSiC and SCS-6™/NBSN CFCCs

CFCC Filter Preform Fabrication

Subtask Objectives

The principal objectives of this subtask were as follows:

1. To fabricate Dualite®- loaded SCS-6™/NBSiC and SCS-6™/NBSN 38 mm (1.5 inch) disk specimens for corrosion and permeability testing at Westinghouse STC;
2. To adapt and modify microballoon-loaded NBSiC and/or NBSN dispersions to permit direct filament winding of CFCC filter preforms with no intermediate operator handling steps (such as tape lay-up and ply orientation);
3. To select tooling materials and designs that could accommodate pressureless slip casting and facilitate physical release of tubular CFCC filament preforms from the filament winder mandrels; particularly for closed-ended CFCC tubes; and,
4. To initiate trials for fabrication of subscale tubular CFCC filter elements with a candle filter type geometry.

Technical Approach

For the fabrication of 38 mm (1.5 inch) disk-shaped coupons for permeability and corrosion testing, Textron modified a processing approach that had been used successfully in the past to prepare flat panels of standard SCS-6™ reinforced NBSiC and NBSN CFCCs. The methodology combined elements of filament drum wrapping (winding a parallel array of fiber on a large diameter drum, at a closely controlled fiber-to-fiber spacing, to produce a fiber-only ply) and conventional slip casting as follows:

(1) Dualite®-loaded NBSiC or NBSN slurries were prepared and allowed to equilibrate as described previously. Loadings of 10-14 weight percent microballoons were investigated for these CFCC coupon processing trials.

(2) Drum wrapping of SCS-6™ mats and uniaxial tapes was carried out at spacings of anywhere from 30 to 40 SCS-6™ filaments per centimeter (75-100 filaments/inch) of drum width. For ply thicknesses in the vicinity of 0.25-0.30 mm (0.010-0.012 inch) this typically yielded SCS-6™ filament volume fractions in the 8-18% range for finished panels. The overall dimensions of the planar test coupons made from the NBSiC and NBSN CFCC matrix compositions above were mostly in the range of 10 cm (4 inch) width by 15 cm (6 inch) in length and from 0.4-0.7 cm (0.160-0.280 inch) in thickness. For this particular effort, all CFCC coupons tested were 0°/90° lay-ups.

(3) The drum wrapped filaments were then taped and cut into dry plies, into which NBSiC and NBSN microballoon-loaded slurries were impregnated by doctor blading. After impregnating the plies with slurry, the fiber plies were laid up and lightly pressed between two Potter's plaster platens in a small laboratory laminate press. The green body was then allowed to cast and dry for about one hour and was then removed from the plaster.

(4) Those panels which successfully survived processing to this step were, as before, rested on setter plates, inserted in the nitridation furnace and then exposed to a computer-controlled ramp/soak cycle ending at a peak temperatures in the vicinity of 1350-1380°C (2462-2516°F). Bottled or purified house nitrogen gas was flowed by the specimens at small rates, generally in the few liter per minute range. Sample temperatures were measured directly during nitridation via physical contact with a Type "C" sheathed thermocouple.

As-nitrided monolithic NBSiC and NBSN porous flat panels were first weighed to determine nitridation conversion efficiencies, and were then sectioned into 38 mm (1.5 inch) disks for eventual corrosion and permeability testing at Westinghouse STC. Unfortunately, however, by the time we were able to make self-supporting CFCC filter disks, the Phase 1 development program funding was expended and the contract subsequently terminated. As a result, no corrosion or permeability data were generated on this class of materials and results of work performed on this subtask will refer only to characterization of basic physical properties and representative microstructures. Routine characterization of sample microstructures were performed with scanning electron microscopy (SEM), optical microscopy and other relevant physical measurement (i.e., bulk density) techniques.

Direct filament winding was used to construct tubular SCS-6™ reinforced CFCC filter preforms which were approximately 30 cm (12 inch) long, 5 cm (2 inch) in diameter and 3-8 mm (0.118-0.315 inch) wall thickness. Porous gypsum molds were used as filament winding mandrels, which defined the overall geometry and inner diameter of the tubular preform. The gypsum molds also served as inner diameter slip casting molds for the combined filament winding/slurry deposition process. The main complicating factor here was the need to extricate the preform from the gypsum tool after winding and casting. Several different methods were investigated to fabricate collapsible and multi-piece mandrels that could be disassembled after preform construction was complete. Provisional wet filament winding trials were performed with water-based NBSiC slurries onto these cylindrical gypsum mandrels.

Key steps for the fabrication of NBSiC or NBSN CFCC filters were as follows:

(1) Dualite®-loaded NBSiC or NBSN slurries were prepared and allowed to equilibrate as described previously. Loadings of 10-14 weight percent microballoons were investigated for these CFCC filter fabrication trials.

(2) SCS-6™ filaments were wrapped onto a Potter's plaster mandrel with approximately one kg (2.2 pounds) of tension in a 90°/±45°/90° architecture to define the CFCC preform geometry. The Dualite®-loaded NBSiC or NBSN slurries were simultaneously introduced with the

monofilaments by forcing the slurry through a syringe-type applicator which was immediately above the filament being paid out onto the plaster mandrel.

Once the feasibility of on-line slurry impregnation and preform construction had been demonstrated, modifications to the filament winder payout head were undertaken which permitted handling of one to three spools of SCS-6TM fiber at once. SCS-6TM spool carriers were built to follow the motions of the payout head during filament winding and also to allow for tension adjustments to be made on the filaments. Feed rates of the filaments were thus slaved to the rotational rates of the mandrel. Our first computer programs written specifically for winding of CFCC preforms were kept intentionally simple, as we wanted to demonstrate process feasibility and document items of interest such as slurry drying rates and reinforcement handling behavior as the preforms were built up. Both 90°/±45°/90° or 90°/±30°/90° reinforcement architectures were evaluated during this filament winding development effort. Relatively low fiber volume fractions (less than 10%) were also used in order to minimize winding times and keep preform costs as low as possible.

(3) Wet slurry winding was continued until the CFCC preform geometry was completed and the preform was allowed to air dry for about one day, when the preform would be ready for extraction from the mandrel and nitridation.

Results

Fabrication of CFCC flat panel specimens using NBSN or NBSiC matrices and drum wrapped fiber mats turned out to be a difficult proposition, with most of the problems encountered being attributable to the low strength of the green matrix materials. Processing trials for panels with less than 10-12% microballoon loadings showed some promise, but it was not always possible to separate the slip cast panels from the plaster plates used to form the cross-plyed green bodies. Inter-ply failures of the matrix materials and matrix cracking were frequently observed. Cracking of the green NBSN and NBSiC matrices was recognized from the onset as a potential problem. The densities of the Dualite[®]-loaded matrix materials were generally quite low due to the high pore volume and had a tendency to shrink much more than standard NBSiC and NBSN mixes during drying. Since SCS-6TM monofilaments obviously do not shrink during drying, matrix microcracking frequently occurred since the intrinsically weak matrix material was subjected to residual tensile stresses due to the restraint of the fibers. A few panels were, however, successfully slip cast but were never subjected to any detailed testing or microcharacterization other than measurement of bulk density.

As nitrided SCS-6TM-reinforced NBSiC panel densities were in the 0.55-1.3 g/cc (0.02-0.05 pounds/in³) range, while the as-nitrided NBSN matrix CFCC densities were generally ~10 % higher (Table 2-3). A few sample disks of CFCC material with approximately 10% microballoon loadings were successfully cored out with a 38 mm (1.5 inch) diameter diamond drill. These samples have been retained at Textron and are available to DOE for testing purposes if interest warrants.

Table 2-3
Summary of Nitridation Data on CFCC Hot Gas Filter Materials

Fabrication Process	Materials Systems	Bulk Density Range (gm/cm ³)	Si to Si ₃ N ₄ Conversion (% theor.)	Nitridation Results
<i>Drum Wrap Fiber & Slip Cast</i>	• SCS-6™/NBSiC	• ~0.55-1.3	• 95-99 %	<ul style="list-style-type: none"> • Laminar defects difficult to eliminate • Better penetration around SCS-6™ fibers.
	• SCS-6™/NBSN	• ~0.6-1.4	• 88-93%	

Composite forming complications were also encountered at microballoon loadings of 12 weight percent and higher. At these higher microballoon loadings, "sieving" by the fiber plies of the matrix particulates and microballoons occurred. This caused the presence of laminar porosity in as-slip cast panels, which lowered matrix green strength to nearly unhandleable levels.

The first exploratory wet filament winding trials employing modified slip casting methods and Dualite[®] loaded NBSiC slurries were unsuccessful. Excessive cracking of the CFCC green bodies was found at microballoon loadings above 12-14 weight percent, and therefore, extraction of the preforms from the mandrels was impossible. At microballoon loadings below 12 weight percent, macro-cracking of the green matrix, although less prevalent, was still a problem which prevented consistent mandrel extraction. It is believed that part of the problem was due to the fact that Potter's plaster mandrels appear to absorb water from the microballoon-loaded dispersions relatively rapidly, generating anisotropic drying stresses in the green matrix material. At the very end of this effort, Textron began to investigate the use of fugitive mandrel materials which could be burned out or carbonized prior to nitridation to facilitate removal of the mandrel from the fragile CFCC green body. Although a number of single-ended mandrels were fabricated from phenolic foam, they were never actually tested in filament winding trials.

Conclusions

Adaptation of the McClean-Anderson winder to suit the processing needs of our Phase 1 Program required significant modifications of CFCC processing technology that had been developed on the Textron Phase 1 CFCC program. The magnitude of the modifications needed to successfully fabricate CFCC hot gas filters was initially underestimated, thus adding to the difficulties which were already being experienced with the handling of microballoon-CFCC filter preforms.

Wet filament winding of NBSiC or NBSN CFCC hot gas filter preforms is technically feasible with suspensions containing less than 10-12% microballoons, but is essentially unworkable when using slurries exceeding these loadings. Although part of the problem is certainly due to the anisotropic drying stresses in the green matrix material generated by the plaster mandrels, significant microcracking occurs due to the matrix weakness and the restraint imposed by the fiber array.

The ability to fabricate prototype-scale tubular CFCC filter components was not convincingly demonstrated on this subtask. Significant amounts of additional dispersion formulation and CFCC tooling development efforts would be required in order to produce crack-free porous green bodies using SCS-6 monofilaments and microballoon-loaded NBSiC or NBSN matrices as the constituent phases.

2.3 *In-Situ* Pore Forming Agents

2.3.1 Process Overview

The objective of this work, which was commenced late in the program, was to investigate an alternative methodology for introducing porosity in NBSiC and NBSN monolithic and CFCC materials. The intent was to make use of in-situ pore forming agents which would essentially cause formation of bubble networks in the ceramic matrices that would be stable through the entire processing sequence.

We first considered employing emulsions as a route to fabricate open cell pore networks. In aqueous dispersions, simple emulsions can be produced by mixing water, particulate, oil and a suitable emulsifying agent. With agitation or mixing of all three ingredients dilute emulsions can be produced wherein small water droplets are physically dispersed in the oil phase. The viscosity and internal structure of such emulsions can be varied by changing water/oil ratios, and it is even possible to form open cell foam structures with tailorable internal structures.

Another approach that was pursued creating stable pore networks in aqueous dispersions was to induce gas bubble formation in the presence of plasticizing or binding agents that would rigidize the bubble network as the green body dried. In the case of Textron's NBSiC and NBSN slurries, we attempted to form stable bubble networks by adjusting pH in slips which contained polymeric binders like polyvinyl alcohol or polyethylene oxide.

It was somewhat unfortunate that work on his pore-forming methodology occurred so late in the program, as it appeared to offer a greater promise of making reasonably strong CFCC filter materials with either NBSiC or NBSN ceramic matrices.

2.3.2 Monolithic NBSiC and NBSN - Preform Fabrication Trials

Subtask Objectives

The principal objectives of this subtask were to comparatively evaluate two distinct approaches for forming stable pore networks in NBSiC and NBSN dispersion via in-situ methods and to find the materials combinations and processing conditions which yielded open cell pore networks with permeabilities of less than 10 iwg/10 fpm. Emulsion and polymeric additive methods were both examined.

Technical Approach

As in the previous work involving microballoons, we first prepared high-solids content (75-88 weight percent), water-based NBSiC and NBSN dispersions and allowed particulate surface chemistry to equilibrate by low speed roller-mixing for a few days with rubber ball media. After the dispersions reached a stable value of pH, we added emulsifying or polymeric additives which served as the precursors for creating bubble networks.

The emulsion-based pore forming approach involved use of a silicone oil additive and sodium hexametaphosphate surfactant. These two constituents were added to stabilized NBSiC and NBSN dispersions at less than 1 weight percent levels and the resultant mixtures were mixed in a high shear lab mixer for periods ranging from 15 minutes to 1 hour. The resultant foamy dispersions were then allowed to age for about one hour and bodies were then slip cast onto No. 1 Potter's plaster. The as-cast samples were then removed from the plaster and subjected to nitridation treatments identical to those described earlier.

The polymeric pore-former approach entailed addition of less than 0.5 weight percent polyvinyl alcohol or polyethylene glycol to fully-stabilized NBSiC or NBSN dispersions. After a few hours of mixing, the pH of the dispersions was adjusted upwards with minor additions of ammonium hydroxide. When the pH of the dispersions reached 9-11 copious gas evolution was observed, inducing formation of a bubble network. The dispersions were then either immediately slip cast or allowed to age for 1-3 hours and were then slip cast as various shaped green bodies onto No. 1 Potter's plaster. After drying for 12-24 hours the samples were removed from the molds, dried and then nitrided as in the process trials described previously.

Results

The outcome of this effort showed some promise, although additional work on mixing techniques and compositional variations would be required to optimize the pore size distribution using either in-situ pore forming approach. What was particularly encouraging was that both the NBSN and NBSiC suspensions did not show a marked tendency to crack upon drying, at least as monolithic bodies.

For both the emulsion-based and polymer-based pore forming approach, however, pore size distributions were rather wide, with very large as well as very small scale bubbles in the population. At present, the largest pores appear to be much too large in scale to effectively filter out particulate, though formation of these pores may have been due to a surface energy driven, Ostwald ripening-type effect wherein the larger bubbles would tend to grow at the expense of the smaller bubbles over time. It is likely that smaller median size, more nearly monomodal, pore size distributions could be obtained by parametrically varying mixing time, surfactant selection and polymer or emulsion weight fractions. What would actually seem to be desirable is a pore size distribution of the types exhibited by the microballoon-loaded NBSiC and NBSN ceramics.

Nitridation results were excellent, and there was no evidence of reaction poisoning from the small amounts of either silicone oil or polyvinyl alcohol added to the NBSiC or NBSN dispersions.

Weight gains of 97-99% of theoretical were achieved for all materials combinations fabricated in this effort, which is typical of what is obtained with standard NBSiC and NBSN dispersions. The skeletal strength of the NBSiC and NBSN monolithic bodies, based on handlability, was significantly higher than for microballoon-loaded ceramic matrices at all loading levels. Optical metallographic examination of the NBSiC and NBSN materials also showed that the pores were not plugged with alpha silicon nitride whiskers.

Bulk densities of as-nitrided monolithic specimens, however, ranged from 0.8-1.6 g/cc (0.03-0.06 pounds/in³), which is probably too high for percolation effects to become relevant and for linkage of porosity to occur; an obvious requirement for producing permeable matrices.

2.3.3 SCS-6™/NBSiC CFCC Processing Trials

One sample of SCS-6 reinforced NBSiC with ~0.5 weight percent polyvinyl alcohol as a pore former/plasticizer was slip cast in a 0/90 fiber lay-up using the fabrication methods previously mentioned. The sample was readily extracted from the plaster mold and did not show any signs of macro-cracking in the NBSiC matrix due to differential shrinkage effects. The porosity distribution was rather gross in scale, so additional processing trials would be needed to optimize the pore size distribution. The sample also nitrided to greater than 98% weight gain and maintained good matrix strength. It would thus appear that any future efforts concerning development of porous ceramic matrices with elastically stiff reinforcements like SCS-6™ would be more fruitful if *in-situ* pore forming methods were pursued.

Conclusions

The outcome of these extremely preliminary processing trials with *in-situ* pore-forming methods suggest that, in hindsight, this may have been the preferred approach to begin with for fabricating structurally robust and thermodynamically stable CFCC hot gas filters using modifications of Textron's CFCC fabrication route.

