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Project No. A-3868 — GTRI/~~GTRC~~ — DATE 6 / 26 / 84

Project Director: Tom Starr — ~~School~~/Lab EMSL

Sponsor: Naval Surface Weapons Center; White Oak; Silver Spring, MD 20910

Type Agreement: P.O. No. N60921-84-M-3992

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Title: "Fiber Reinforcement of Slip-Cast Fused Silica"

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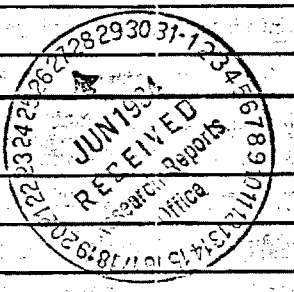

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Project Director(s) Tom Starr GTRC /~~XXX~~

Sponsor Naval Surface Weapons Center

Title "Fiber Reinforcement of Slip-Cost Fused Silica"

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INTERIM TECHNICAL REPORT

SURFACE LAUNCHED WEAPONRY MATERIALS
TECHNOLOGY (SURFMAT) PROGRAM

FIBER REINFORCEMENT OF SLIP-CAST FUSED SILICA

Thomas L. Starr and Joe N. Harris
Georgia Institute of Technology
Georgia Tech Research Institute
Atlanta, Georgia 30332

September 28, 1984

Contract Number N60921-84-M3992

Prepared for

NAVAL SURFACE WEAPONS CENTER
White Oak Laboratory
Silver Spring, Maryland 20910

GEORGIA INSTITUTE OF TECHNOLOGY
A Unit of the University System of Georgia
Engineering Experiment Station
Atlanta, Georgia 30332

1984

SURFACE LAUNCHED WEAPONRY MATERIALS TECHNOLOGY (SURFMAT) PROGRAM

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fused silica, ceramic matrix composites, fiber reinforced fused silica, glass matrix composites

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

While improvement in the toughness and rain erosion resistance of slip-cast fused silica (SCFS) have resulted from low loadings of reinforcing fiber, the increased porosity resulting from higher loadings limits these gains. SCFS composites with up to 27% v/v of fiber and only 16% porosity have been obtained by inpregnating the green body with a silica precursor resin prior to firing.

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William Messick	(202) 394-1137	NSWC (K-06)

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INTRODUCTION

Slip-cast fused silica (SCFS) is the only operational radome material with adequate thermal shock resistance and high temperature dielectric properties to be considered for advanced application at velocities in the range of Mach 6 to Mach 8. However, in order to provide maximum mission capabilities under all weather conditions at these velocities, the mechanical/structural properties of this material must be improved.

Others have attempted to improve the strength and rain erosion resistance of SCFS by blending chopped, high modulus fibers into the slip and, then, casting and firing in the usual manner. Higher strength, increased work of fracture, and improved rain erosion resistance have been obtained with fiber contents less than 10% (1,2,3). Above this level, the porosity of the body increases and the properties degrade as a result. It is reasonable to expect continued improvement in the strength and toughness of fiber reinforced SCFS at higher fiber loadings if this porosity can be reduced.

In our recent work on improved silica materials (4), we have developed a silica precursor resin that can be used to increase the green density of silica powder compacts. This resin is prepared by careful hydrolysis of ethyl silicate in alcohol. Upon solvent evaporation, the resin ultimately attains a silica density of 0.85 g/cc or 40% of full silica density. This resin decomposes to a dense particulate silica at moderate temperature (<1000°C). By impregnating a porous powder/fiber compact, this resin can be used to increase the green density and, thus, the fired density of silica composites.

This interim report presents the results of the first three months of a six month program. In this first half of the program, we have focused on obtaining reduced porosity at higher fiber loadings. In the second phase, we will confirm the expected improvement in mechanical properties by flexure testing of composite bars.

EXPERIMENTAL

Nextel ^{R} 312 alumina-boria-silica fibers* were blended with commercial high purity fused silica slip**. Typical properties of the fiber and slip are shown in Tables 1 and 2.

