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Nitride-Bonded Silicon Carbide Composite Filter

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TEXTRON Specialty Materials
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Lowell, MA 01851

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PB.5 Nitride-Bonded Silicon Carbide Composite Filter

CONTRACT INFORMATION

Contract Number	DE-AC21-92MC31213
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Other Funding Sources	
Contract Project Manager	Bruce N. Thomson
Principal Investigator	Stephen G. DiPietro
METC Project Manager	Theodore J. McMahon
Period of Performance	September 30, 1994 to September 30, 1997
Schedule and Milestones	

FY 95 Program Schedule

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                  O   N   D   J   F   M   A   M   J   J   A   S

Test Plan         -------------
Fabrication               -------------------------------------
Testing                        -----------------------------------------
Analysis                              ---------------------------------
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OBJECTIVES

The overall objective of the program is to develop and demonstrate an advanced hot gas filter, using ceramic composite technology, with enhanced durability to provide increased resistance to crack propagation and thermal fatigue, the primary modes of failure. More specifically, the objective is to modify a continuous fiber ceramic composite (CFCC) material which has already demonstrated a satisfactory level of durability in order to incorporate the required level of permeability and filtering efficiency. This material is silicon carbide (SiC) fiber reinforced nitride bonded silicon carbide (NB-SiC).

BACKGROUND INFORMATION

It is widely 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 systems. Significant gains have been made in recent years in demonstrating hot gas filtering media. Ceramic materials which are currently being used as cross flow filter materials include alumina/mullite, cordierite, aluminosilicate foam, cordierite-silicon nitride, and reaction bonded or sintered silicon nitride. Porous ceramic candle filters are made from clay bonded silicon carbide, alumina/mullite, clay bonded alumina, and recrystallized silicon carbide, as well as some developmental materials.

While monolithic ceramic hot gas filters are able to perform the filtration function, they do not provide adequate durability to withstand the intended operating environment for extended periods of time. In addition to the high temperature particle removal requirement, these filters are continuously subjected to thermal cycling through pulse gas cleaning or system transients during process operation and to mechanical stresses at attachment points.

An ideal solution is the application of ceramic composite technology to provide an acceptable level of material durability. The prospect of this approach is particularly attractive in light of the fact that in a separate program (Ref. 1) Textron is successfully fabricating closed end ceramic composite tubes similar in size and shape to the proposed candle filters. The composite material is nitride bonded silicon carbide (NB-SiC) with a silicon carbide reinforcing fiber. A high level of strength and toughness is provided by multidirectional fiber reinforcement.

Textron's methodology for fabricating continuous fiber ceramic composites via gas phase reaction synthesis is based on combining high performance ceramic reinforcements with silicon carbide and/or silicon nitride-containing ceramic matrices by gas phase reaction synthesis. This process, which converts metallic Si to silicon nitride via the reaction $3\ Si + 2\ N_2 = Si_3N_4$ is a net shape process that requires no pressure to effect matrix densification. Thus, complex ceramic composite parts can be made very rapidly with no restraint tooling. Additionally, no sintering aids are required to effect matrix densification, and thus matrix phase purity can be very high - consisting of mixtures which vary from combinations of $SiC + Si_3N_4$ to basically pure Si_3N_4 (NBSN). This is important to hot gas filters as there is a fair body of experimental evidence to suggest that the elevated temperature gaseous corrosion resistance of Si-based ceramics is strongly affected (if not dominated) by the presence of metallic impurities or sintering aids. Previous hot corrosion testing conducted by Blanchere et al(Ref 2) on silicon nitride and silicon carbide ceramics showed that high purity CVD silicon nitride exhibited the best and most predictable corrosion behavior from amongst a group of sintered and hot pressed SiC or silicon nitride materials. Given the high degree of phase purity that can be obtained with this fabrication process, ceramic matrices based on tailorable mixtures of Si_3N_4 + SiC are expected to perform well in the envisioned gaseous corrosion environments.

Using a four axis McClean-Anderson filament winder, SCS-6™ silicon carbide monofilament-reinforced, non-porous tubular components have been fabricated with integral flanges and closed ends that have been up to one meter in length and 15 cm in diameter. Total fabrication times (including preform winding, binder removal and gas phase nitridation) are on the order of two to three days. The nitrided ceramic matrices normally contain 12-20% porosity and have densities in the 2.5 - 2.8 g/cc range. No dimensional alteration of the part occurs after the CFCC preform is constructed and no repeated infiltration/densification cycles are required to achieve matrix densification. This technology forms the basis of the composite filter development activity.