The purity of the emulsion-derived or polymer-derived pore forming additives is quite high, as neither species appears to have any measurable effect on nitridation kinetics. This is contrasted with the outcome of the microballoon-based pore forming approach, where evidence was gathered to support the idea that the calcium carbonate sizing on Dualite® may have had a negative influence on nitridation, and eventually matrix strengthening behavior.

While the *in-situ* pore forming approach as a route for producing porous NBSiC or NBSN ceramic matrices appears technically promising, additional basic processing studies would be required in order to establish emulsifier/water ratios, polymer/water ratios, and mixing procedures that promote formation of stable bubble networks with the desired size distributions for filtration and program permeability requirements.

3.0 PERMEABILITY AND CORROSION TEST RESULTS

3.1 Introduction

Westinghouse was issued a subcontract from Textron under DOE/METC's Advanced Hot Gas Filter Development Program.⁸ Under the subcontract, Westinghouse was to conduct preliminary permeability and particulate collection efficiency testing on discs and/or cylindrical sections of candle filter material provided by Textron, select material properties that were required for the filter material(s) (i.e., bulk strength of the filter matrix at process operating temperature; stress strain and creep characteristics; and static fatigue), conduct high temperature flow-through testing, and expose Textron filter material(s) at 870°C (1600°F) for 400 hours to steam/air or gas phase alkali/steam/air conditions. In addition, Westinghouse would conduct post-test characterization of the flow-through exposed material(s) (i.e., microstructural evaluation via scanning electron microscopy/energy dispersive x-ray analyses (SEM/EDS); x-ray diffraction (XRD) analyses; room temperature and process temperature flexural and/or compressive and tensile strength testing; hoop strength), and identify the response of the material(s) to the steam/air and alkali/steam/air flow-through test environment.

3.2 Room Temperature Gas Flow Resistance Measurements

During this Phase 1 effort, Textron supplied Westinghouse with monolithic samples of two general materials classes:

- Nitride bonded silicon carbide (NBSiC) previously loaded with Dualite[®] microballoons; and,
- Nitride bonded silicon nitride (NBSN)) previously loaded with Dualite[®] microballoons.

The samples were in the form of 38 mm (1.5 inch) diameters discs and were supplied to Westinghouse for measurement of room temperature gas flow resistance. In addition, sections of several disc materials were subjected to high temperature, static air conditions containing equilibrium concentrations of gas phase alkali.

Achievement of an acceptable gas flow resistance through the porous ceramic filter matrix,⁹ and performance of the porous ceramic as a complete barrier filter to fine particulates are considered by Westinghouse to be essential initial steps in the development of an acceptable filter matrix, prior to the manufacture and qualification testing of full body, prototype, filter elements.

⁸ DOE/METC Contract No. DE-AC21-94MC31213.

⁹ Gas flow permeability measurements ~ Inverse of the gas flow resistance measurements.

Initial permeability testing was conducted on nitride bonded silicon nitride discs that were supplied by Textron on January 31, 1995. The materials are identified as

- NBSN + 8 weight percent Dualite: (a less than 45 micron SN + less than 10 micron Si starting powder NBSN previously loaded with 8 weight percent Dualite M6017AE)
- NBSN + 12 weight percent Dualite: (a less than 45 micron SN + less than 10 micron Si starting powder NBSN previously loaded with 12 weight percent Dualite M6017AE)
- NBSN + 20 weight percent Dualite: (a less than 45 micron SN + less than 10 micron Si starting powder NBSN previously loaded with 20 weight percent Dualite M6017AE)

In comparison to Westinghouse's gas flow resistance criteria of 1 iwg/fpm for a ~6 mm (~0.25 inch) thick disc of filter material, all of the monolithic nitride bonded silicon nitride materials were shown to be relatively non-permeable (Table 3-1). Additional porosity is needed in the nitride bonded silicon nitride matrices to be considered as acceptable hot gas filter materials.

The gas flow resistance ranges that are shown in Table 3-1 for each disc are based on testing each sample twice (i.e., both surfaces in the direction of the gas flow). This is generally done for two reasons:

- To indicate whether an applied membrane, if present, had any effect on the gas flow resistance measurement. The January 31, 1995 discs were manufactured without a membrane.
- Any minor chips, out-of-roundness, etc., could be easily detected when the discs were initially tested, subsequently taken out of the holder, and retested.

Since the samples had variable thicknesses, a gas flow resistance adjusted for sample thickness is provided in Table 3-1 for comparison purposes (i.e., iwg/fpm-in). From either the actual or adjusted gas flow resistance data, minor variations exist between the discs that were produced in the same production batch. What is interesting is that by adding 12 weight percent Dualite, the gas flow resistance of the nitride bonded silicon nitride discs dramatically decreases, and perhaps with the inclusion of 20 weight percent Dualite, acceptable or nearly acceptable gas flow resistance measurements may have been achieved for the as-manufactured filter matrix.

Table 3-1
Room Temperature Gas Flow Resistance of NBSN Filter Materials

Disc Sample Identification Number, NBSN weight percent M6017AE	Gas Flow Resistance, iwg/fpm	Thickness, mm (inch)	Adjusted Gas Flow Resistance, iwg/fpm-in
8 weight percent Disc 1 (a)	127.17 -128.63	5.33 (0.21)	605.6-612.5
8 weight percent Disc 2	123.81-126.61	4.57 (0.18)	687.8-703.4
12 weight percent Disc 1	NT (c)	4.70 (0.185)	--
12 weight percent Disc 2 (a, b)	61.24-70.47	7.79 (0.307)	199.5-229.6
12 weight percent Disc 3	20.86-21.20	7.79(0.307)	67.9-60.04
20 weight percent Disc 1	NT (d)	--	--

NT: Not Tested.

(a) Adequate Disc Edge For Gas Tight Sealing; Very Smooth Surface; Surface Porosity Not Visually Evident.

(b) Inhomogeneity Between Fabricated Disc Samples.

(c) Chipped Sample.

(d) Broken Sample.

Three additional sets of filter discs were supplied by Textron on March 20, 1995. These materials were identified as:

- (A) NBSiC + ~14 weight percent M6017AE
- (B) NBSiC + ~14 weight percent M6017AE + M6033AE
- (C) NBSN + ~10 weight percent M6017AE

The thickness of the four "A" filter discs ranged between 4-8 mm (0.16-0.20 inch). One of the discs cracked during delivery to Westinghouse, while a second disc had a section of material removed from its outer edge. Only two of the "A" discs were subjected to room temperature gas flow resistance measurements. The thickness of the two "B" filter discs was ~6.6 mm (0.170 inch). One disc which remained intact was subjected to room temperature gas flow resistance measurements. In contrast all three "C" filter discs remained intact after shipment to Westinghouse, and were subjected to room temperature gas flow resistance measurements. The thickness of the "C" filter discs ranged from 0.22 to 0.24 inches.

All intact samples were tested twice, positioning both surfaces of each disc to the direction of the gas flow. As shown in Table 3-2, variations exist in the resulting gas flow resistance measurements for the three filter sample types, which may be due to intrinsic density variations or perhaps edge damage effects. Both NBSiC materials (i.e., discs "A" and "B") had a measured gas flow resistance of less than 1 iwg/fpm which is within the Westinghouse tolerance for an 0.25 inch thick sample disc. The measurements seem to indicate that a Dualite® microballoon loading in the

vicinity of 12 weight percent for the NBSiC ceramics must be near the percolation threshold, the point at which porosity becomes interconnected and accessible to the outside environment.

**Table 3-2
Room Temperature Gas Flow Resistance of NBSiC and NBSN Filter Materials**

Disc Sample Identification Number	Gas Flow Resistance, iwg/fpm
(A) NBSiC + ~14 weight percent M6017AE (Batch No. 010595-1)	0.14- 0.21 0.37-0.38
(B) NBSiC + ~14 weight percent M6017AE + M6033AE (Batch No. 010595-1)	0.13-0.18
(C) NBSN + ~10 weight percent M6017AE (Batch No. 01295-1)	12.69-18.93 13.16-13.76 22.62-25.02

(A) and (B): Possible Gas Flow Leaks Around The Edge Of The Sample; Very Fragile Material; Surface Porosity Visually Evident.
(C): Smoother Surface Finish Than (B); Adequate Disc Edge For Gas Tight Sealing.

In contrast, however, the NBSN discs ("C" samples), had relatively high gas flow resistance in comparison to acceptable gas flow resistance criteria. This would suggest that the NBSN-based materials have a tighter pore network per unit microballoon loading level as compared to the NBSiC compositions (bulk density measurements also seem to bear this conclusion out). Further effort would therefore be needed to introduce porosity and permeability into the NBSN filter compositions in order to satisfy program defined requirements. The scanning electron micrographs are presented in Figures 3-1 and 3-2, illustrating the microstructure of the cross-sectioned NBSiC and NBSN filter materials.

Two additional porous ceramic filter discs, Nos. 1 and 2, were sent to Westinghouse on June 8, 1995 for room temperature gas flow resistance measurements. Both had the same composition (NBSiC + ~16 weight percent M6036 + M6017 + M6001), but were fabricated in different batches.

Room temperature gas flow resistance testing indicated that Disc No. 2 slightly exceeded the Westinghouse gas flow resistance tolerance of 1 iwg/fpm, while the room temperature gas flow resistance of Disc No. 1 was twice that of the Westinghouse gas flow tolerance criteria (Table 3-3). Both discs were assumed to be manufactured identically, and therefore variations within the fabricated filter discs were considered to have resulted.

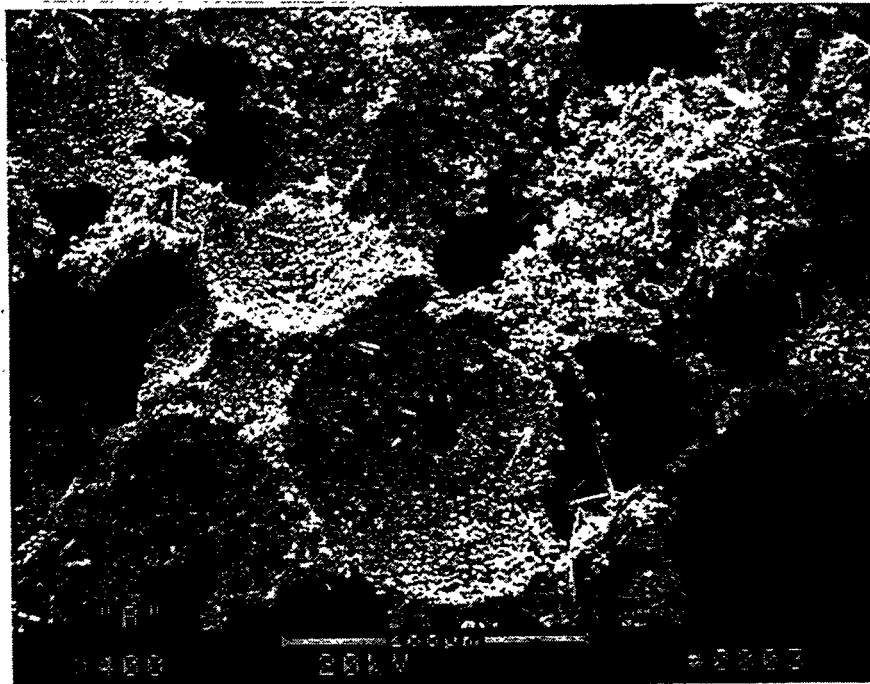
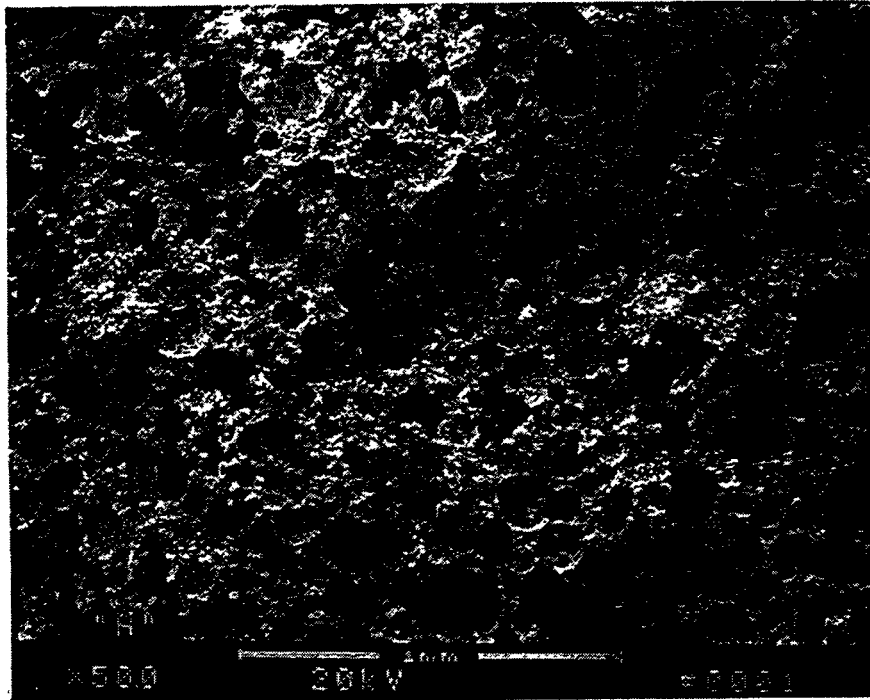


Figure 3-1: NBSiC + 14 Weight Percent Dualite[®] M6017AE

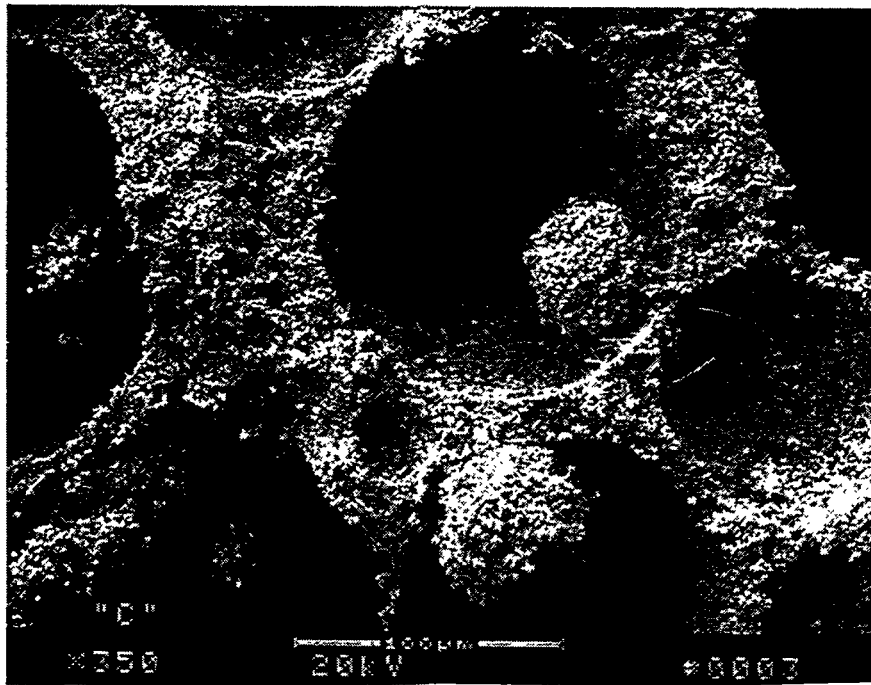
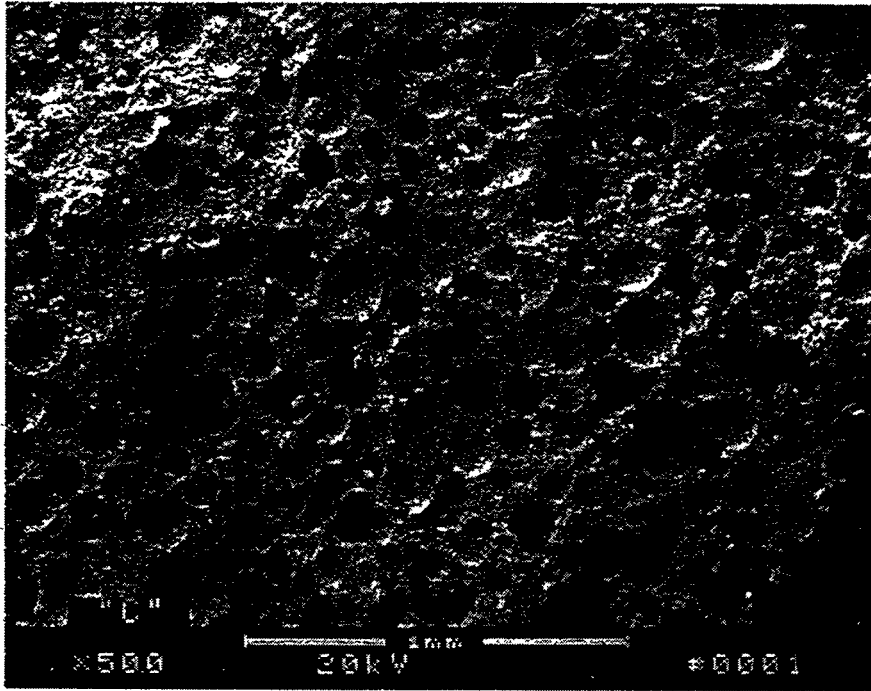


Figure 3-2: NBSN + 10 Weight Percent Dualite[®] M6017AE

Table 3-3
Room Temperature Gas Flow Resistance of NBSiC Filter Materials

Disc Sample Identification Number	Gas Flow Resistance, iwg/fpm
(1) NBSiC + ~16 weight percent M6036 + M6017 + M6001 + Lattice NT050	2.12
	1.99
(2) NBSiC + ~16 weight percent M6036 + M6017 + M6001 + Lattice NT050	1.17
	1.13

- (1) Warped Surface Containing Depressions; Very Fragile Matrix.
(2) Densified Section Along One Edge; Gaps In Matrix Apparent; Very Fragile Matrix.

