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Development of a Monolithic Ceramic Cross Flow Filter

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DISCLAIMER

PB.3 Development of a Monolithic Ceramic Cross Flow Filter

CONTRACT INFORMATION

Contract Number	DE-FG02-94ER18718
Contractor	Blasch Precision Ceramics, Inc. 580 Broadway Albany, NY 12204 (518)436-1263 (telephone) (518)436-0098 (telefax)
Other Funding Sources	None
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Period of Performance	August 15, 1994 to March 10, 1995
Schedule	Phase I Completed March 10, 1995 Awaiting Approval of Phase II

OBJECTIVES

The objective of this SBIR Phase I project was to demonstrate feasibility of forming a permeable, porous ceramic material using the unique and proprietary Blasch process, to meet the permeability and other material property requirements of cross flow filters. This objective was accomplished by: (1) using this process to form and fire matrices of over 100 ceramic test compositions into test specimens, and (2) performing appropriate testing to determine feasibility for cross flow filter application.

The specific criteria considered in this project to determine if a ceramic composition is feasible for cross flow filters include:

(a) Composition must be able to be formed and fired successfully using the unique and proprietary Blasch process.

(b) Permeability must meet Westinghouse's specifications for cross flow filters. This was determined to be 1 iwg/fpm maximum by Westinghouse.

(c) Apparent porosity, according to Westinghouse, should be approximately 40-50 %.

(d) Strength property requirements, although unknown, were arbitrarily targeted at minimum of 1000 psi for both room temperature and hot (870° C) modulus of rupture (MOR).

(e) Bonding phase preferably should be a non-glassy type that will be less likely to be attacked by alkali or steam in a hot gas stream environment.

(f) Pore size, according to Westinghouse experience, should be in the approximate range of 20 microns for best filtration and to eliminate the need for a membrane filtration layer.

BACKGROUND INFORMATION

High temperature, high pressure (HTHP) particulate control is required to protect turbine equipment and to meet environmental stack emissions standards in coal-fueled power systems. Ceramic cross flow filters were designed with a high surface area per unit volume to be a highly efficient means to remove particulates from these hot gas streams. Previously developed cross flow filters were segmented; several thin porous ceramic plates with channels formed by ribbed sections were stacked atop each other and fired, to form a "monolithic filter". This filter was not truly monolithic, however, as it experienced seam delamination while in service at operating temperature. This delamination of cross flow filters degraded the filter system's performance allowing particulates in the hot gas stream to by-pass the filter. With a sufficient amount of delamination of filter elements in a system, this leakage of particulates could lead to very costly (and perhaps catastrophic) downstream turbine damage, and failure to meet environmental stack emission standards.

Therefore, an important need has been identified for a one-piece monolithic ceramic cross flow filter, rather than the present built-up segmented filter. Current ceramic technology has proved incapable of forming a complex one-piece shape such as this, with an acceptable, permeable, porous ceramic material. Blasch Precision Ceramics has a unique proprietary injection mold ceramic forming process that has been used for many years to commercially produce complex one-piece monolithic shapes, but of a non-permeable nature.

In this SBIR Phase I project, feasibility was to be demonstrated for the development of a permeable, porous ceramic material formed using this unique Blasch process, targeted to meet the permeability and other material property requirements of cross flow filters. With this

material and process, a more reliable, effective monolithic cross flow filter could evolve in Phases II and III.

PROJECT DESCRIPTION

Work Plan Overview

The project objective, as stated earlier, was to demonstrate feasibility of forming a permeable, porous ceramic material using the unique and proprietary Blasch process, to meet the permeability and other material property requirements of cross flow filters. To accomplish this, the following tasks were performed:

(a) Molds were designed and fabricated for the forming of ceramic disks and plates to be used for Westinghouse disk permeability and hot modulus of rupture (MOR) testing. Molds already existed for the forming of test bars and cubes for room temperature MOR and cube permeability.

(b) A test matrix was formulated of different ceramic compositions of various particle packing schemes, different fillers (pore formers) and amounts of fillers, and firing cycles. Ceramic disks, bars, and cubes were formed and fired of each composition, using the Blasch forming process.

(c) Measurements of room temperature MOR, apparent porosity, and cube permeability were made at Blasch on the compositions in this test matrix.

(d) Measurements of disk permeability were made at Westinghouse on selected compositions in this matrix.

(e) Using earlier obtained data as a basis, adjustments were made to ceramic compositions and firing schedules to form a second refined test matrix. Test bars, cubes, plates, and disks were made and fired.