PROJECT DESCRIPTION

The work is to be accomplished in two phases. The objective of the first phase is to develop and demonstrate at the coupon size level the feasibility of a hot gas filter material which will have acceptable performance and suitable manufacturing characteristics for fabricating hot gas filters. The objective of the second phase (optional) is to demonstrate the fabrication and performance of full size candle filters. This is to be accomplished by scaling up the phase one material processing approach to produce full scale filters and testing these to again validate acceptable performance. An additional part of this work will be to address quality control/quality assurance (QC/QA) issues, manufacturing cost and commercialization.

The successful accomplishment of these objectives will be demonstrated with ceramic hot gas filters which meet New Source Performance Standards and gas turbine inlet stream requirement limits of 10 ppm by weight, have a pressure drop of less than 5 inches of water at a face velocity of 10 feet per minute under standard temperature and pressure conditions, sufficient durability to resist pressure surges and thermal shock, and environmental resistance to steam and alkali. The fabrication of fifty (50) hot gas filters for pilot plant testing is an additional optional task.

During the first phase, the initial work has concentrated on establishing an acceptable level of permeability for the material. The current effort is directed toward the fabrication and testing of corrosion coupons.

RESULTS

The primary focus to date for the fabrication of fiber reinforced hot gas filter material is to intentionally incorporate porosity into the ceramic matrix of the slurry formulations used in the modified slip casting technique used in fabrication. The technique entails addition of microspheres or microballoons to existing slurry formulations. The microspheres are fugitive and thus are removed via a burnout step. Microballoons are an attractive means to intentionally incorporate porosity in the matrix of CFCC filter materials for the following technical and economic reasons:

- A very wide variety of microballoon sizes and compositions (i.e., acrylic, glass, phenolic, etc.) are available in large quantities at reasonable cost.

- Microballoon size distributions and volume loadings in the NB SiC or NBSN slurry mixtures can be tailored to achieve different combinations of matrix strength and gas permeability. This can be accomplished by controlling the packing density of balloon additions near or above the "percolation threshold," or the point at which microballoons just begin to contact each other.

- Microballoons can be chosen with very low residual ash contents after burnout, thus alleviating concerns about introducing contaminants that can have a deleterious effect on high temperature corrosion behavior.
- The rheological and handling characteristics of NBSiC or NBSN slurries loaded with microballoon additions are very similar to slurries which do not contain these foam-formers. This is very advantageous since Textron's proven methods for fabricating large non-porous CFCC components can directly be adapted to the manufacture of CFCC hot gas filter components.

For initial studies, nitride bonded silicon nitride (NBSN) and nitride bonded silicon carbide (NBSiC) samples were prepared which contained microballons but were unreinforced. The purpose in preparing and testing of these samples was to get insight into the range of composition which would provide acceptable permeability. The samples were cast as round disks 38mm diameter by approximately 5mm thick. Permeability tests were conducted at Westinghouse Electric Corporation Science and Technology Center.

Test results for the initial round of coupons are shown in Table 1. The range that is shown for each disc is based on testing the samples with both surfaces in the direction of the gas flow. This is generally done for two reasons; (1) to indicate whether an applied membrane has any effect on flow (which in this case, no membrane has been applied), (2) any minor chips, disc out-of-round, etc. could be easily detected when the disc is initially tested, and subsequently taken out of the holder and retested. Since the samples had variable thicknesses, the flow resistance measured was adjusted for thickness for comparison purposes (in-wg/fpm-in).

The coupon with 20 weight percent microballoons did not have sufficient structural integrity without fiber reinforcement and broke. The other samples had relatively high flow resistance, when compared to a target value of 1 in.-wg./fpm for a 0.25 inch thick disk of filter material, and a higher porosity material was therefore required.