3.3 Corrosion Testing

3.3.1 Gas Phase Alkali Corrosion of NBSN

High temperature, static air, corrosion testing was conducted using NBSN matrices which contained 8 weight percent M6017AE and 12 weight percent M6017AE (Table 3-1). Testing was conducted for 92 hours at 870°C (1600°F) in the presence of equilibrium concentrations of gas phase sodium chloride. Post-test inspection indicated that both matrices glazed and were adherently attached to the supporting platinum wire mesh screen (Figure 3-3). Bubbles were also evident along the outer surfaces of both materials, particularly along the surface that had been directly positioned along the platinum mesh screen.

As shown at low magnification in Figure 3-4, the outer periphery of the cross-sectioned NBSN + 8 weight percent M6017AE matrix was encapsulated by the "bubble-like" glaze or glass phase. The scanning electron micrographs (SEM) shown in Figures 3-5a through 3-5c indicate that the "bubble" formation was evident through the relatively dense, amorphous (~100 µm-1 mm thick) glaze. Energy dispersive x-ray analysis (EDS) of the 321-NBSN matrix directly below the glaze in Figure 5b, Area 1, identified the presence of 57.67% Si, 37.48% O, 3.31% Na, and 1.54% Ca (i.e., atomic percent basis; gold was utilized to coat the samples and therefore may mask the actual concentration of the light elements). A micrograph montage shown in Figure 3-5c illustrates the glass/matrix interface. Figure 3-5c, Area 1, was identified to contain 40.92% Si, 34.66% O, 20.27% Na, 2.60% Ca, and 1.55% Cl, while Area 2 contained 50.24% O, 46.74% Si, 1.57% Na, 1.10% Ca, and 0.35% Al.

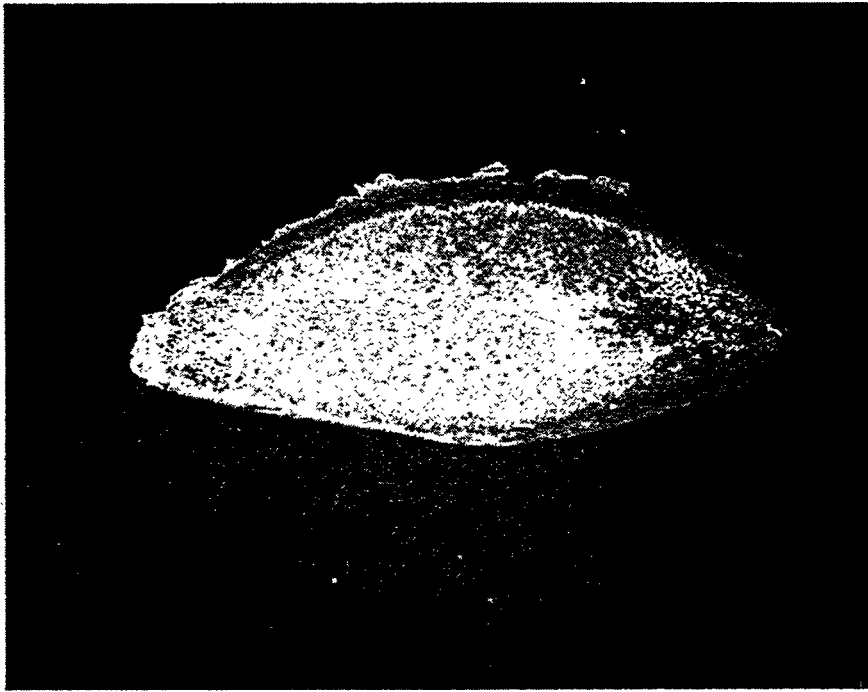


Figure 3-3: Morphology Of The NBSN + 8 Weight Percent M6017AE After 92 Hours Of Exposure To Equilibrium Gas Phase Concentrations Of Sodium Chloride At Temperatures Of 870°C (1600°F) In A Static Air Furnace. Bottom Photograph Illustrates The Extensive Bubble Formations Along The Surface Of The Material That Was In Direct Contact With The Platinum Mesh Screen.

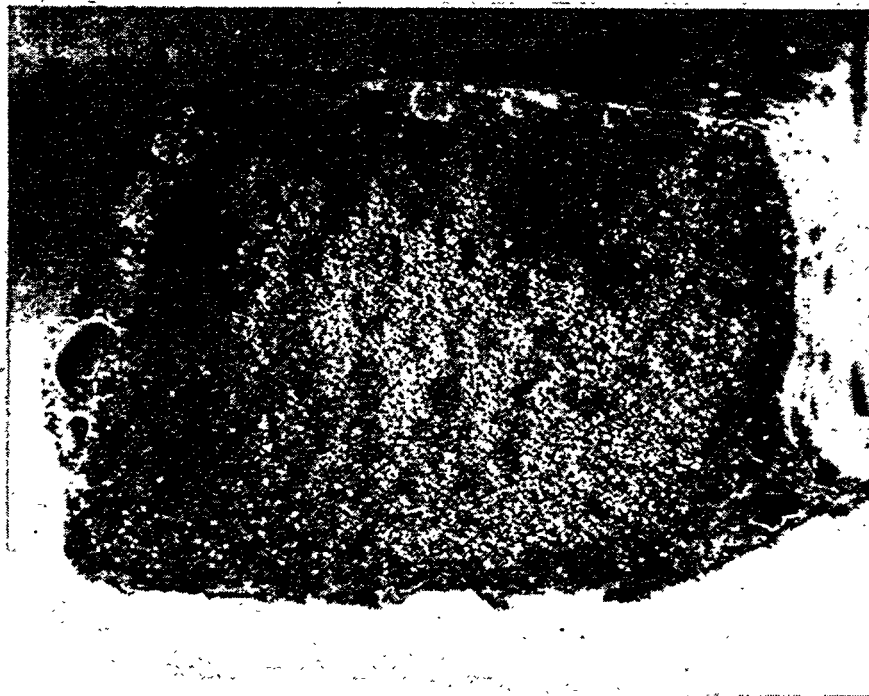


Figure 3-4: Glazed Surface Of The 321-NBSN + 12 Weight Percent M6017AE Matrix After 92 Hours Of Exposure To Equilibrium Gas Phase Concentrations Of Sodium Chloride At Temperatures Of 870°C (1600°F) In A Static Air Furnace

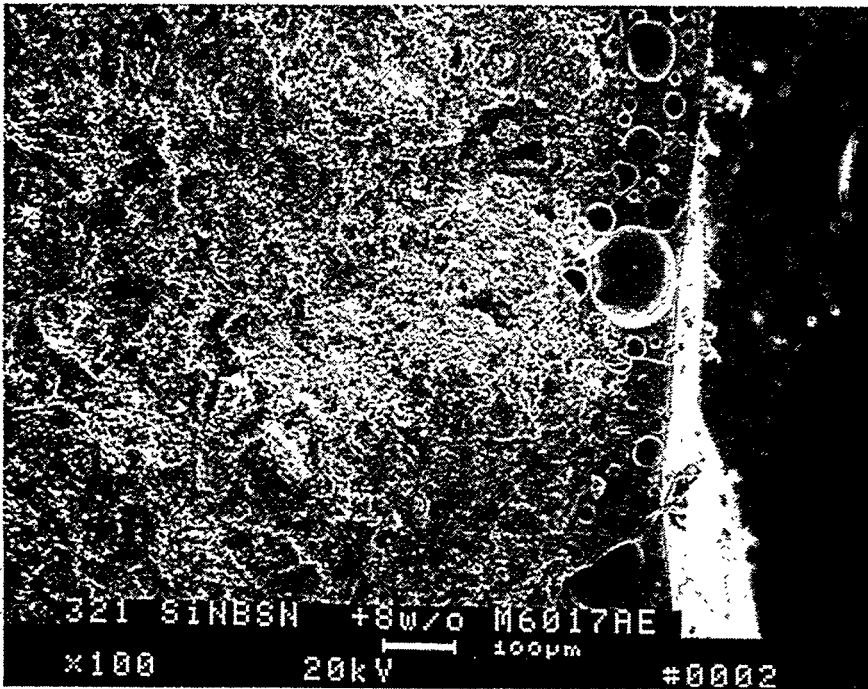


Figure 3-5a: Cross-Sectioned Alkali-Exposed NBSN + 8 Weight Percent M6017AE Matrix

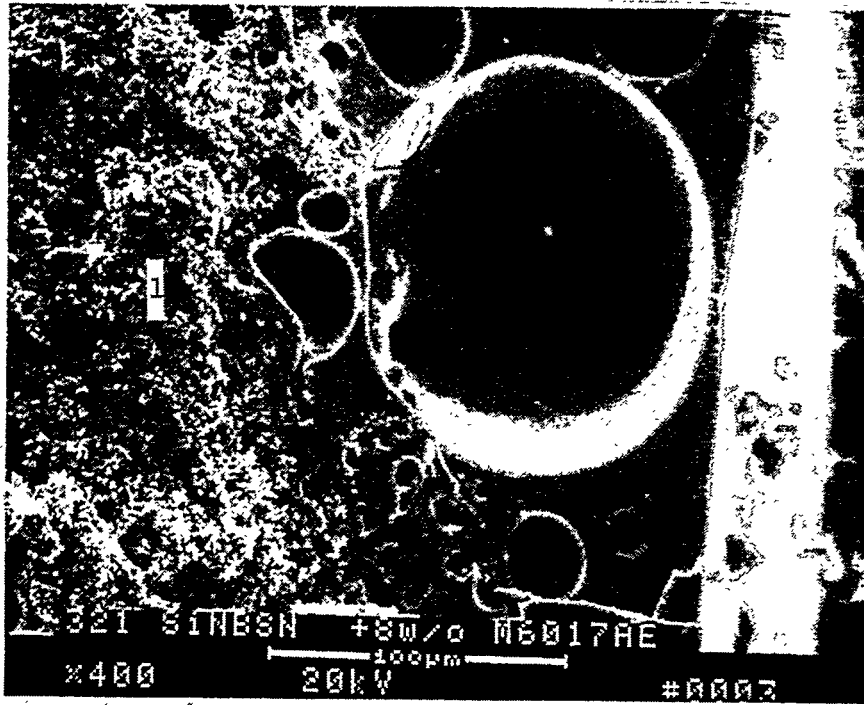


Figure 3-5b: Higher Magnification Micrographs Illustrating The Glass Formation Along The Surface Of The Alkali-Exposed NBSN + 8 Weight Percent M6017AE Matrix

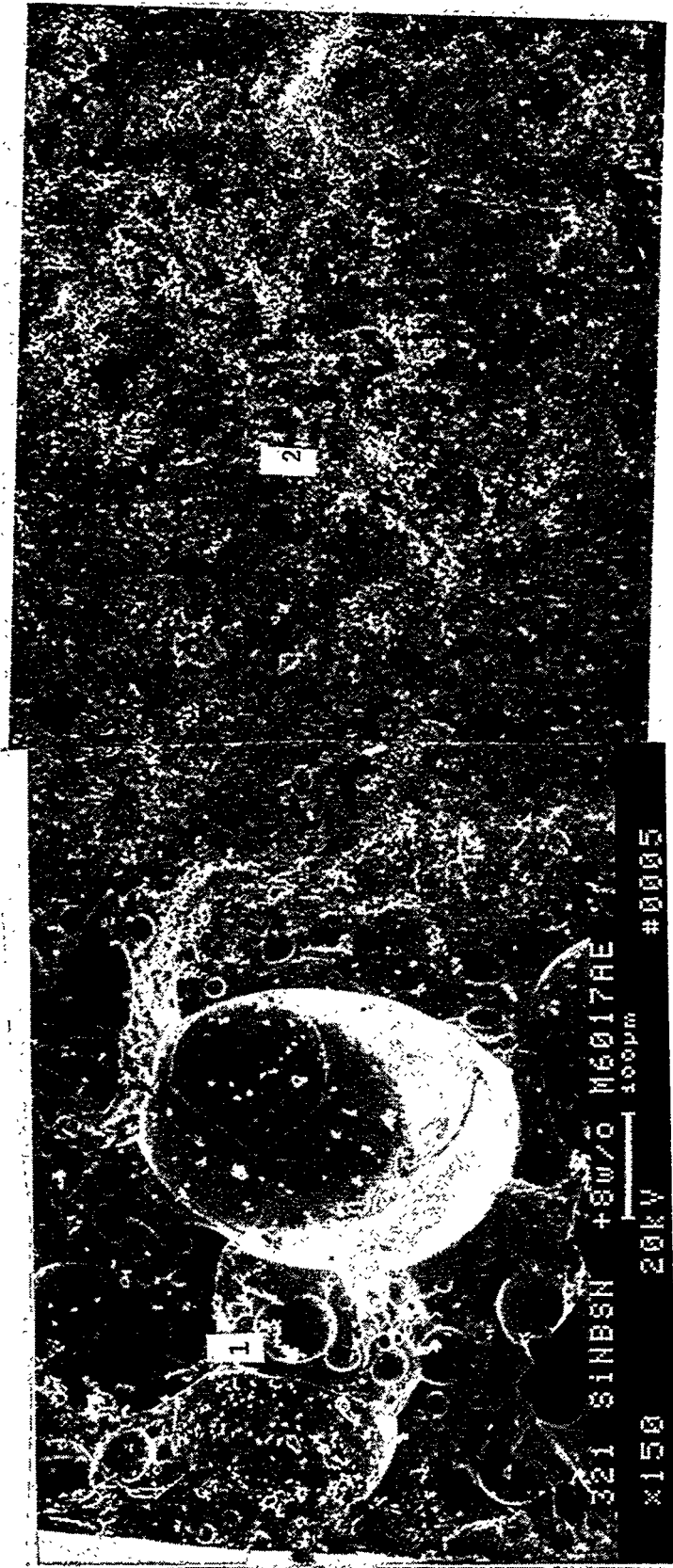


Figure 3-5c: Montage Illustrating The Cross-Sectioned Morphology Of The Glass/Matrix Interface After 92 Hours Of Exposure In The 870° C (1600°F) Alkali-Laden Static Air Environment

Moving to the center of the NBSN + 12 weight percent M6017AE matrix (Figure 3-6a), a relatively dense matrix was apparent. Porosity existed within the microstructure with "whisker-like" formations protruding into the pore cavities (Figure 3-6b). Qualitatively, the composition of the "whisker-like" area shown was identified to consist of 51.19% Si, 48.09% Si, and 0.72% Ca.

Figure 3-7 illustrates the morphology of the amorphous or glass area which formed along the surface of the NBSN material. Cracks and limited bubble formations were evident in this area. EDS analysis of the glass shown in this region indicates the presence of 57.71% O, 21.37% Na, 18.29% Si, 1.0% Fe, 0.85% Ca, 0.59% Cl, and 0.20% Al. The presence of iron along the surface of the glass phase may have resulted from contamination.