(f) Measurements of room temperature MOR, apparent porosity, and cube permeability were made at Blasch on the compositions in this refined test matrix.

(g) Measurements of disk permeability and hot MOR were made at Westinghouse on selected compositions in this refined matrix. Additionally, x-ray diffraction, scanning electron microscopic analysis, and mercury porosimetry analysis were performed by other labs on selected compositions.

General Procedure

Matrices of various ceramic compositions were devised and each composition was formed into a full set of test specimens: bars (five 1″x1″x7.5″size), ceramic cubes (three 2″cubes), and disks (four 1.5″dia x 0.25″th).

The process used for producing these test specimens was the lab scale version of the unique and proprietary Blasch process, which includes: batching/weighing, wet batch mixing, injection of ceramic slurry into molds, solidification, removal of mold, drying, and firing.

The variables in these matrices included:

*numerous particle packing schemes
*maximum particle sizes from 20 mesh down to 325 mesh
*alumina-silica compositions
*alumina-silica-silicon carbide compositions
*various types fiber pore former additions
*ground walnut shells pore former additions
*fumed silica addition
*various rheology enhancement

additions
*firing temperatures of 2700°F or 3000°F

A total of over 100 ceramic compositions were made using these variables as the basis.

Testing

Each composition in these matrices was tested at Blasch as follows: room temperature modulus of rupture, apparent porosity, bulk density, and permeability. Based on the results of these initial tests, several of the ceramic compositions were submitted for further permeability testing by Westinghouse. Some promising compositions were then selected for further testing (XRD phase determination, mercury porosimetry, scanning electron microscopy to illustrate physical structure, and hot modulus of rupture at 870°C).

Initial testing was done by Blasch Precision Ceramics. Room temperature MOR was done using hydraulic force and a 3 point fixture with a 4" span, on test bars formed to 1"x1"x7.5". Apparent porosity was performed by weighing and measuring a ceramic piece, filling the pores with water, and then re-weighing the saturated specimen. Bulk density was determined by measurement of dimensions and weighing of ceramic bars. Permeability was done by ASTM standard method C577 "Standard Test Method for Permeability of Refractories". In this method, flow of nitrogen gas is measured through 2" ceramic cubes while controlling the pressure differential with a mercury or water filled manometer. The readings were translated to centidarcy units, as is explained in the ASTM standard:

$$K = (MQL/ A\Delta P) \times 100$$

where:

K = permeability, centidarcies
M = gas viscosity, cP
Q = flow rate, cm^3/s
L = sample length, cm
A = sample area, cm^2
ΔP = absolute pressure drop across the sample, atm

On chosen ceramic compositions, a second tier of permeability testing was completed on the 1.5"dia x 0.25" disks by Westinghouse. Westinghouse determines permeability by the measurement of flow of nitrogen gas through the ceramic disk at specified pressure differentials, to yield a reading in units "iwg/fpm" (inches water gage /feet per minute).

Based upon the results of this testing, ceramic compositions were chosen for XRD phase analysis, mercury porosimetry, SEM (scanning electron microscope) microstructure photos, and hot MOR testing. The XRD analyses and SEM photos were done by Washington Mills Electro Minerals in Niagara Falls, NY. Mercury porosimetry was performed by Micromeretics in Norcross, GA, using their AutoPore II 9220 equipment. Westinghouse did the hot MOR tests at 870°C, using a 4 point fixture with a 1.57" span on test bars cut to 0.25"wide x 0.08"thick cross-section.

Next, ceramic disk test specimens were made from selected ceramic compositions (independently from the original specimens) so Westinghouse could determine if the earlier permeability measurements were repeatable with new batches of specimens.

RESULTS

Discussion of Results

The particle packing scheme and top end

particle size that yielded both acceptable room temperature MOR strength and permeability was 100/200 mesh top end particle size, with a particle sizing gap in the compostion. The coarser (>100/200 mesh) top end particle sizes yielded lower than acceptable room temperature (R.T.) MOR strength (<1000 psi). Finer (<100/200 mesh) top end particle sizes all yielded high room temperature MOR strengths (>2000 psi), but had unacceptably low permeabilities (<200 centidarcies). In general, mixes without a particle size gap resulted in higher R.T. MOR strengths, with unacceptably lower permeabilities. Table 1 indicates mix numbers and properties of the "selected five compositions" in these matrices (out of over 100 compositions total), based on meeting these requirements for R.T. MOR strength and permeability as measured at Blasch Precision Ceramics. All of these "selected compositions" had top end particle size of 100/200 mesh with similar particle sizing gaps, and yielded the targeted results for R.T. MOR of >1000 psi and permeability of >200 centidarcies.