The as-received fiber (1/8 inch chopped fiber) was dispersed and further chopped in an Osterizer blender with water, washed with hydrochloric acid to remove metal contamination from the blades, and dried. After this treatment, the fiber exhibited a free settling density of 0.19 g/cc or 6.9% of theoretical. This corresponds to an average length to a diameter (L/D) ratio of 65:1 (5), or an average fiber length of 650 μm. This agrees roughly with microscopic examination although there is a wide range of individual fiber lengths, generally between 200 and 1200 μm.

---

* 3M Company, St. Paul, Minnesota

** Thermo Materials Corporation, Atlanta, Georgia

The chopped fiber was blended with slip using a two blade, counter rotating mixer, with small water additions to maintain fluidity. Three slips were prepared in the range 15 to 35% fiber (volume percent of total solids). Several bars and plates, at a nominal 1/4 inch thickness, were cast on plaster and dried at 150°C.

The bars and plates were impregnated with silica precursor resin, then calcined to remove residual organic material. This cycle was repeated until constant density was achieved. Two impregnation techniques were utilized - vacuum impregnation with concentrated resin and impregnation by boiling the bars (plates) in dilute resin solution.

Fully impregnated/calcined bars were fired in vacuum at 1200° and 1250°C. The firing cycle consisted of (1) heat at 100°C/hr to firing temperature, (2) hold for four hours, (3) cool at 300°C/hr.

Characterization of green and fired bars (plates) consisted of measuring the bulk dimensions, weighing, and density and open porosity determination by Archimedes' method.

RESULTS

The composition and performance data for three slips are summarized in Table 3. These slips exhibited sufficient fluidity to cast in the normal manner, although this became more difficult at the higher loadings. The fibers appeared to be well dispersed but tended to settle if left standing for several minutes.

GREEN DENSITY

The green density of cast bars and plates decreases with increasing fiber loading. The porosity in the green state, calculated from the cast density and the theoretical density at the composite composition, is plotted in figure 1 as a function of the fiber loading. The point at 100% fiber represents the free settling density of the fibers. Plotted on the same figure is the volume fraction of fiber relative to the bulk volume of the body. Note that this value must reach a maximum at some point. Indeed, if the porosity continues to rise as a linear function of the fiber loading, this maximum occurs at 0.42 where the bulk loading factor is 0.19. Thus, increasing the fraction fiber (relative to total solids) from 0.27 to 0.42 increases the fraction fiber (relative to the bulk volume) only from 0.17 to 0.19. The remainder of the volume is porosity which increases from 0.34 to 0.54.

Impregnation will reduce the porosity but will not increase the bulk loading factor for the fiber. Since this likely will determine the bulk loading factor in the fired body, we would not expect significant change by increasing the loading of fiber in the slip beyond 0.25.

IMPREGNATION

The results of impregnating these composites are shown in figure 2. With both methods the porosity is reduced to a level similar to green SCFS after two or three cycles. The vacuum method appears to be somewhat more effective than the boiling method although both give similar ultimate densities.

FIRING

Impregnated bars cast from slips #1 and #2 (16 and 27% fiber) were fired at 1200 and 1250°C, and achieved densities shown in table 4. For comparison, the density of SCFS fired under these conditions is 1.95 g/cc with 12% porosity.

Figure 3 compares these results to those in references 1 and 3. The reduced porosity at high fiber loading as a result of impregnation is readily apparent.

CONCLUSIONS

We have demonstrated the feasibility of fabricating fiber reinforced SCFS with low porosity at high fiber loading. Continued improvement of the mechanical properties still must be shown.

It appears that a fiber loading of 25% of the total solids is the practical maximum for the fibers used in this study. This results in a bulk loading in the final fired body of 17% v/o. Further reduction of the average fiber length or pressing of the cast body prior to impregnation may result in higher loadings.

REFERENCES

1. F.P. Meyer, "Effects of Various Additions on the Properties of Slip Cast Fused Silica", XV Symposium on EM Windows, Georgia Institute of Technology, June, 1980.

2. W.J. Corbett, A.T. Sales, and J.D. Walton, "Improving the Mechanical Properties of Slip-Cast Fused Silica by Fibrous Reinforcement", Georgia Tech Final Report, Project A-793, Contract no. 16-2092 for Sandia Corporation, August, 1965.

3. F.P. Meyer, G.D. Quinn, and J.C. Walck, "Fiber Reinforced Fused Silica for Hypersonic Radome Applications" XVII Symposium on Electromagnetic Windows, Georgia Institute of Technology, July, 1984.