Moving to the opposite surface of the alkali-exposed NBSN sample (i.e., surface that was in direct contact with the platinum mesh screen), large concave bubbles and a "frothy" appearance of the glass or glazed surface resulted (Figure 3-8a). EDS analysis of the "frothy" glaze shown in Figure 3-8b, Area 1, identified the presence of 42.14% O, 34.39% Si, 19.06% Na, 2.91% Cl, and 1.50% Ca, while the composition of the concave bubble surface included 53.44% O, 21.62% Si, 21.52% Na, 1.19% Ca, 1.16% Cl, and 1.06% Fe (Area 2).

Similar "glass-like" formations resulted along the surface of the NBSN + 12 weight percent M6017AE matrix that was exposed for 92 hours to the 870°C (1600°F) gas phase sodium chloride environment. Various thicknesses of the glass phase were observed along the outer periphery of the sample.

The NBSN + 12 weight percent M6017AE matrix had an apparent higher porosity (Figure 3-9) in comparison to the NBSN + 8 weight percent M6017AE matrix (Figure 3-5a). Both the existence of porosity, as well as the glass/matrix interface are shown in the micrograph montage provided in Figure 3-10. EDS analysis of an area located directly below the glass phase formation indicated the presence of 66.98% Si, 31.37% O, and 1.65% Ca, while the glass phase was identified to contain 50.05% O, 28.52% Si, 19.79% Na, 0.97% Ca, and 0.67% Cl.

The porosity of the NBSN + 12 weight percent M6017AE matrix in the center of the cross-sectioned sample is shown in Figure 3-11. The "whisker-like" features that were evident along the pore cavity of the NBSN + 8 weight percent M6017AE matrix were also present in the 321-NBSN + 12 weight percent M6017AE matrix (Figure 3-12).

Further analyses of the glass/matrix interface along the surface of the NBSN + 12 weight percent M6017AE matrix that was in direct contact with the platinum mesh screen indicated the presence of 55.33% Si, 37.45% O, and 7.23% Na, while the glass layer was identified to contain 39.25% O, 38.93% Si, 18.68% Na, 1.65% Cl, and 1.48% Ca.

The morphology of the glass phase surface that encapsulated the entire 321-NBSN + 12 weight percent M6017AE matrix after 92 hours of exposure to the gas phase sodium chloride environment at 870°C (1600°F) was characterized by bubble formations, as well as cracks within the resulting glass phase. EDS analysis of the glass phase indicated the presence of 58.55% O, 20.08% Na, 19.27% Si, 0.87% Ca, 0.85% Fe, and 0.39% Cl.

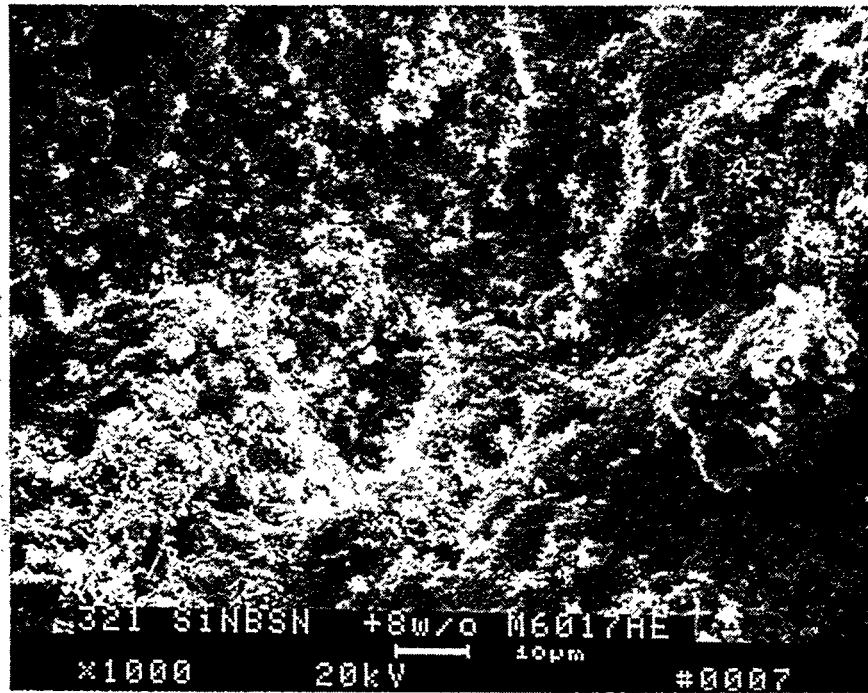
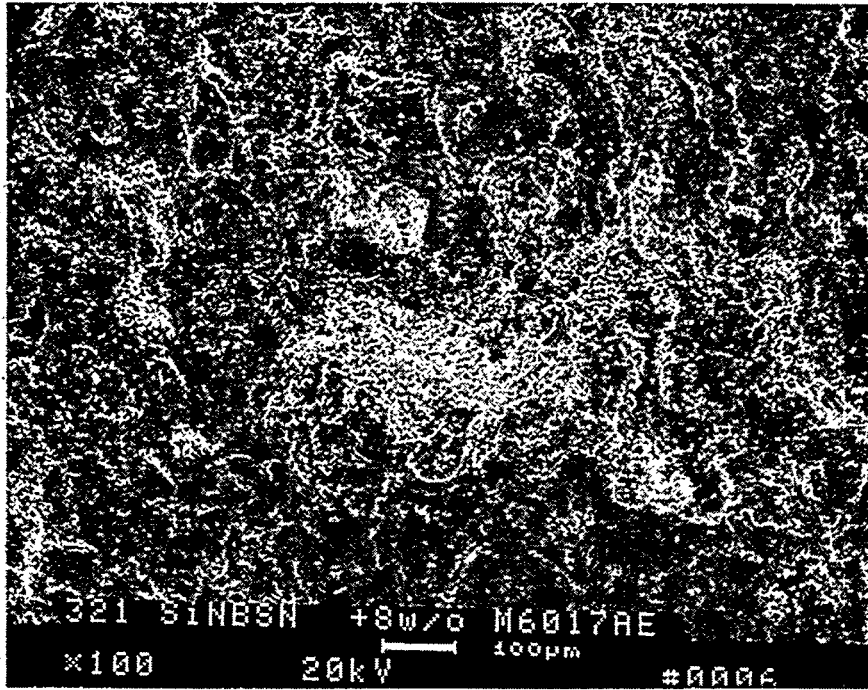


Figure 3-6a: Cross-Sectioned Center Of The Alkali-Exposed NBSN + 8 Weight Percent M6017AE Matrix

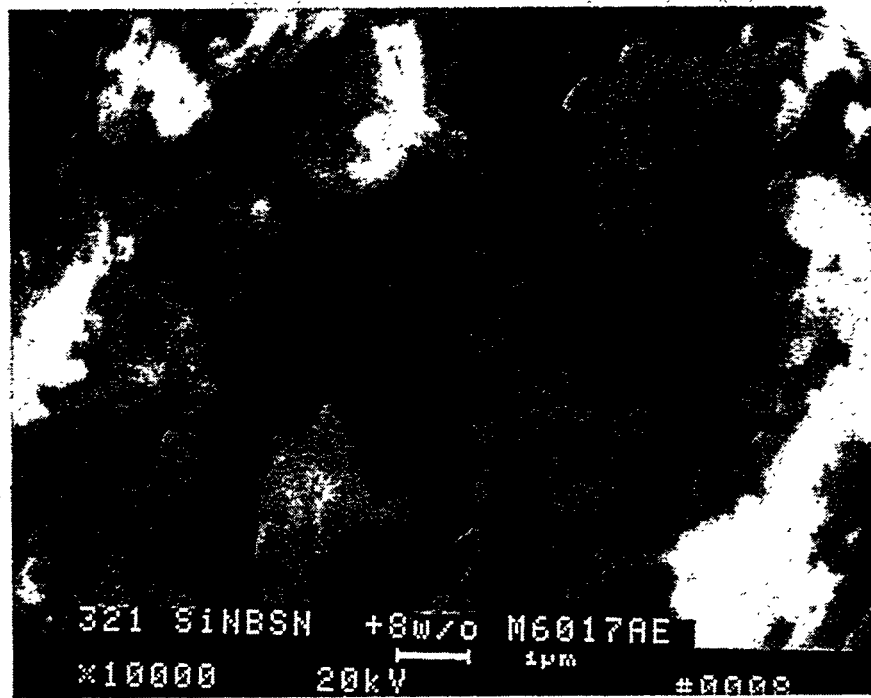


Figure 3-6b: Higher Magnification Micrograph Illustrating The Morphology Of The Pore Cavity In The Center Of The Cross-Sectioned Alkali-Exposed NBSN + 8 Weight Percent M6017AE Matrix

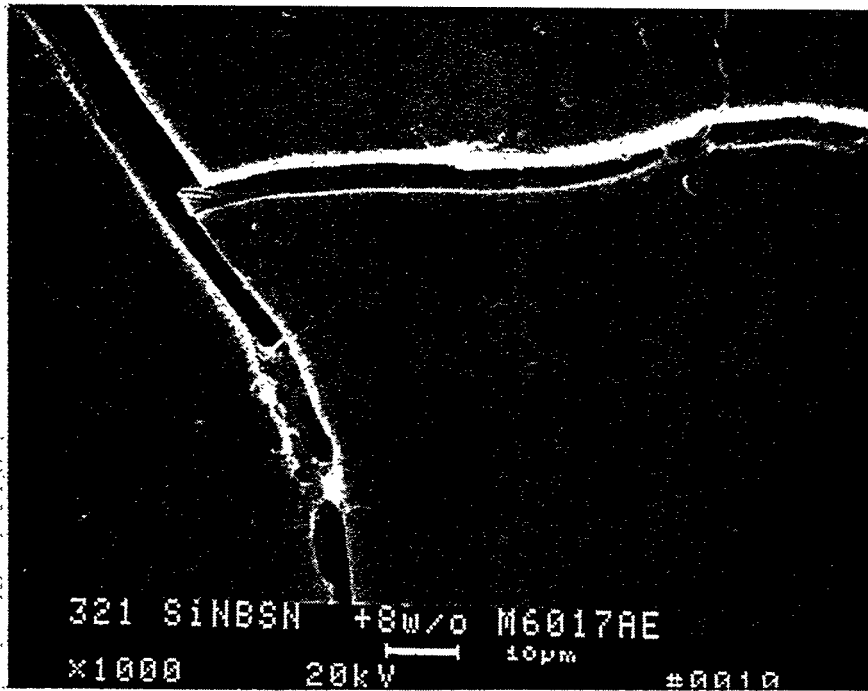
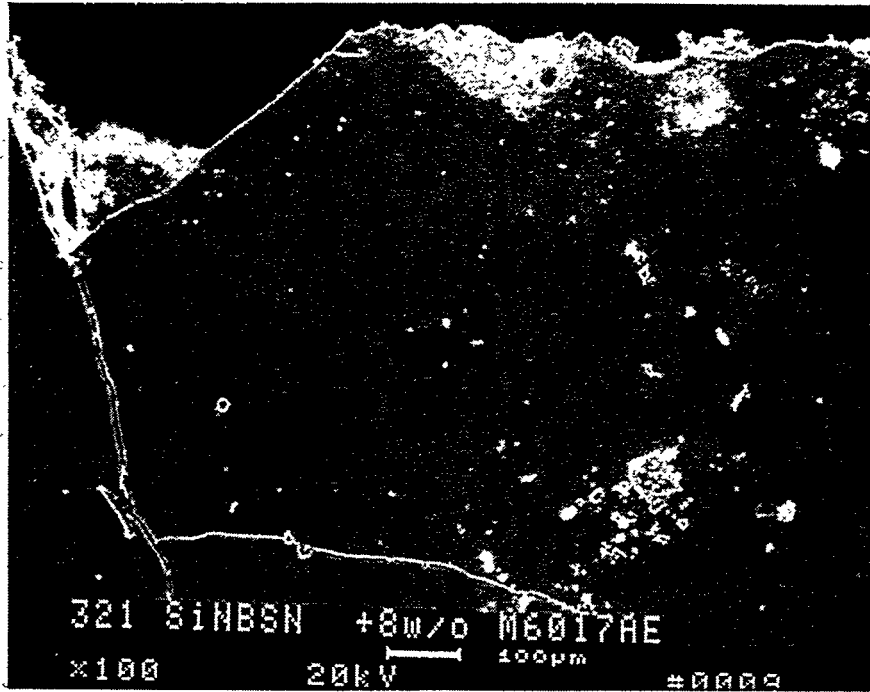


Figure 3-7: Morphology Of The Glazed Outer Surface Of The Alkali-Exposed 312 NBSN + 8 Weight Percent M6017AE Matrix

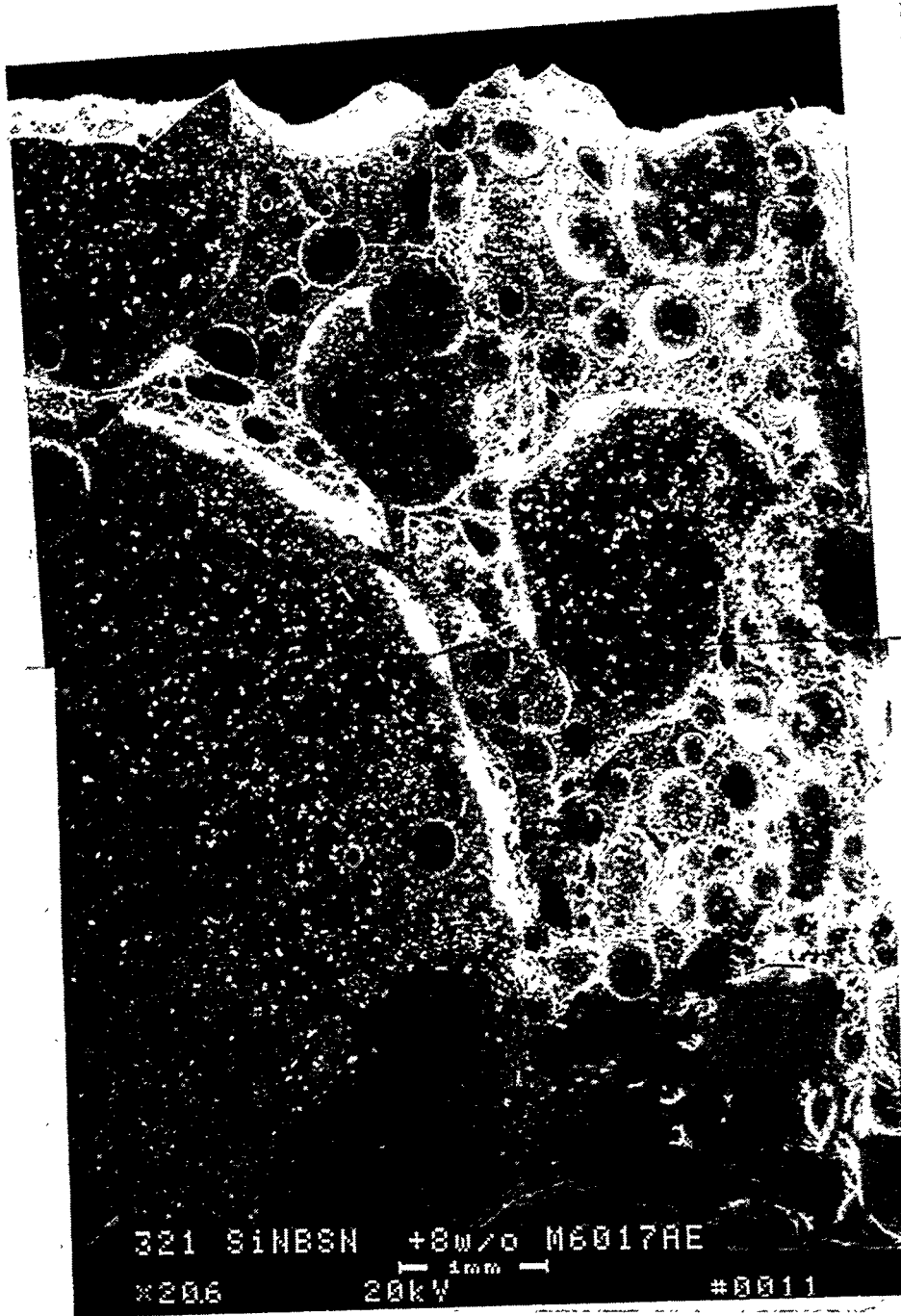


Figure 3-8a: Bubble Formations In The Glass Phase That Formed Along The Surface Of The NBSN + 8 Weight Percent M6017AE Matrix That Was In Direct Contact With The Platinum Mesh Screen During High Temperature Exposure To The Gas Phase Sodium Chloride Environment