The "selected compositions" designated in Table 1 are all combinations of alumina and silica based raw materials, plus pore forming additives.

The substitution of 20 wt% SiC grain for similar size tabular alumina in the particle size range of 20/100 mesh was tried in ten compositions. Some of these compositions yielded adequate R.T. MOR strength, but none had acceptable permeability. It was noteworthy that, when fired @ 3000°F, these compositions glazed, apparently due to oxidation of the SiC. Further work would be required to determine if it possible to attain the needed strength and permeability with an alumina/SiC composite.

Variations of different pore forming additives were attempted in many of the compositions. Various fiber types of pore formers were tried: both organic and inorganic. Additionally, other pore forming additions were tried, such as ground walnut shells and fumed silica. Amounts and sizes of pore forming additives were varied, as well as use of combinations of the most promising candidates. Again, the objective was to attain both acceptable R.T. MOR strength and permeability with the composition. Several of the pore forming additives yielded acceptable permeability but unacceptable R.T. MOR strength, or vice versa. The ground walnut shells were used at a relatively high concentration (>15 wt%) to attain the needed permeability, but this caused the R.T. MOR strength to plummet unacceptably to below 600 psi. Fumed silica additions even in small amounts (0.5 wt%) had a very deleterious effect on R.T. MOR (result: <300 psi).

The pore formers that showed the most promise in these matrices were fibers. These were present in each of the "selected compositions" (Table 1) as combinations of different types of fibers, and resulted in ceramic compositions with both acceptable permeability (>200 centidarcies) and R.T. MOR strength (>1000 psi).

Firing temperatures were 2700°F and 3000°F in these matrices. There seemed to be little if any difference in permeability of the same composition fired @ 2700 vs. 3000°F, as is shown in identical mixes 4-300 and 4-270 (Table 1) that were fired at these different temperatures. Although when fired lower (mix 4-270), the R.T. MOR strength was lower (1011 vs 1218 psi), there is insufficient data to determine if this is really an effect of the firing temperature. Hot MOR testing indicated that these mixes 4-300 and 4-270 had nearly identical hot MOR @ 870°C (650 vs 686 psi), based again on a limited amount of data (Table 1). XRD analyses (Table 2) showed that mix 4-300 (fired at 3000°F) had 25% mullite formation, while identical mix 4-270 (fired at 2700°F) had 20% mullite formation. Neither had any free crystalline silica detectable by XRD. Further development work would be necessary to determine if higher temperature firing yields

higher room temperature and hot MOR strengths.

The "Properties of Selected Compositions", Table 1, lists the mix numbers of the best compositions in all matrices based on attaining targeted room temperature MOR (>1000 psi) and permeability (>200 centidarcies) in measurements performed at Blasch Precision Ceramics. Other properties shown on Table 1 are Blasch measurements of apparent porosity and bulk density, as well as Westinghouse measurements of permeability and hot MOR (@ 870°C). The targets were achieved for all compositions except the Westinghouse permeability reading for one mix (#1-300) was not acceptable. The hot MOR strength measurements by Westinghouse were lower than the original arbitrary target of 1000 psi (results: 650 to 805 psi; Table 1). However, hot MOR requirements for cross flow filter application are unknown and hot strength viability can only be accurately determined by full scale filtration testing (proposed as part of Phase II).

Ceramic specimens of compositions 2-300 and 4-300 were chosen for scanning electron microscope (SEM) surface microstructure photographs. SEM photos of these compositions (Figures 4 and 5) are at 100X magnification. The 2-300 and 4-300 compositions were similar, but they contain different combinations of types of fiber pore formers. The SEM microstructures of these specimens look very similar. Both have uniform pore structure and size, and many pores in the 7 to 40 micron range.

Mercury porosimetry was performed on ceramic specimens of compositions 2-300, 4-300, and 4-270. Compositions 2-300 and 4-300 were mentioned previously; composition 4-270 was identical to 4-300, except it was fired at a lower temperature (2700 vs 3000°F). Figures 1, 2, and 3 are graphs of this porosimetry work, while Table 3 is a summary table of porosimetry data and physical properties as measured by Micromeretics, Inc. All three specimens were very similar in porosimetry characteristics. All had a majority of pores in the 7 to 40 micron diameter range, with median pore diameters as follows: Sample 2-300: 16 microns; Sample 4-300: 22.4 microns; Sample 4-270: 18.8 microns.