Table 1. Flow Resistance of Initial Filter Materials

Composition and Weight % of Microballoons	Flow Resistance, in-wg/fpm	Thickness, in.	Adjusted Flow Resistance, in-wg/fpm-in
NBSN + ~ 8 w/o Disc 1	127.17-128.63	0.21	605.6-612.5
Disc 2	123.81-126.61	0.18	687.8-703.4
NBSN+~ 12 w/o Disc 1	(a)	0.185	
Disc 2	61.24-70.47	0.307	199.5-229.6
Disc 3	20.86-21.20	0.307	67.9-60.04
NBSiC+~ 20 w/o Disc 1	(b)		

(a) Chipped
(b) Broken

Two additional type samples were prepared; a nitride bonded silicon carbide (NBSiC) with 14 weight percent of microballoons and a pure silicon nitride (NBSN) with 10 weight percent microballoons.

The samples are identified as follows:

(A) NBSiC + approximately 14 w/o microballoons.
(B) NBSiC + approximately 14 w/o microballoons.

(C) NBSN + approximately 10 w/o microballoons.

The difference between A and B is that B has a bimodal distribution of microballoons.

The thickness of the four "A" filter discs ranged between 0.17 and 0.2 inches. One of the discs cracked apparently during delivery to Westinghouse, while the second disc had a section of material broken from its outer edge. Therefore, only two of the "A" discs were subjected to room temperature gas flow resistance measurements.

The thickness of the two "B" filter discs was approximately 0.17 inch. The one disc which remained intact was 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 2, variation exists in the resulting gas flow resistance measurements for the three filter sample types. Both NBSiC materials (i.e., discs "A" and "B") have a measured gas flow resistance of <1 in-wg/fpm which is within the Westinghouse tolerance for a 0.25 inch thick sample disc. In contrast, however, the NBSN discs ("C" samples) which remained fully intact, have a relatively high gas flow resistance in comparison to the targeted, as manufactured resistance measurements. While the NBSiC material with 14 weight percent of microballoons has an acceptable gas flow resistance, further effort is needed to introduce porosity and/or permeability into the NBSN filter disc series and to perform duplicate experiments to verify the previous results.

The scanning electron micrographs are presented in Figures 1 through 3, illustrating the cross-sectioned morphology of the NBSiC and NBSN filter materials. The NBSiC material (Figures 1 and 2) shows interconnected porosity, whereas the NBSN material (Figure 3) is slightly below this level. The lack of gross amounts of whiskers is also evident.

Table 2. Flow Resistance of Additional Filter Materials

Composition and Weight % of Microballoons	Flow Resistance in-wg/fpm	Thickness, in
NBSiC + ~ 14 w/o Disk 1 Disk 2	0.14 - 0.21 0.27 - 0.38	0.17 - 0.20
NBSiC + ~ 14 w/o	0.13 - 0.18	0.17
NBSN + ~ 10 w/o Disk 1 Disk 2 Disk 3	12.69 - 18.93 13.16 - 13.76 22.62 - 25.02	0.22 - 0.24

A second additional batch of unreinforced samples of nitride bonded silicon carbide (NBSiC) were prepared based on mixtures of microballoons and microcrystalline starch particulate with graded particle size distributions. The mixes contained four component pore former additions. These were chosen to maximize the packing efficiency of the pore formers in order to achieve the required permeability at the lowest possible weight fraction of the pore former. The purpose was to get the highest possible solids loading to minimize shrinkage during drying, and therefore the tendency towards cracking during the casting process.

Two general formulations were prepared; one at 14 weight percent pore formers and one at 16 weight percent. Both used a distribution of pore formers as shown in Table 3. The disks of these materials are being tested at Westinghouse for permeability and will be reported at a later date.

Table 3. Pore Former Additions

Component Description	Weight Percent
Latex microballoon with max size of 70 microns	42
Latex microballoon with max size of 40 microns	24
Latex microballoons with max size of 20-25 microns	13
Microcrystalline, roughly spherical shaped starch additive with a median size of approximately 8-10 microns	21

In addition to the tests on unreinforced material, experiments were initiated to incorporate fiber reinforcement into the filter. Various approaches were tried to make flat panels which could be subsequently machined to produce flat disks for permeability, filtering efficiency and corrosion testing. These included both casting and pressure casting of the matrix into collimated arrays of SCS-6 fiber reinforcement. These attempts were only partially successful because it was difficult to achieve uniform and complete filling of the fiber array with matrix material. Since the hot gas filter configuration is tubular and the only purpose in making flat panels was to produce coupons, the decision was made to proceed directly to the fabrication of cylindrical shapes representative of candle filters. These shapes are being made by a wet filament winding approach which has proven successful in the fabrication of non-porous tubes and will be tested at Westinghouse as minicandles or sections of minicandles for permeability, filtering efficiency and corrosion behavior.