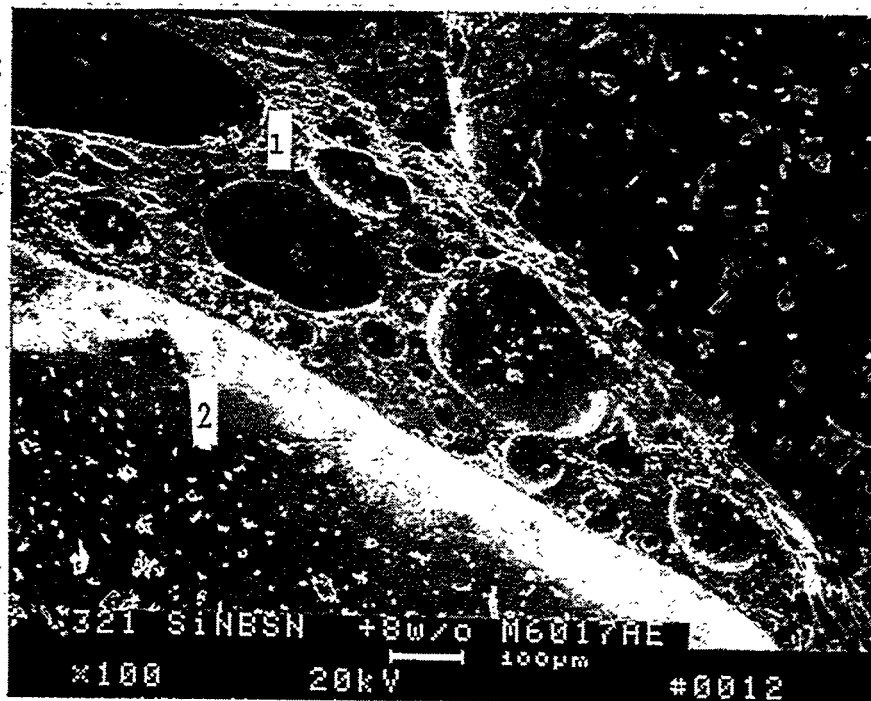
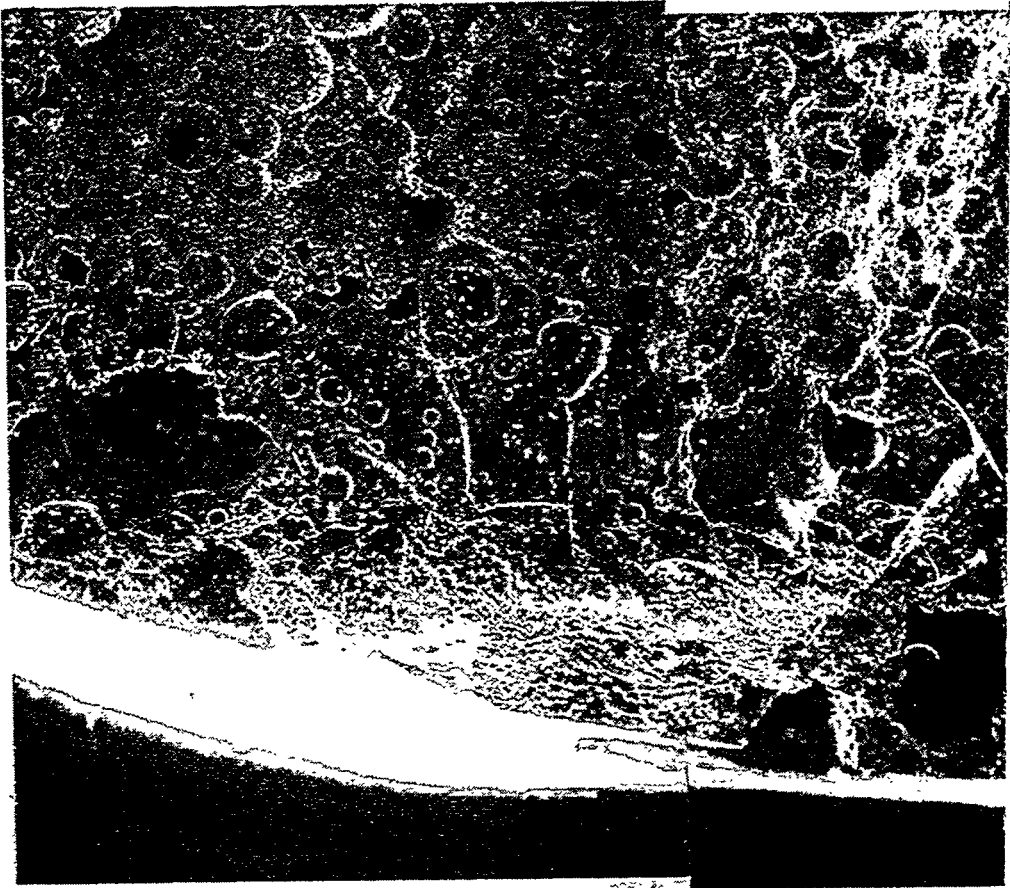


Figure 3-8b: Higher Magnification Of The Glass And Bubble Formations That Resulted Along The Alkali-Exposed NBSN + 8 Weight Percent M6017AE Matrix



Figure 3-9: Cross-Sectioned Alkali-Exposed NBSN + 12 Weight Percent M6017AE Matrix



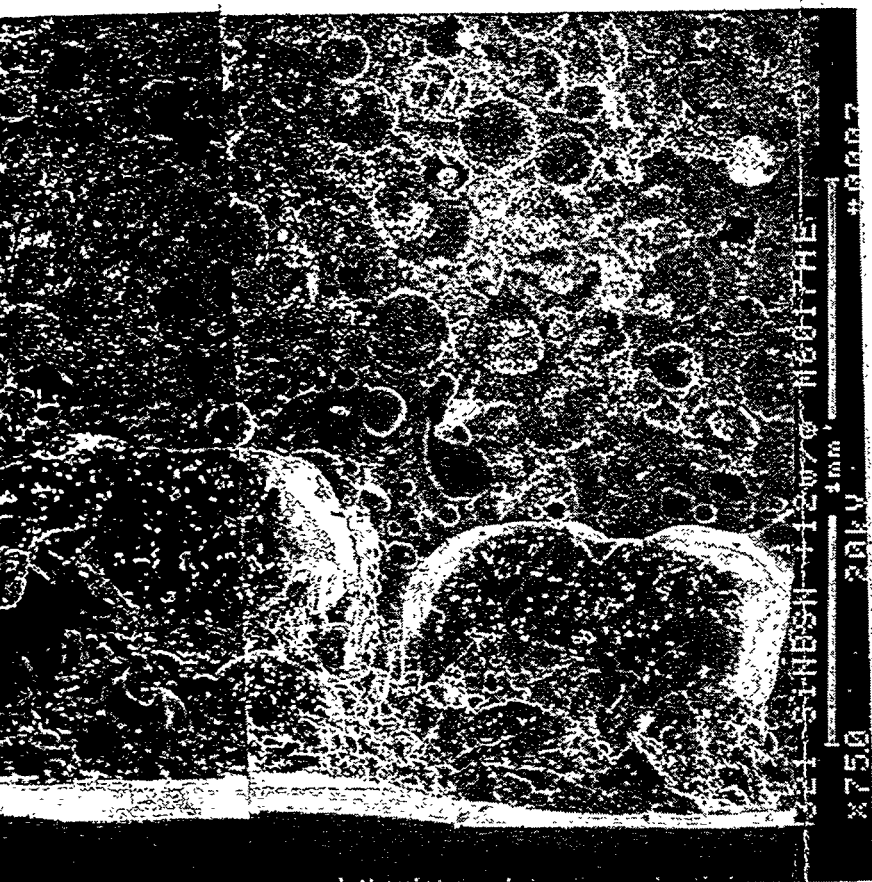


Figure 3-10: Micrograph Montage Illustrating The Glass/Matrix Interface That Formed Along The Outer Surface Of The NBSN + 12 Weight Percent M6017AE Matrix After 92 Hours Of Exposure at 870°C (1600°F) To Equilibrium Gas Phase Concentrations Of Sodium Chloride

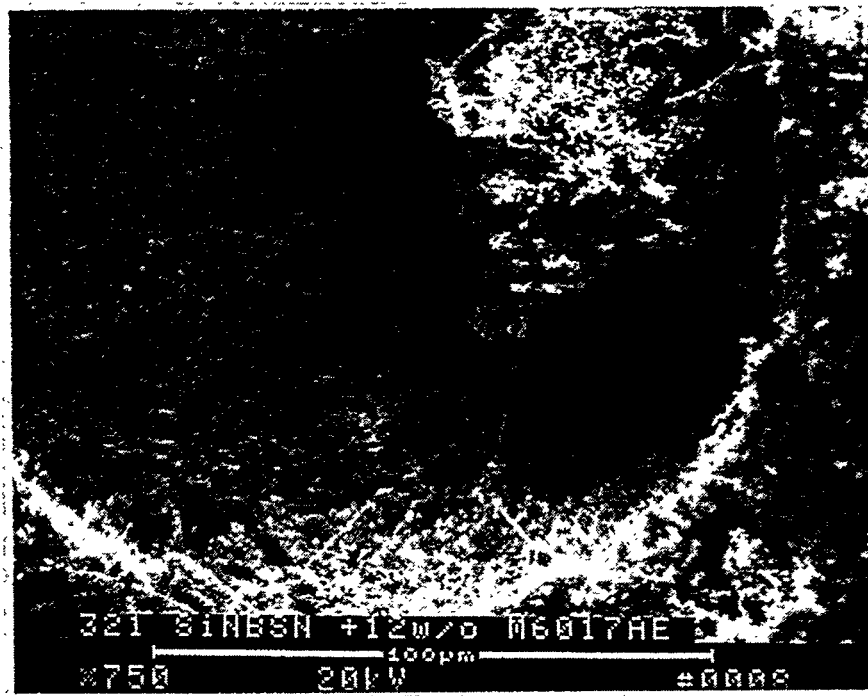


Figure 3-11: Morphology Of The NBSN + 12 Weight Percent M6017AE Matrix At The Center Of The Cross-Sectioned Alkali-Exposed Sample

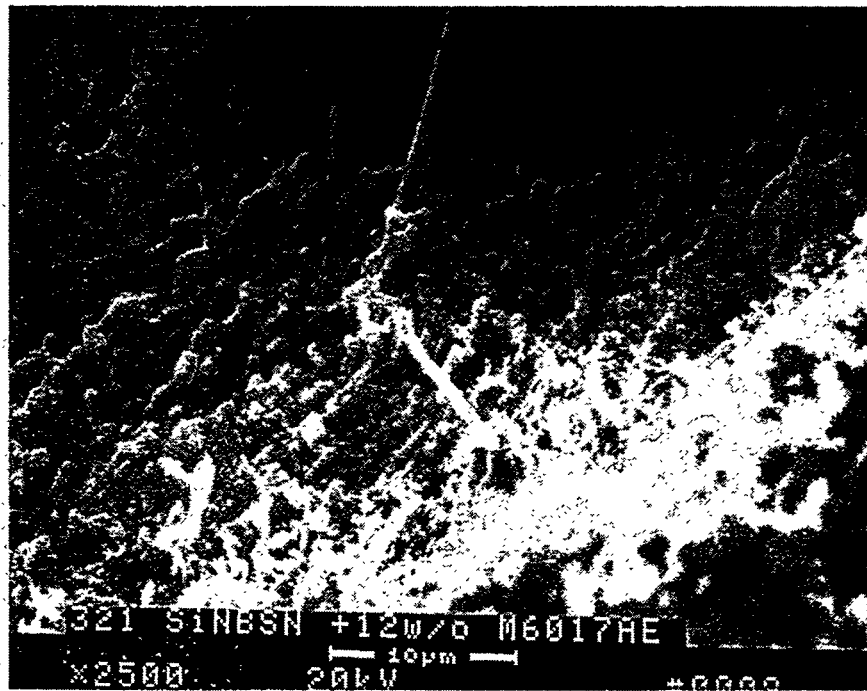


Figure 3-12: Higher Magnification Micrograph Of The Pore Cavity Surface At The Center Of The Cross-Section NBSN + 12 Weight Percent M6017AE Matrix

Comments And Summary

- Since gold was utilized to coat the alkali-exposed NBSN materials in order to produce high quality micrographs, the reported atomic percent concentrations should be viewed as qualitative, since gold masks or reduces the concentrations of the light elements (including oxygen and sodium).
- The qualitative atomic compositions show the potential for accelerated oxidation in the presence of high gas phase alkali concentrations
- Reaction of the various materials with gas phase alkali in a flow-over mode is virtually limited to the outer periphery of the NBSN filter matrices.
- The NBSN + M6017AE matrices have a high potential to sorb alkali. This is similar to the response of alternate nonoxide ceramic filter materials that have been tested at Westinghouse. Low concentrations of chlorine were also sorbed via the NBSN matrix during high temperature exposure to the gas phase sodium chloride-containing environment.
- Calcium was detected within the NBSN matrix, and is perhaps the result of the Dualite microballoon calcium carbonate sizing described earlier. The presence of iron may be a result of the manufacturing process, or may be an artifact of contamination.

3.3.2 Gas Phase Alkali Corrosion of NBSiC and NBSN

Sections of the following discs were also subjected to high temperature, static air, flow-over, corrosion testing:

- NBSiC + ~14 weight percent M6017AE (Batch No. 010595-1)
- NBSiC + ~14 weight percent M6017AE + M6033AE (Batch No. 010595-1)
- NBSN + ~10 weight percent M6017AE (Batch No. 01295-1).

After 100 hours of exposure at 870°C (1600°F) in a static air furnace which contained 5-10 grams of sodium chloride, glazing, holes and void formations were evident in the alkali-exposed NBSiC samples. Surface sealing and glazing resulted during exposure of the NBSN sample. Scanning electron microscopy/energy dispersive x-ray analyses (SEM/EDS) were conducted to identify the morphology and elemental composition of the high temperature, alkali-exposed NBSiC and NBSN materials.

NBSiC & ~14 Weight Percent M6017AE (Batch No. 010595-1)

The NBSiC + ~14 weight percent M6017AE (Batch No. 010595-1) matrix which was exposed for 100 hours at 870°C (1600°F) to gas phase sodium chloride developed a glaze along the outer

surface of the sample. Voids and hole formations were evident (Figure 3-13). As shown at higher magnification (Figure 3-14), the glaze extended ~100-300 μm into the matrix. The composition of the glaze shown in this region was identified by EDS to consists of 42.71% Si, 37.87% O, 15.75% Na, 2.01% Ca, and 1.66% Cl (atomic percent basis).¹⁰

Figure 3-15 illustrates the morphology of the NBSiC + ~14 weight percent M6017AE (Batch No. 010595-1) matrix near the center of the sample. Pores were detected in only localized area of the matrix. Although the glassy formation was not as pronounced, sorption of gas phase alkali into the interior of the matrix resulted (Figure 3-15, Area 1 (pore cavity)): 51.10% Na, 39.10% Cl, 5.57% O, 3.38% Si, 0.85% Ca; Area 2 (fractured ligament): Si, most likely as the nitride bonded SiC matrix).

NBSiC + ~14 Weight Percent M6017AE + M6033AE (Batch No. 010595-1)

The NBSiC + ~14 weight percent M6017AE + M6033AE (Batch No. 010595-1) matrix also developed a glaze along the outer surface of the sample that had been exposed for 100 hours at 870°C (1600°F) to the gas phase sodium chloride-containing environment. As shown in Figure 3-16, one surface of the alkali-exposed surface was uniformly glazed, while voids and pit formations were evident along the opposite surface.