For the "selected compositions" designated in Table 1, another set of disk specimens for each were made (processed separately from the earlier sets) and submitted to Westinghouse for permeability testing to determine repeatability as compared to earlier specimens. This comparison is shown in Table 4. The results showed good batch to batch repeatability, although compositions 1-300 and 2-300 showed greater variability than the other compositions. It is theorized that the reason for this variability for these two compositions is either lack of consistency of one type of fiber raw material used in both of these mixes, or ineffective dispersion of these fibers into the mix. It is noteworthy that neither batch of composition 1-300 met Westinghouse's permeability specification of <1.00 iwg/fpm, while all batches of the other four compositions in this table met this specification.

Blasch's permeability readings of 200 or greater centidarcies (cd) generally correlated with acceptable Westinghouse permeability readings of <1.00 iwg/fpm. Blasch achieved permeability values of 202 to 404 centidarcies in 23 compositions. Disk specimens of these 23 compositions were submitted to Westinghouse for their permeability testing. Westinghouse found 19 to be acceptable, 2 to be marginal, and 2 to be unacceptable. One of the two determined to be unacceptable was composition 1-300, where Blasch measured permeability of 234 cd and Westinghouse's measurement was 1.36 iwg/fpm (Table 1). This may be due to non-uniformity in this batch, possibly related to the earlier mentioned lack of consistency of the specific fiber pore former raw material or ineffective dispersion of this fiber into the mix.

Summary and Conclusion

Mullite bonded, porous, permeable alumina ceramics were made on a lab scale with the unique and proprietary Blasch injection forming process. Permeability as well as the other initial targeted property requirements for the cross flow filter were achieved. These include permeability of >200 cd (or <1 iwg/fpm) and room temperature MOR of >1000 psi. The compositions that met these requirements had the following characteristics in common:

*Alumina-silica raw material base composition
*100/200 mesh top end particle size
*Gap in particle sizing
*Small percent of fiber pore forming additions
*Firing temperature of either 2700 or 3000°F

It is concluded that it is feasible to use the unique and proprietary Blasch process to form ceramic shapes of a permeable, porous nature, targeted for use in monolithic ceramic cross flow filters.

FUTURE WORK

The future work planned is dependent upon DOE's approval of an SBIR Phase II proposal submitted by Blasch in mid April, 1995. If this Phase II is approved, the effort would occur over a two year period commencing Summer 1995. The major objectives for this Phase II proposed work include:

1. Design (with input from Westinghouse) prototype full size monolithic ceramic cross flow filter ceramic shape to be produced using the Blasch process and permeable ceramic compositions developed in Phase I.

2. Design and build a mold system capable of forming this prototype full size monolithic ceramic cross flow filter.

3. Characterize permeable ceramic compositions to be used in prototype monolithic ceramic cross flow filters, to include room temperature permeability, particulate collection efficiency, and corrosion testing.

4. Produce prototype full size monolithic ceramic cross flow filter by upscaling the lab scale process developed in Phase I.

5. Evaluate performance of these prototype filters in filtration testing and characterize after testing (testing by Westinghouse).

REFERENCES

1. Discussions with Ms. Mary Anne Alvin and Dr. Tom Lippert of Westinghouse Electric Corporation, Science and Technology Center, Pittsburgh.

2. Discussions/meeting with Mr. Ted McMahon, Mr. Harvey Ness, Mr. Richard Dennis, Mr. Norman Holcombe, and Mr. Thomas Keech, Jr., all of DOE METC, September 1993.

3. Discussions with Mr. Ted McMahon of DOE METC throughout Phase I, September 1994 through February 1995.

4. Lippert, T.E., Alvin, M.A., Smeltzer, E.E., Bachovchin, D.M., and Meyer, J.H., Subpilot Scale Gasifier Evaluation of Ceramic Cross Flow Filter, Final Report-February 1, 1988-December 31, 1992: DOE/MC/24021-3544. August, 1993.

5. Lippert, T.E., Smeltzer, E.E., Alvin, M.A., and Bachovchin, D.M., Long-Term Durability Testing of Ceramic Cross-Flow Filter: Final Report-September 29, 1987-December 31, 1992: DOE/MC/24022-3654. August, 1993.