FUTURE WORK

Future testing will validate that the material will have acceptable performance under the intended power plant operating conditions and suitable manufacturing characteristics for fabricating hot gas filters. This includes the testing of minicandles or sections of minicandles for permeability, filtering efficiency and corrosion behavior. The demonstration of the fabrication and testing of full scale hot gas filters will take place during the second phase of the work. The fabrication of fifty (50) hot gas filters for pilot plant testing is an additional optional task.

REFERENCES

1. Continuous Fiber Ceramic Composites Program with the Department of Energy; Cooperative Agreement #DE-FC02-92 CE 41001.

2. Blanchere, etal, High Temperature Corrosion of Ceramics; (Noyes Data Corp.; 1989)

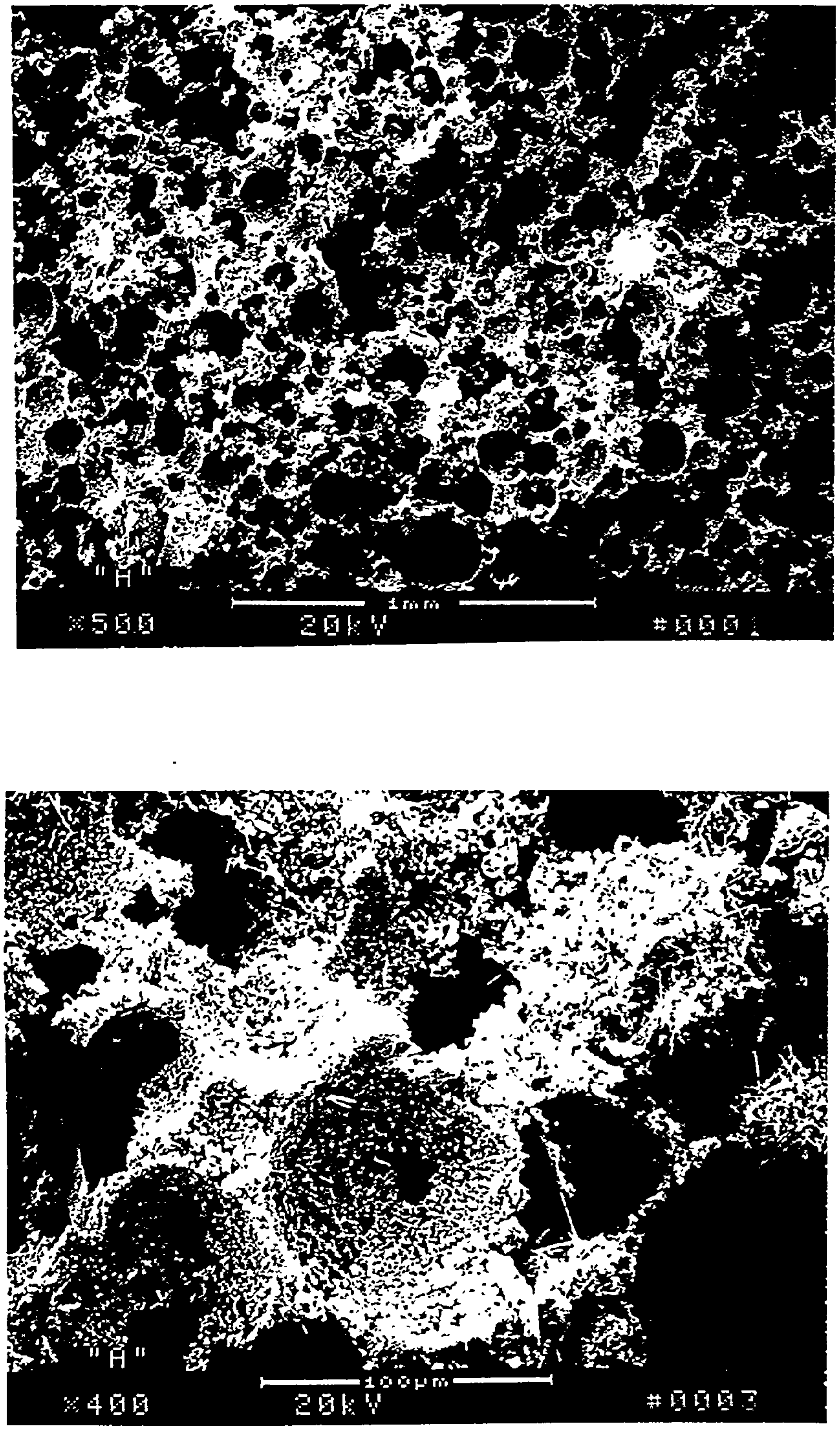

Figure 1. NBSiC + ~ 14 w/o Microballoons

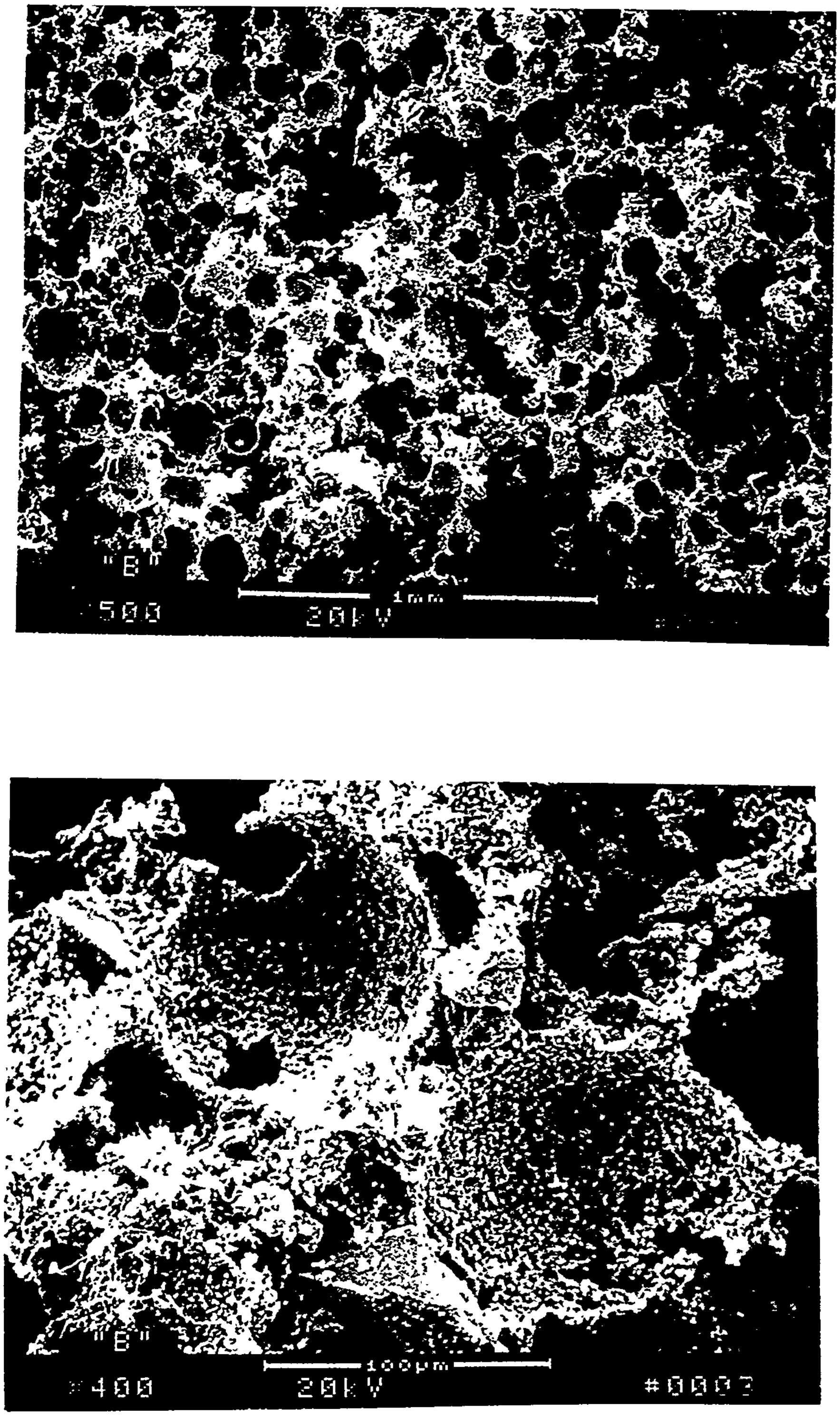

Figure 2. NBSiC + ~ 14 w/o Bimodel Distribution of Microballoons

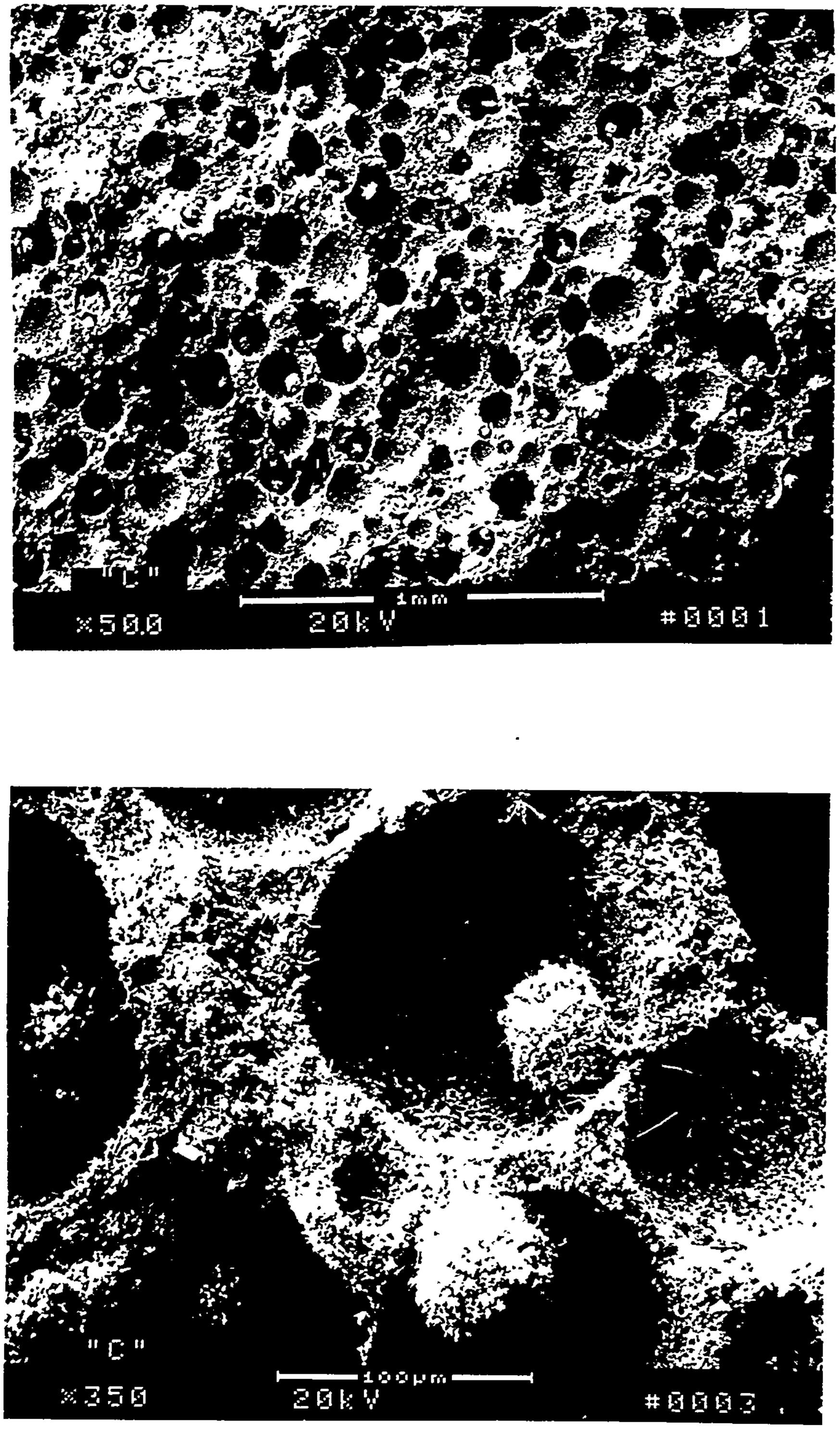

Figure 3. 321 RBSN + ~ 10 w/o Microballoons