The morphology of the cross-sectioned NBSiC + ~14 Weight Percent M6017AE + M6033AE (Batch No. 010595-1) matrix is shown at higher magnification in Figure 3-17. EDS analysis of the crystal formation shown in Area 1 indicated the presence of sodium chloride (i.e., 50.49% Na, 48.58% Cl, and 0.93% Si).

Figure 3-18 illustrates the morphology of the NBSiC + ~ 14 weight percent M6017AE + M6033AE (Batch No. 010595-1) matrix directly below the “melt-like” outer surface. The pore cavity walls appeared to be nearly entirely smooth, with dendritic “whisker-like” formations evident in many areas of the matrix. Figure 3-18, Area 1 is shown at higher magnification in Figure 3-19. The “melt-like” pore surface (Area 1) was identified to contain 52.24% Na, 42.34% Cl, 5.05% Si, and 0.37% Ca, while the fresh fractured ligament (Area 2) consisted of 72.96% Si, 14.82% Na, 10.14% Cl, and 2.08% Ca.

Similar features were evident in the center of the alkali-exposed NBSiC + ~14 weight percent M6017AE + M6033AE (Batch No. 010595-1) filter matrix. The mottled matrix shown in Area 1, Figure 3-20, was identified to contain 46.05% Si, 40.81% O, 10.20% Na, 1.90% Cl, and 1.05% Ca, while the “melt-like” pore cavity wall (similar to Area 2) consisted of 47.18% Si, 34.70% O, 13.70% Na, 2.76% Cl, and 1.67% Ca.

¹⁰ Gold was used to coat the samples for SEM/EDS analyses.

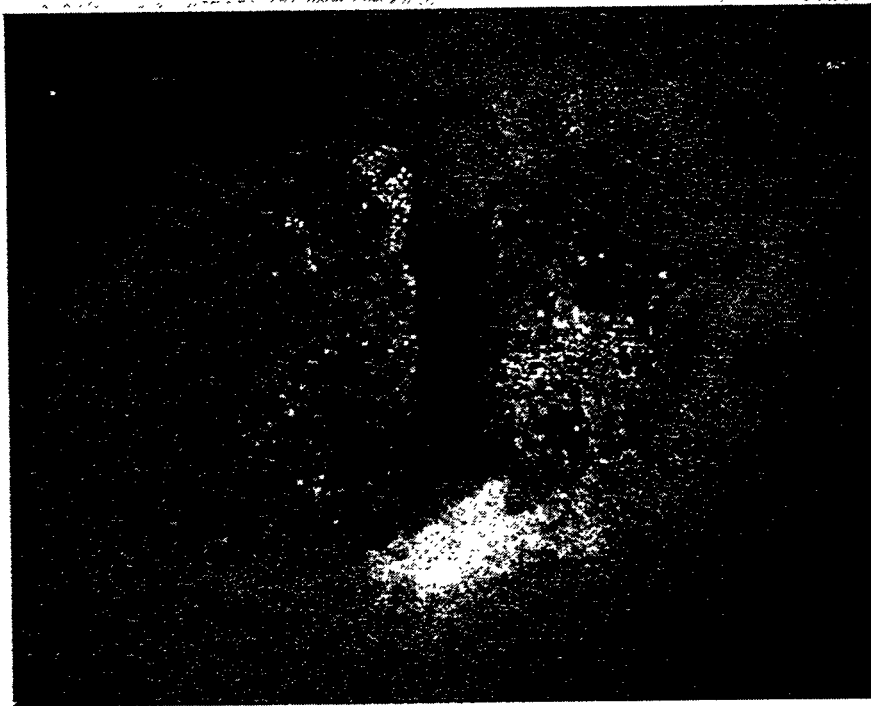


Figure 3-13: Alkali-Exposed NBSiC + ~14 Weight Percent M6017AE (Batch No. 010595-1) Matrix. The Top Photograph Illustrates The Surface Features Of The Exposed Sample Material. The Bottom Photograph Illustrates The Fresh Fractured Cross-Sectioned Matrix.

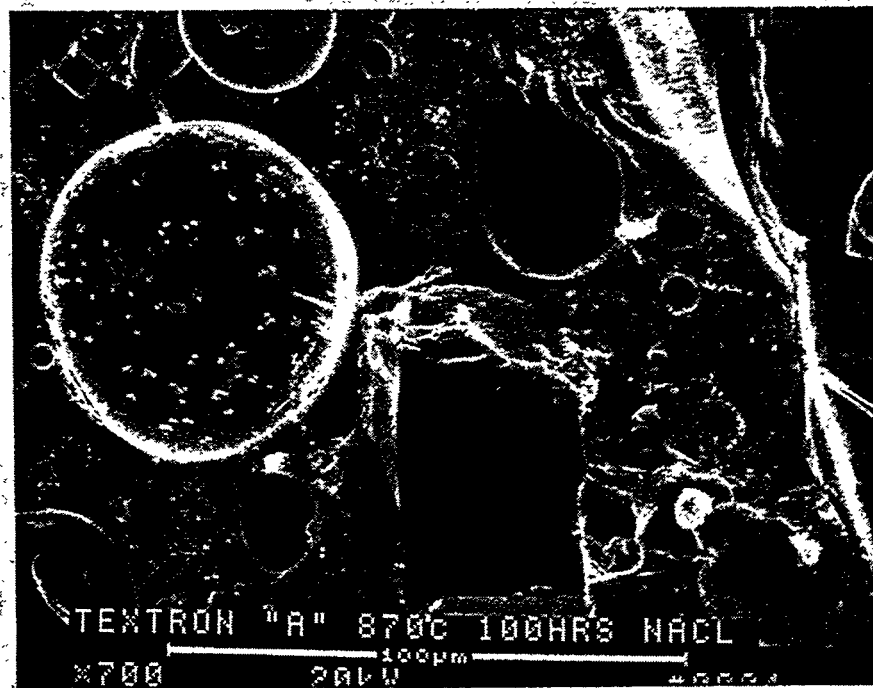
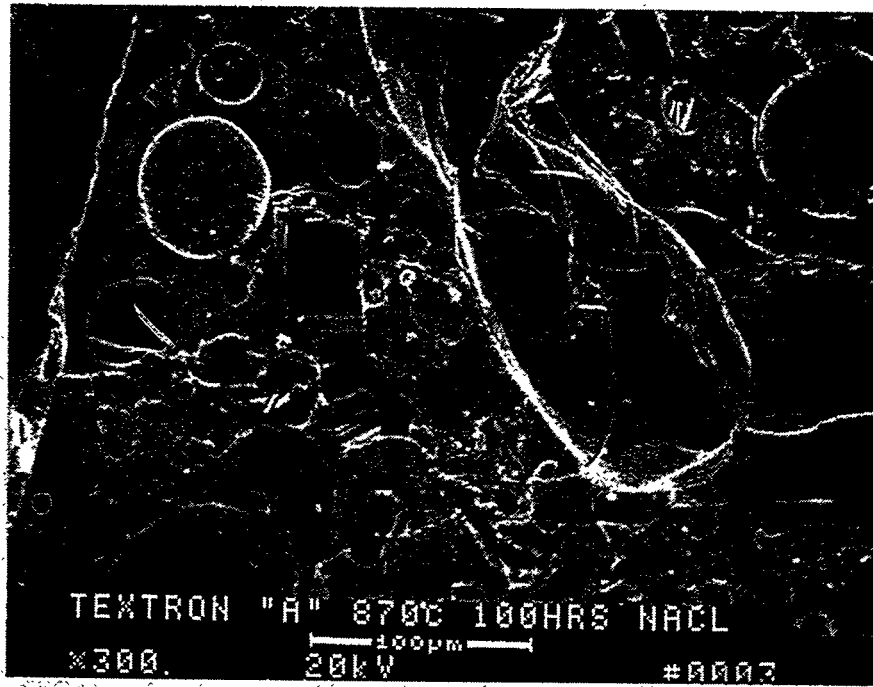


Figure 3-14: Morphology Of The Glazed Surface Which Resulted Along The Alkali-Exposed NBSiC + ~14 Weight Percent M6017AE (Batch No. 010595-1) Matrix

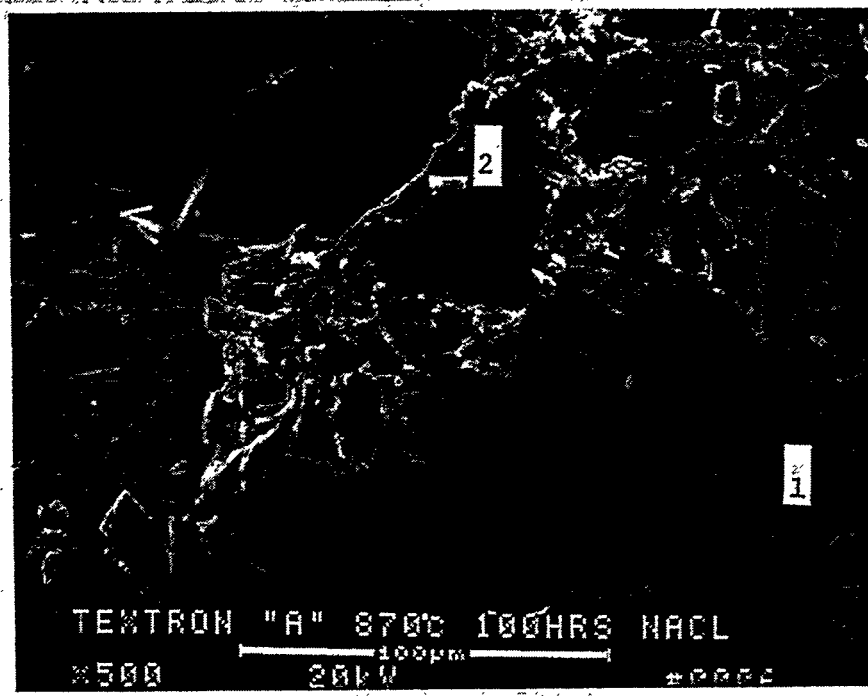
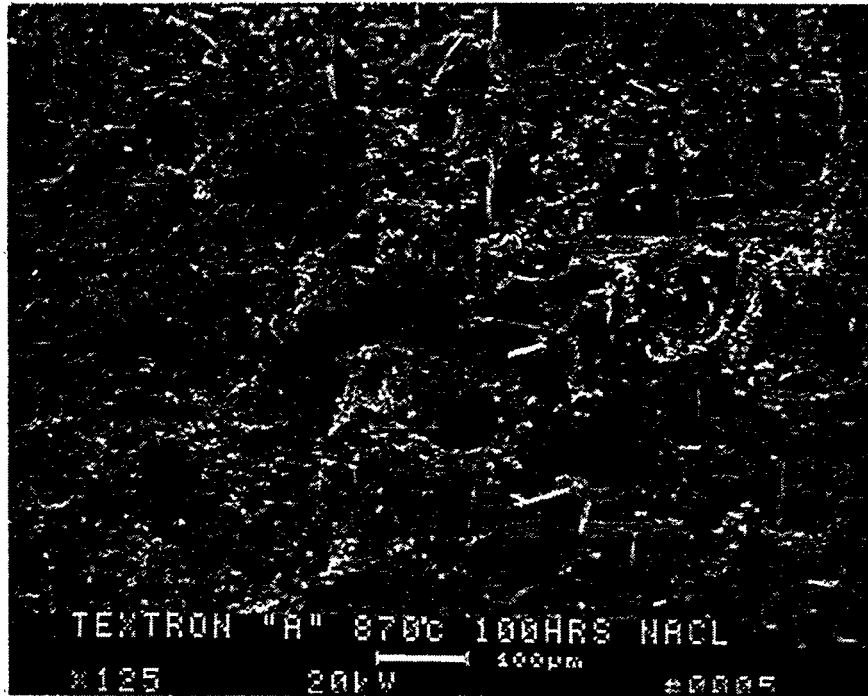


Figure 3- 15: Morphology Of the NBSiC + ~14 Weight Percent M6017AE (Batch No. 010595-1) Matrix Near The Center Of The Alkali-Exposed Sample

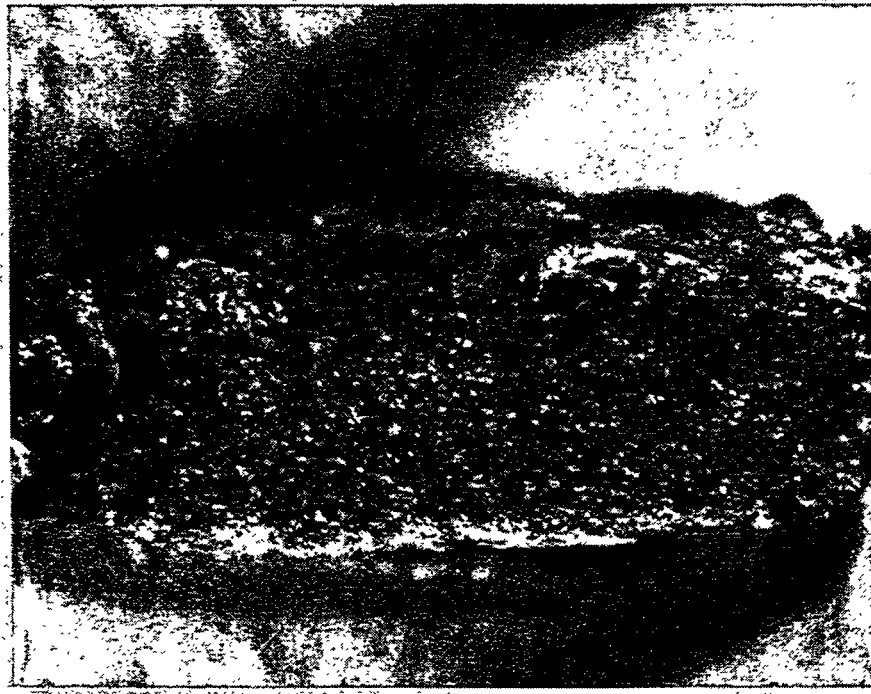
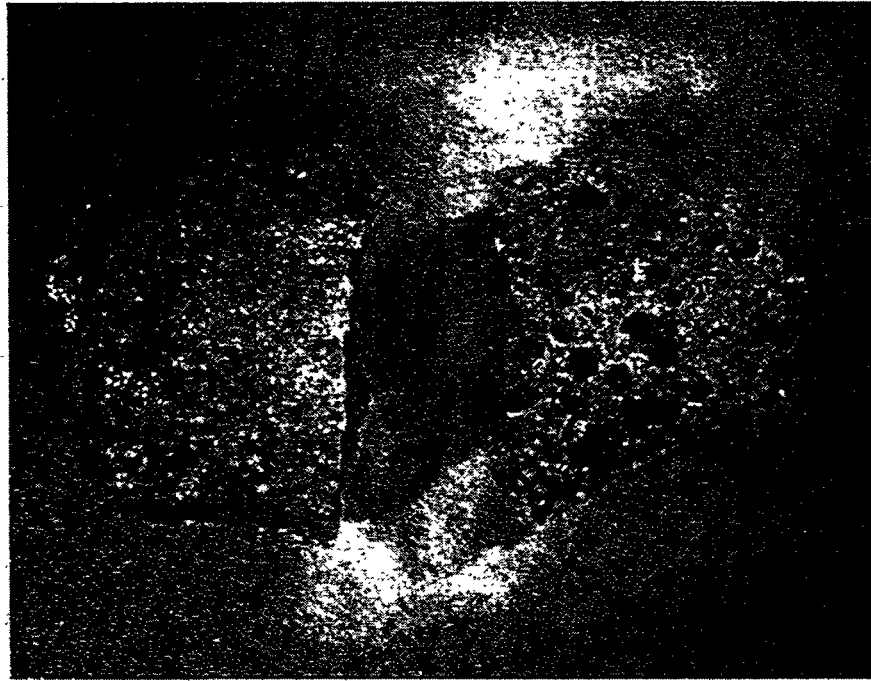


Figure 3-16: Alkali-Exposed NBSiC + ~14 Weight Percent M6017AE + M6033AE (Batch No. 010595-1) Matrix. The Top Photograph Illustrates The Surface Features Of The Exposed Sample Material. The Bottom Photograph Illustrates The Fresh Fractured Cross-Sectioned Matrix.