6. Alvin, M.A., Lippert, T.E., and Lane, J.E., "Assessment of Porous Ceramic Materials for Hot Gas Filtration Applications", Ceramic Bulletin, Vol 70, No. 9, 1991.

7. Bosart, S.J., Cicero, D.C., Zeh, C.M., and Bedick, R.C., Gas Stream Cleanup Technology Status Report: DOE/METC--91/0273. August, 1990.

8. Ventkataraman, V.L., Rath, L.K., Martin, J.W., Bedick, R.C., Proceedings of the Eleventh Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting, Volumes I and II: DOE/METC--91/6123. August, 1991.

9. Webb, H.A., Bedick, R.C., Geiling, D.W., Cicero, D.C., Proceedings of the Eighth Annual Coal Fueled Heat Engines and Gas Stream Cleanup Systems Contractors Review Meeting: DOE/METC--91/6122. July, 1991.

10. 1990 Annual Book of ASTM Standards; Section 15: General Products, Chemical Specialties, and End Use Products; Vol 15.01.

Table 1. Properties of Selected Compositions

Mix No.	BPC Perm (cd)	Whse Perm (wg/fpm)	BPC MOR @70°F (psi)	Whse MOR @870°C (psi)	BPC App Porosity (%)	BPC Bulk Density (g/cc)
1-300	234	1.36 to 1.62	1022	1583	41.3	1.99
2-300	202	0.74 to 0.96	1044	760	43.3	1.92
3-300	287	0.41 to 0.43	1395	805	46.6	1.78
4-300	271	0.43 to 0.58	1218	650	46.5	1.80
4-270	268	0.69	1011	686	45.6	1.84

Notes:

BPC Perm is permeability in centidarcies measured by Blasch.
Whse Perm is permeability in inches water pressure difference per feet/minute velocity measured by Westinghouse.
BPC MOR is modulus of rupture in psi at room temperature using 3 point span measured by Blasch.
Whse MOR is modulus of rupture in psi at 870°C using 4 point span measured by Westinghouse.
BPC App Porosity is apparent porosity in % measured by Blasch.
BPC Bulk Density is in g/cc measured by Blasch.

Table 2. Semi-Quantitative XRD Analyses Results

Composition Number	Firing Temp(°F)	% Alumina	% Mullite	% Crystalline Silica
4-300	3000	75	25	0
4-270	2700	80	20	0
2-300	3000	62	38	0

Table 3. Physical Properties by Micromeretics, Inc

Composition Number	Bulk Density (g/cc)	Open Porosity (%)	Median Pore Diameter (μ)
4-300	1.78	47.9	22.4
4-270	1.86	47.5	18.8
2-300	1.96	45.4	16.0

Table 4. Permeability of Different Batches

Composition Number	Permeability, iwg/fpm: November Batch	Permeability, iwg/fpm: December Batch*
1-300	1.356, 1.346	1.616 ± 0.302
2-300	0.742, 0.761	0.955 ± 0.228
3-300	0.405, 0.430	0.410 ± 0.025
4-300	0.430, 0.581	0.384 ± 0.099
4-270	NA	0.686 ± 0.180

Notes:

Testing by Westinghouse.
Units iwg/fpm represent inches water gage per ft/minute velocity.
* 10 disks supplied; 5 disks randomly selected for testing. Data indicates average and ±1 standard deviation.