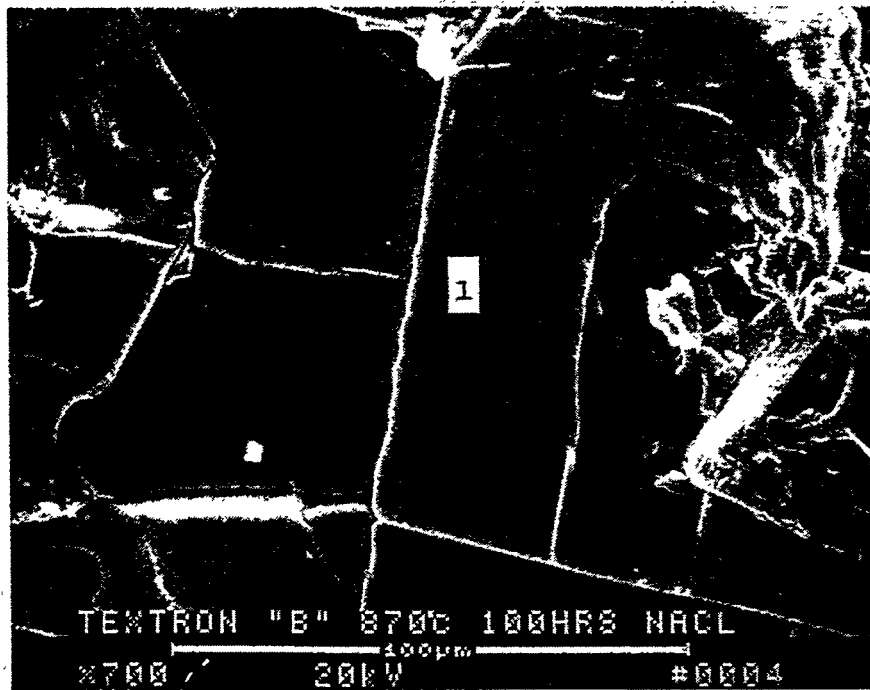
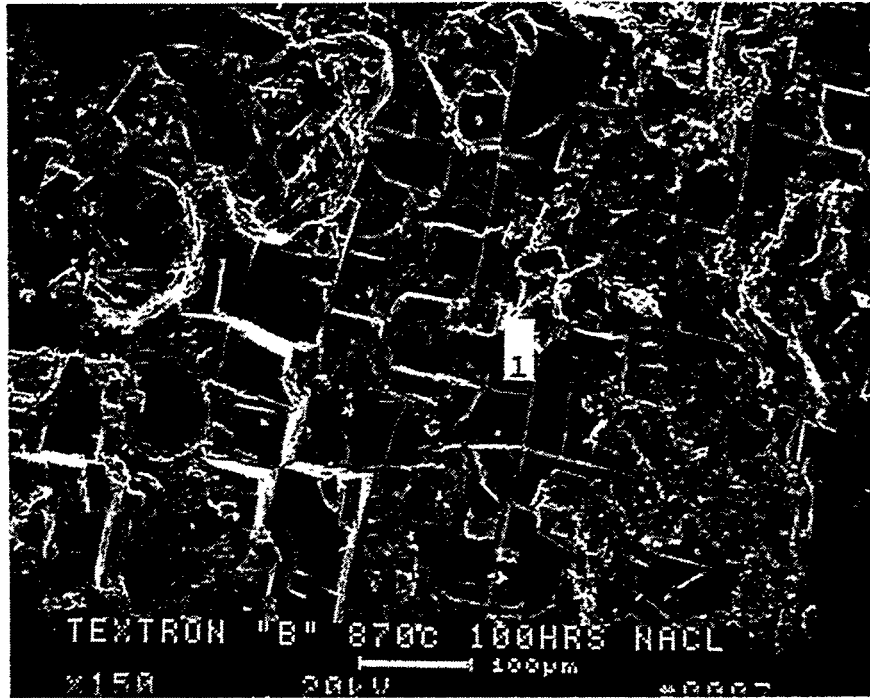


Figure 3-17: Morphology Of The "Melt-Like" Surface Glaze



Figure 3-18: Micrograph Montage Illustrating The Morphology Of The NBSiC +
~14 Weight Percent M6017AE + M6033AE (Batch No. 010595-1) Matrix Below
The Surface Glaze



Figure 3-19: Higher Magnification Micrograph Illustrating The Morphology Of The Pore Cavity Wall And Fresh Fractured Ligament In The Alkali-Exposed NBSiC + ~14 Weight Percent M6017AE + M6033AE (Batch No. 010595-1) Filter Matrix

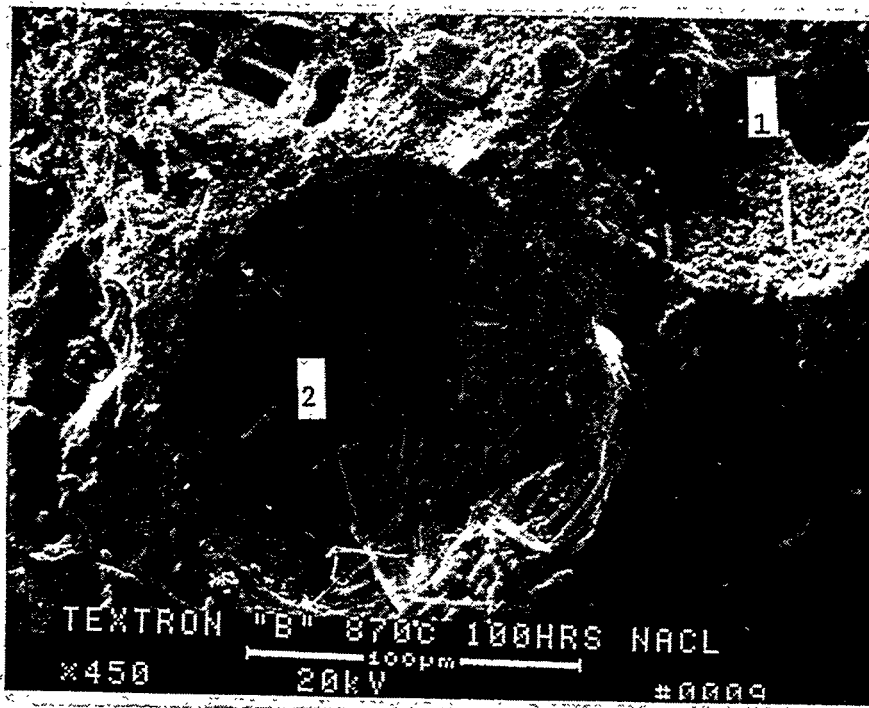
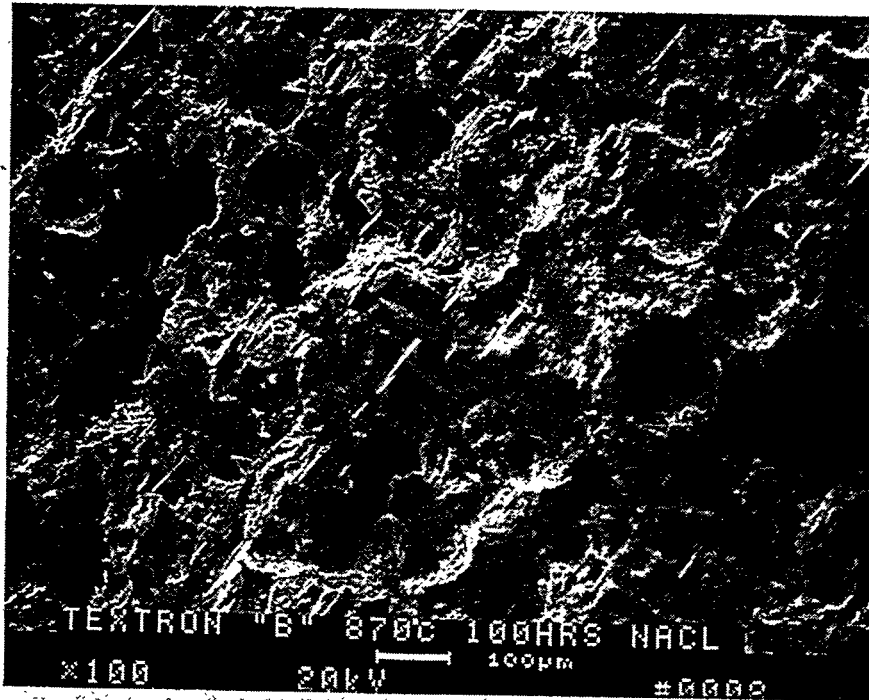


Figure 3-20: Morphology Of The Fresh Fractured NBSiC + ~14 Weight Percent M6017AE + M6033AE (Batch No. 010595-1) Filter Matrix At The Center Of The Alkali-Exposed Sample

NBSN + ~10 Weight Percent M6017AE (Batch No. 01295-1)

The NBSN + ~10 weight percent M6017AE (Batch No. 01295-1) filter matrix formed a significantly greater quantity of the "glassy" material along the surface of the sample after 100 hours of exposure at 870°C (1600°F) to the gas phase sodium chloride-containing environment (Figure 3-21), in comparison to the NBSiC materials. EDS analysis of a section of the transparent glaze that was easily removed from the alkali-exposed sample indicated the presence of 55.68% Cl and 44.32% Na.

The morphology of the fresh fractured alkali exposed NBSN + ~10 weight percent M6017AE (Batch No. 01295-1) filter matrix is shown at higher magnification in the micrographs provided in Figure 3-22. The matrix retained its original, highly porous nature below the ~75-125 µm glassy phase that fully encapsulated the filter sample.

The morphology of the pore cavities located directly below the glaze, close to the outer wall, is shown in Figure 3-23. These pores appeared to contain "melt-like" surface features, while the second and third pore layers had a granular or more mottled appearance, similar to the original filter matrix. The pore cavity close to the outer surface is shown at higher magnification in Figure 3-24. EDS analysis of the glazed, cross-sectioned pore surface (Area 1) identified the presence of 31.50% O, 29.13% Si, 24.68% Na, 13.69% Cl, and 1.00% Ca, while the fractured ligament (Area 2) contained 53.47% Na, 42.95% Cl, and 3.58% Si.

The fresh fractured matrix between the first and second pore layers is shown in Figure 3-25. Although the mottled morphology resembled the original material, it was identified to contain 83.39% Si, 9.84% Na, and 6.77% Cl.

The morphology of the 321 NBSN + ~10 weight percent M6017AE (Batch No. 01295-1) matrix at the center of the alkali-exposed sample is shown in 3-26. The pore cavities in this region were seen to contain "whisker-like" strands, as well as smooth surfaces. The "melt-like" pore cavity surfaces were identified by EDS to contain 48.99% Na, 41.11% Cl, and 9.89% Si, while the fresh fractured ligament contained 64.97% Si, 19.88% Cl, and 15.15% Na.

Summary

- Extensive glazing resulted along the surface of the NBSiC and NBSN materials that were exposed for 100 hours at 870°C (1600°F) to equilibrium concentrations of gas phase sodium chloride. Reaction(s) with the silicon in the filter matrix, followed by continued gas phase sorption and growth of sodium chloride resulted during the 100 hour static air exposure.
- Although glazing predominantly resulted along the surface of the NBSiC and NBSN filter materials, sorption of sodium and/or chloride was evident throughout the matrix.

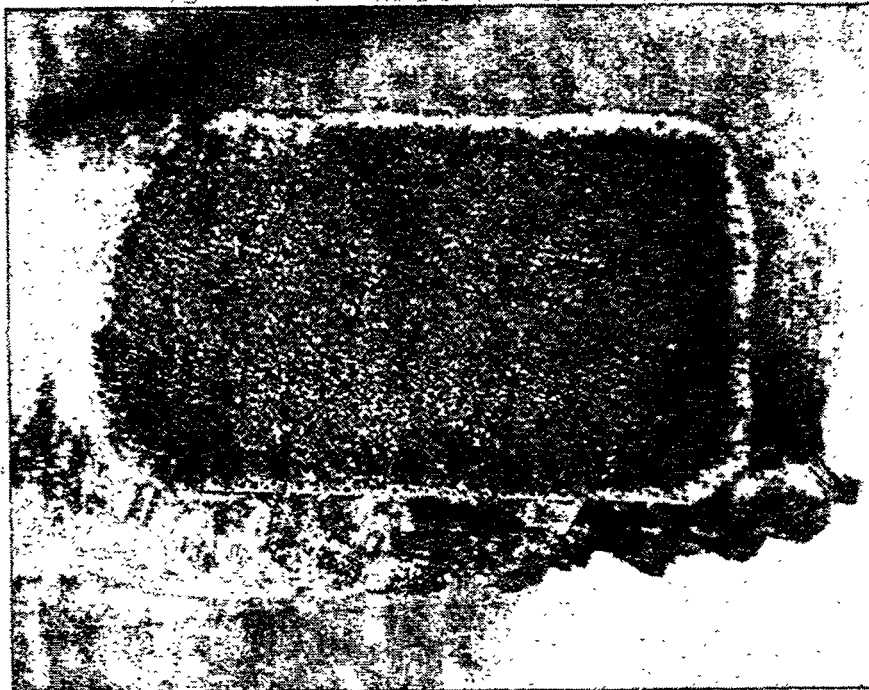


Figure 3-21: Alkali-Exposed NBSN + ~10 Weight Percent M6017AE (Batch No. 01295-1) Matrix. The Top Photograph Illustrates The Surface Features Of The Exposed Sample Material. The Bottom Photograph Illustrates The Fresh Fractured Cross-Sectioned Matrix

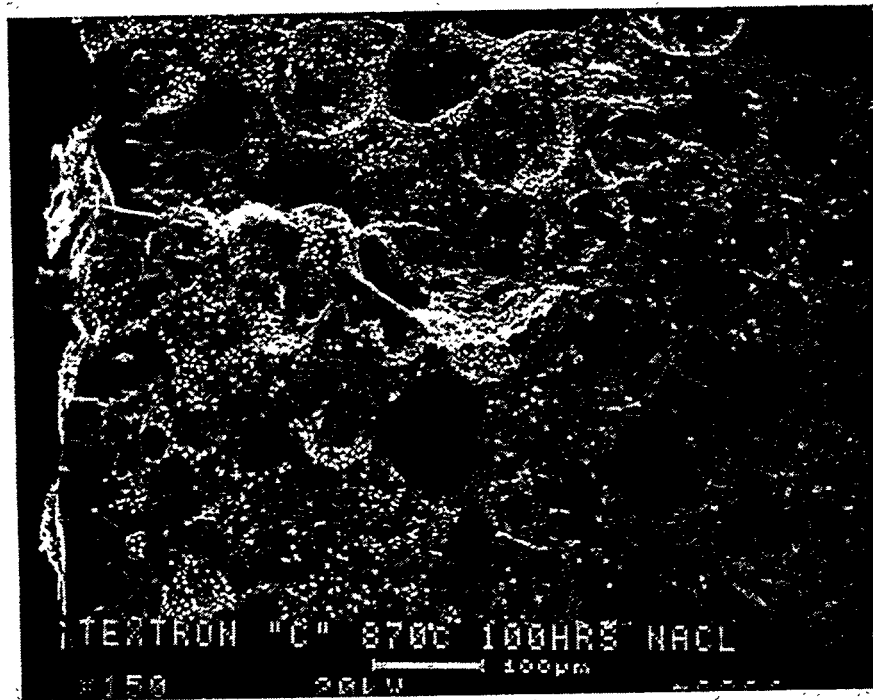
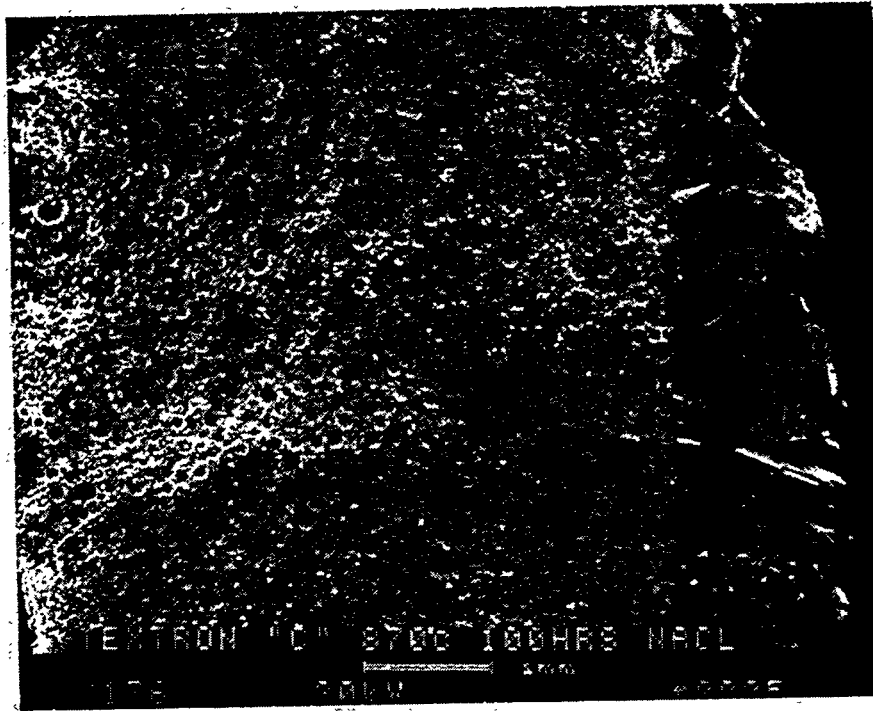


Figure 3-22: Morphology Of The Fresh Fractured Alkali-Exposed NBSN +~10 Weight Percent M6017AE (Batch No. 01295-1) Filter Matrix.