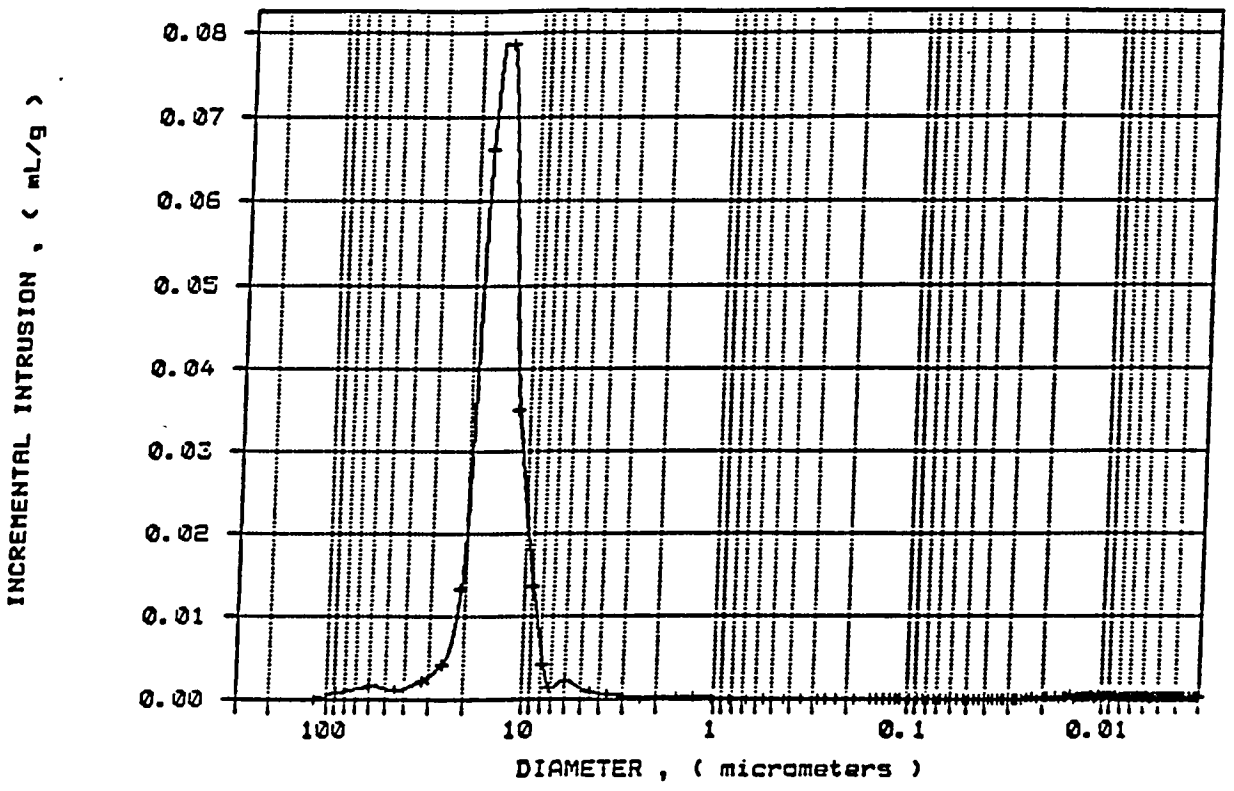

Figure 1. Incremental Intrusion vs Pore Diameter by Mercury Porosimetry Method for Composition 2-300

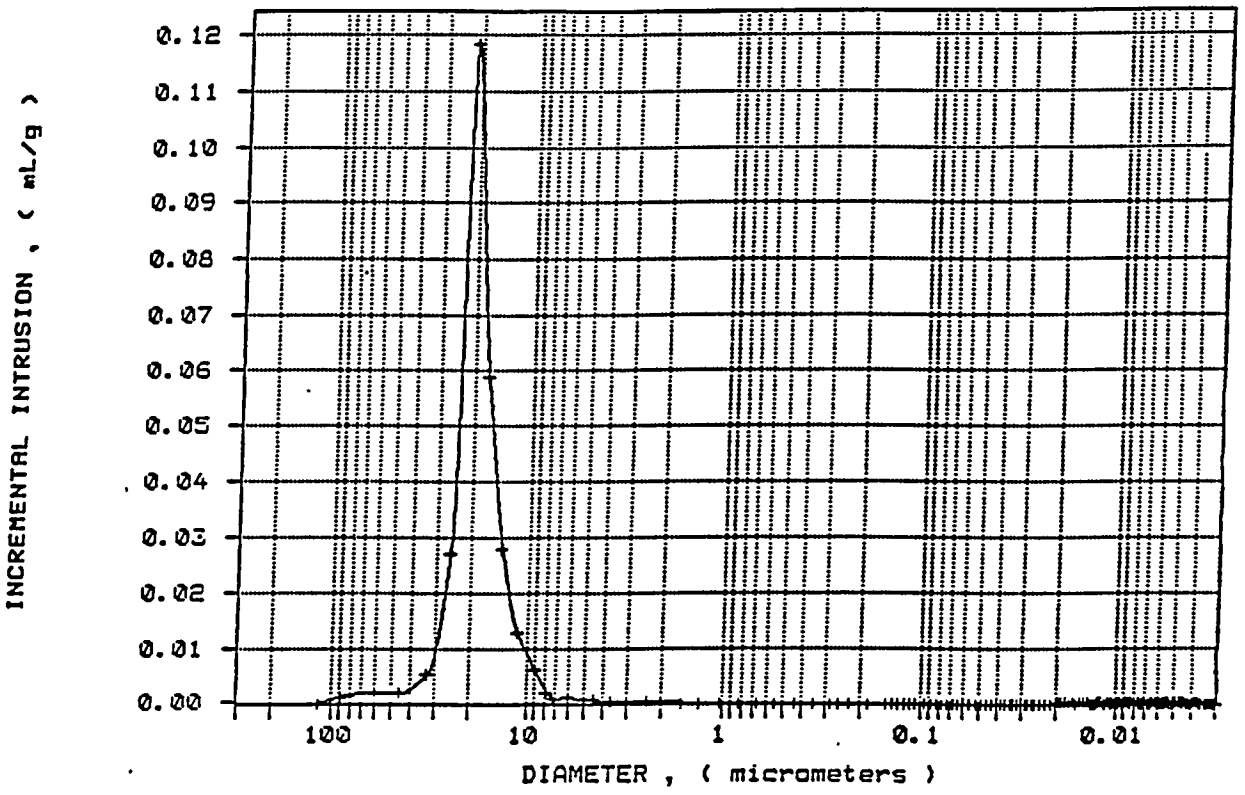

Figure 2. Incremental Intrusion vs Pore Diameter by Mercury Porosimetry Method for Composition 4-300

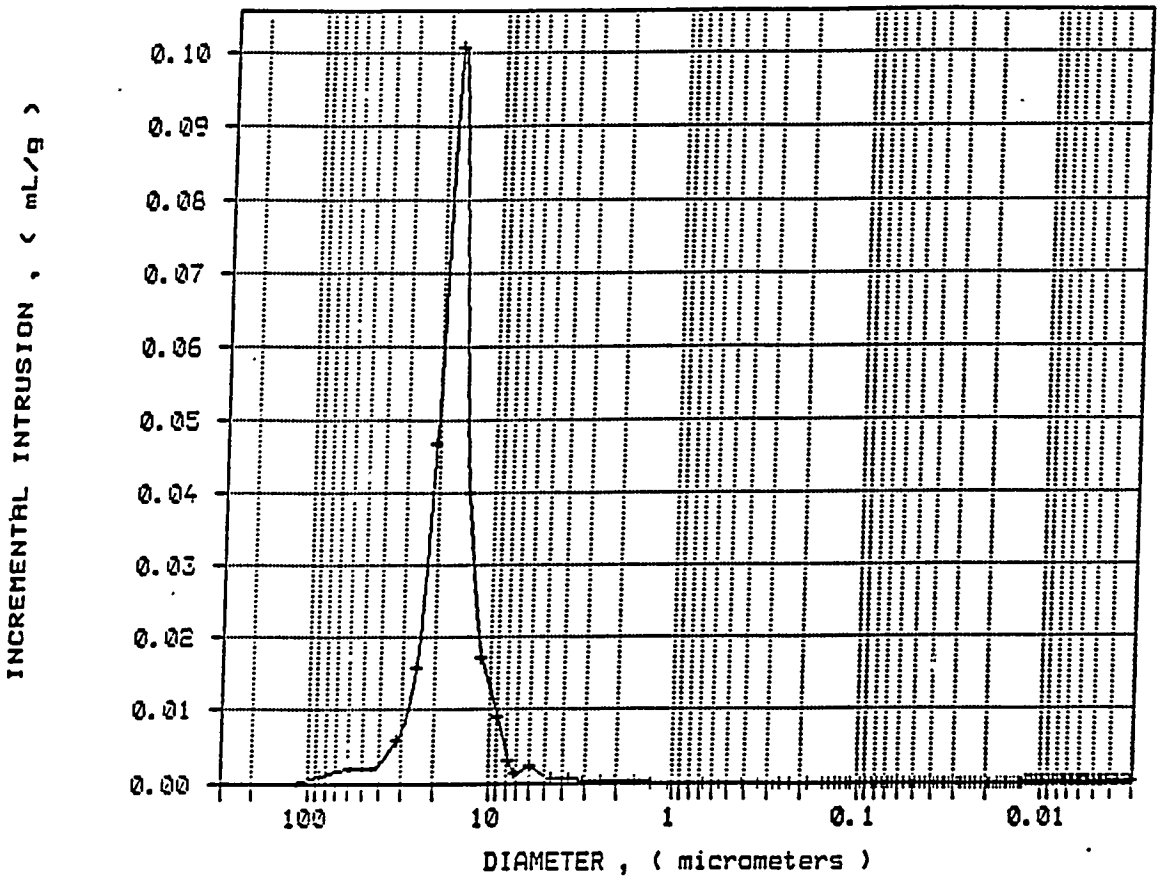

Figure 3. Incremental Intrusion vs Pore Diameter by Mercury Porosimetry Method for Composition 4-270