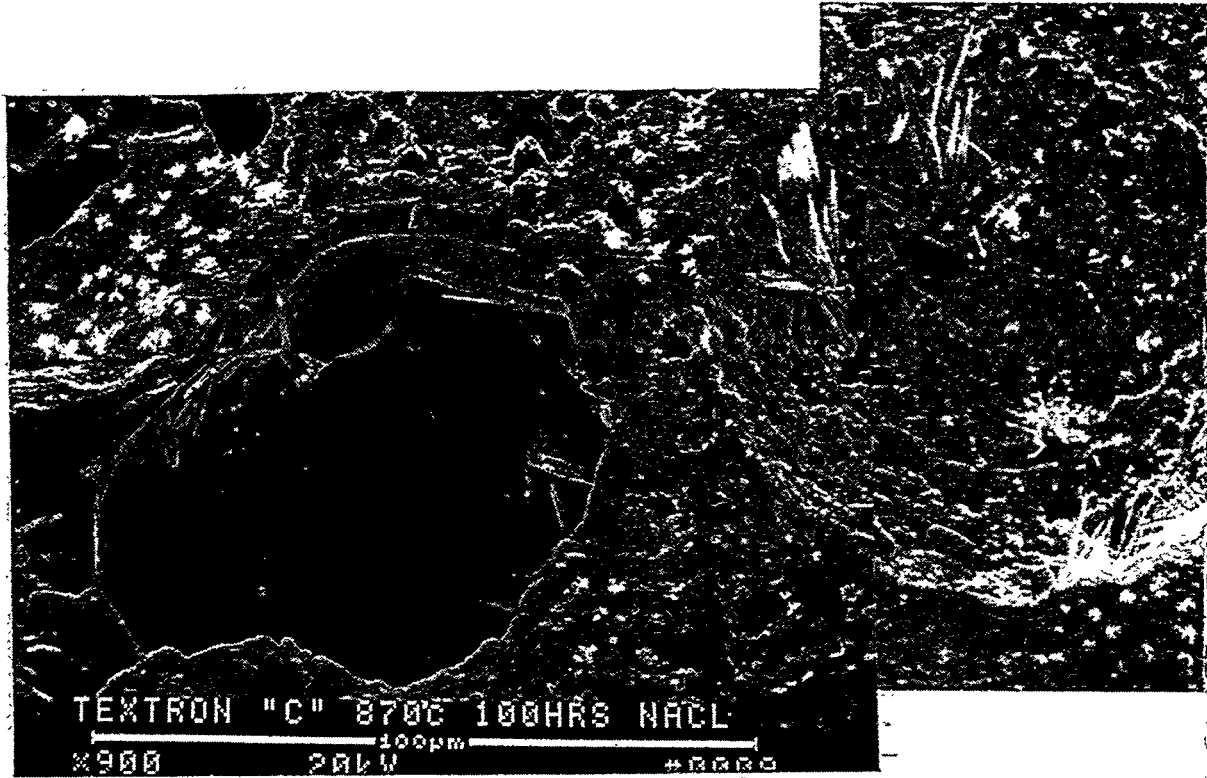
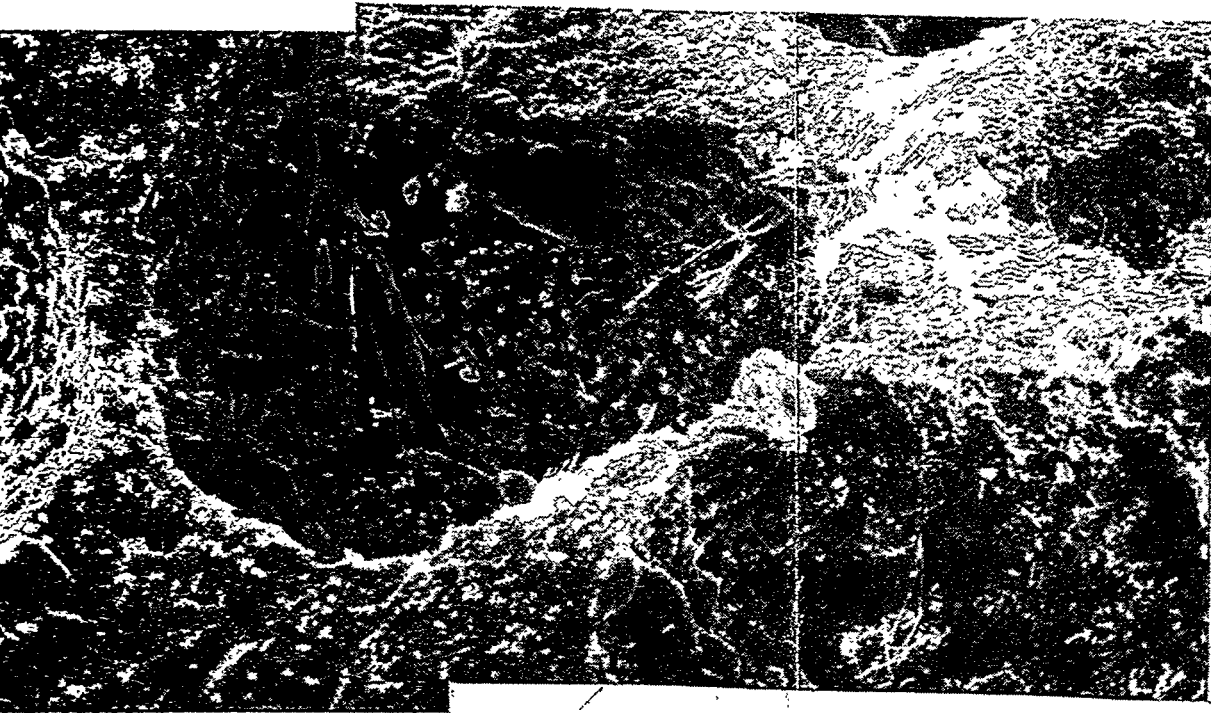


Figure 3-23: First Pore Cavities Below The M6017AE (Batch No. 01295-



Alkali-Exposed NBSN + ~10 Weight Percent
Filter Matrix



Figure 3-24: Morphology Of The First Pore Cavity and Fractured Ligament

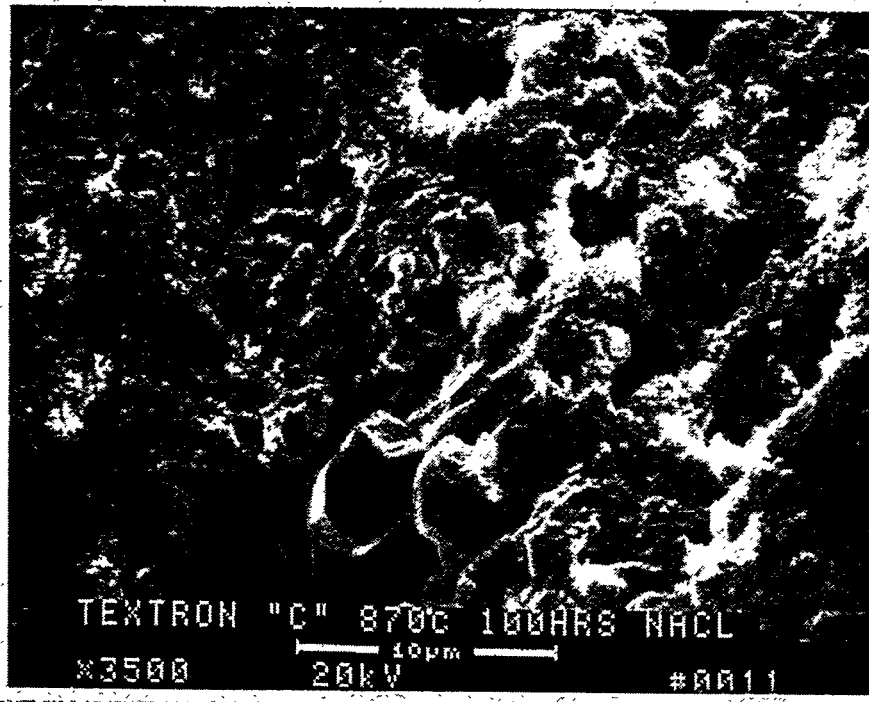


Figure 3-25: Morphology Of The Fresh Fractured Ligament Between The First And Second Pore Cavities In The Alkali-Exposed NBSN + ~10 Weight Percent M6017AE (Batch No. 01295-1) Filter Matrix

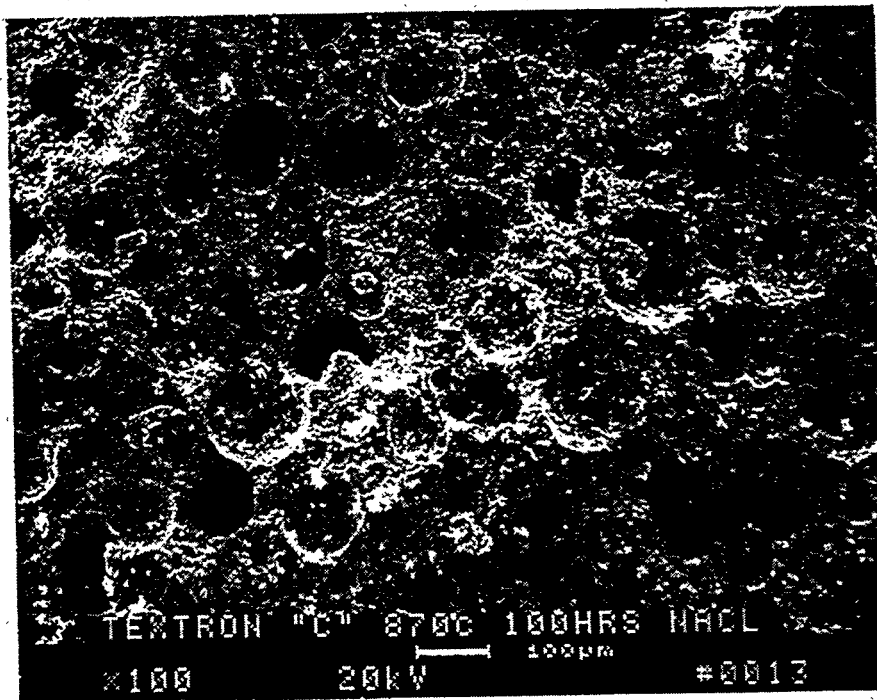


Figure 3-26: Morphology Of The Filter Matrix At The Center Of The Alkali-Exposed NBSN + ~10 Weight Percent M6017AE (Batch No. 01295-1) Sample

4.0 CONCLUSIONS AND RECOMMENDATIONS

Major conclusions from this work appear to be as follows:

Sedimentation-resistant and stable NBSiC and NBSN suspensions can be made over a wide range of particle sizes and relative fractions of Si powder, SiC powders and microballoons, so long as particulate surface chemistry is understood and controlled. Classical electrostatic and possibly polymeric stabilization techniques appear to both be effective at promoting the buildup of mutually-repulsive interparticle forces in NBSiC and NBSN suspensions, thereby allowing preparation of microballoon containing powder suspensions that can be slip cast or filament wound without undue sedimentation occurring.

For cases involving dispersions which contain significant fractions of large (greater than 100 micron (4×10^{-3} inches)) alpha SiC particulate and moderate (less than 10 weight percent) Dualite[®] loadings, we observed that shrinkage of the drying green body was less than a few percent, and also that the amount of binder that was required in order to make a robust preform was lessened. Relatively small additions of binders in aqueous NBSiC suspensions have also been seen to have a potent beneficial effect on green body strength. The same beneficial effects, however, were not seen for NBSiC or NBSN dispersions which were loaded with over 12 to 14 weight percent Dualite[®]. In these latter cases, it was quite difficult to prepare physically robust monolithic green bodies with any combination of starting materials. At microballoon loadings of 18-20 weight percent and higher, the as-cast matrix material was so weak that it could not reasonably be expected to successfully withstand routine composite forming operations like filament winding of candle filters.

Percolation threshold effects on permeability for microballoon loaded NBSiC and NBSN ceramic matrices seem evident. This sort of phenomenon is observed for many systems in which two or more constituents exist with very different intrinsic properties¹¹. In the cases considered here, the two species would be the matrix phase and the microballoon additions. At a microballoon loading level estimated to be in the vicinity of 12 weight percent, percolation in Dualite-loaded NBSiC matrices begins to take place, as these sorts of matrix compositions show gas flow permeabilities in line with program requirements.

Wet filament winding of NBSiC or NBSN CFCC hot gas filter preforms with Textron's SCS-6[™] CVD SiC monofilaments is technically feasible with suspensions containing less than 10-12% microballoons, but is essentially unworkable when using slurries exceeding these loadings. Part of the problem is certainly due to anisotropic drying stresses in the green matrix material, the result of rapid water absorption by the plaster mandrel material.

The ability to fabricate prototype-scale tubular CFCC filter components was not convincingly demonstrated on this Phase 1 development program. Significant amounts of additional dispersion formulation and CFCC tooling development efforts would be required in order to produce crack-

¹¹ Kirkpatrick, S., "Percolation and Conduction," *Reviews of Modern Physics*, Vol. 43, No. 4, 1973.

free porous green bodies using SCS-6 monofilaments and microballoon-loaded NBSiC or NBSN matrices as the constituent phases.

Processing trials with emulsion or polymer-based *in-situ* pore-forming methods suggest that both methods are worthy of further investigation for fabricating structurally robust and thermodynamically stable CFCC hot gas filters.

The purity of the emulsion-derived or polymer-derived pore forming additives is quite high, as either species appears to have no measurable effect on nitridation kinetics. This is to be contrasted with the outcome of the microballoon-based pore forming approach, where evidence was gathered to support the idea that the calcium carbonate sizing on Dualite[®] may have had a negative influence on nitridation (and eventually matrix strengthening behavior).

While the *in-situ* pore forming approach as a route for producing porous NBSiC or NBSN ceramic matrices in monolithic or CFCC materials appears technically promising, additional basic processing studies would be required in order to establish emulsifier/water ratios, polymer/water ratios, and mixing procedures that promote formation of stable bubble networks with the desired size distributions for filtration and program permeability requirements.

Both NBSiC and NBSN-based materials were subjected to high temperature exposure in an alkali-containing environment and experienced accelerated oxidation, resulting in the formation of a low melting temperature eutectic, sodium-enriched silicate phase. As a result, glazing and sealing of the surface, reduced porosity, and extensive bubble formations were evident along the outer surface of the static air-exposed materials. This response is typical of nonoxide filter materials during exposure to alkali-containing environments.

Although significant process-related difficulties had been encountered during attempts to fabricate SCS-6[™] monofilament reinforced CFCC filters, exposure of test coupons of different materials combinations in actual process slip streams (i.e., above the Westinghouse tubesheet at Pinon Pine or at Southern Company Services; in the Westinghouse material evaluation mini-vessel at Pinon Pine; etc.) may still be useful to pursue to provide a point of reference for the laboratory test results. In this manner, the response of the various materials to process gas environments that are directly generated at PFBC or IGCC systems can be evaluated. If the long-term response of the material in the field process gas environments shows negligible degradation, the manufacturing process at Textron should be reevaluated, since it can be modified, to fabricate porous ceramic hot gas filter elements.