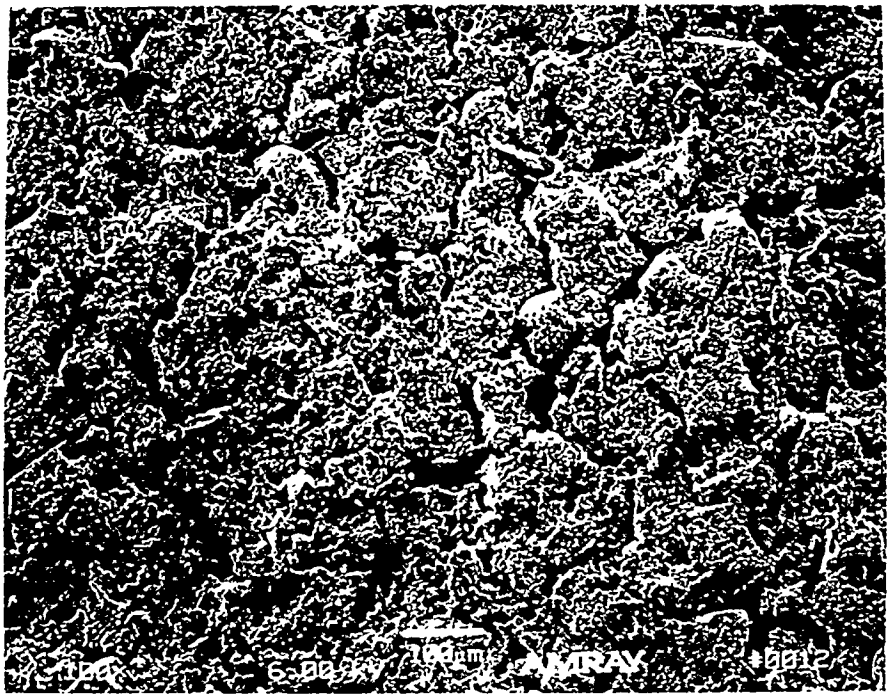

Figure 4. SEM Microstructure of As-Formed Surface of Composition 1-300 @ 100X Magnification

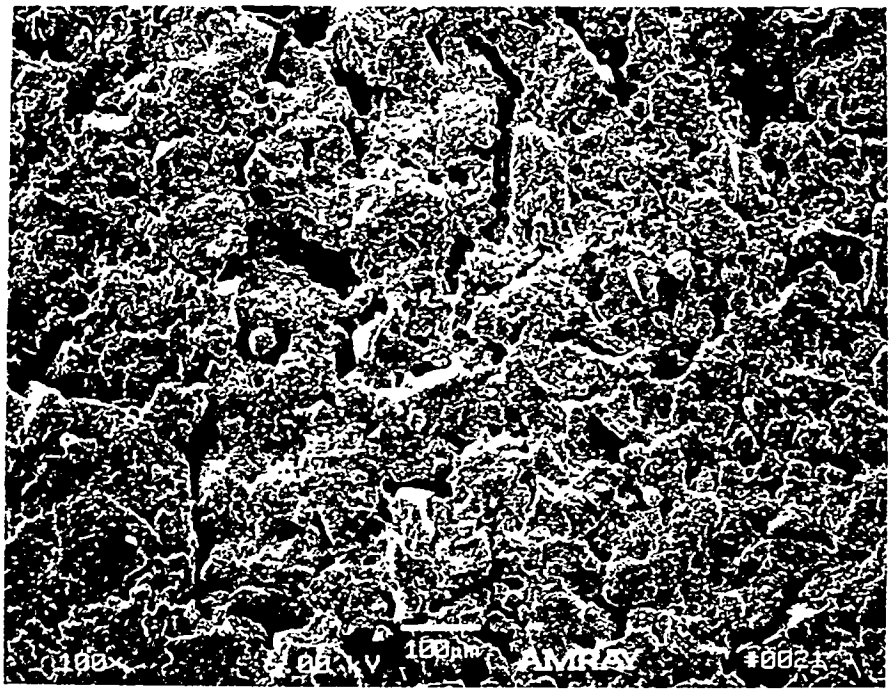

Figure 5. SEM Microstructure of As-Formed Surface of Composition 4-300 @ 100X Magnification