4. T.L. Starr and J.D. Walton, "A Program to Improve the Strength and Toughness of Sintered Fused Silica", Georgia Tech Final Report Project A-3432 under Office of Naval Research contract N0014-83-K-0159, January, 1984.

5. J.V. Milewski, "How to Use Short Fiber Reinforcements Efficiently", 37th Annual Conference, Reinforced Plastics/Composites Institute, the Society of the Plastics Industry, January 11-15, 1983.

Table 1. Nextel fiber properties

Composition	Alumina-boria-silica
Diameter	10-12 μm
Density	2.70 g/cc
Tensile strength	1550 MPa (230×10^3 psi)
Tensile modulus	152 GPa (22×10^6 psi)
Thermal expansion	3×10^6 mm/mm°C
Continuous use temperature	1200°C (2200°F)
Short term use temperature	1650°C (3000°F)
Melting temperature	1800°C (3272°F)

Table 2. High purity silica slip properties

Solid Content (%)	82.8
pH @ 20°C	5.3
Viscosity @ 20°C (centipoise)	
@ 6 rpm	220
12 rpm	187
30 rpm	159
60 rpm	153
Mean Particle Size (μm)	8.0

Table 3. Fiber containing fused silica slips

	#1	#2	#3
fiber volume % of total solids	16	27	33
wt % solids	79.7	77.4	78.5
cast density (g/cc)	1.71	1.47	1.27

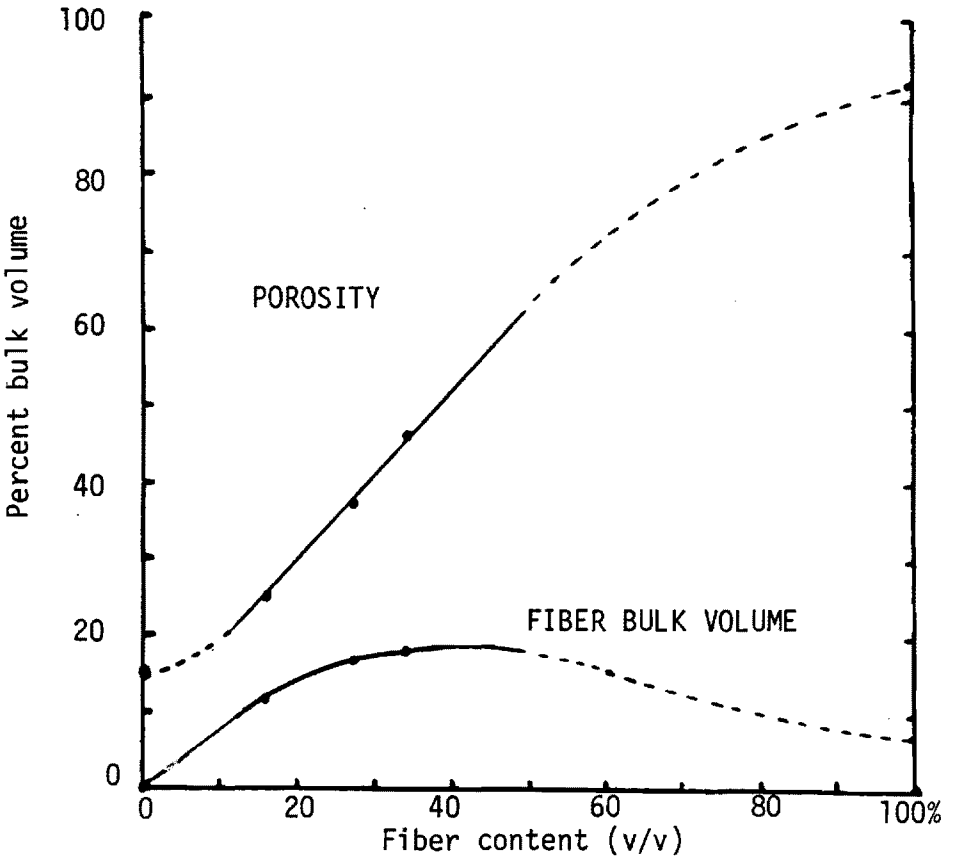

Figure 1. As-cast properties of fiber containing slips

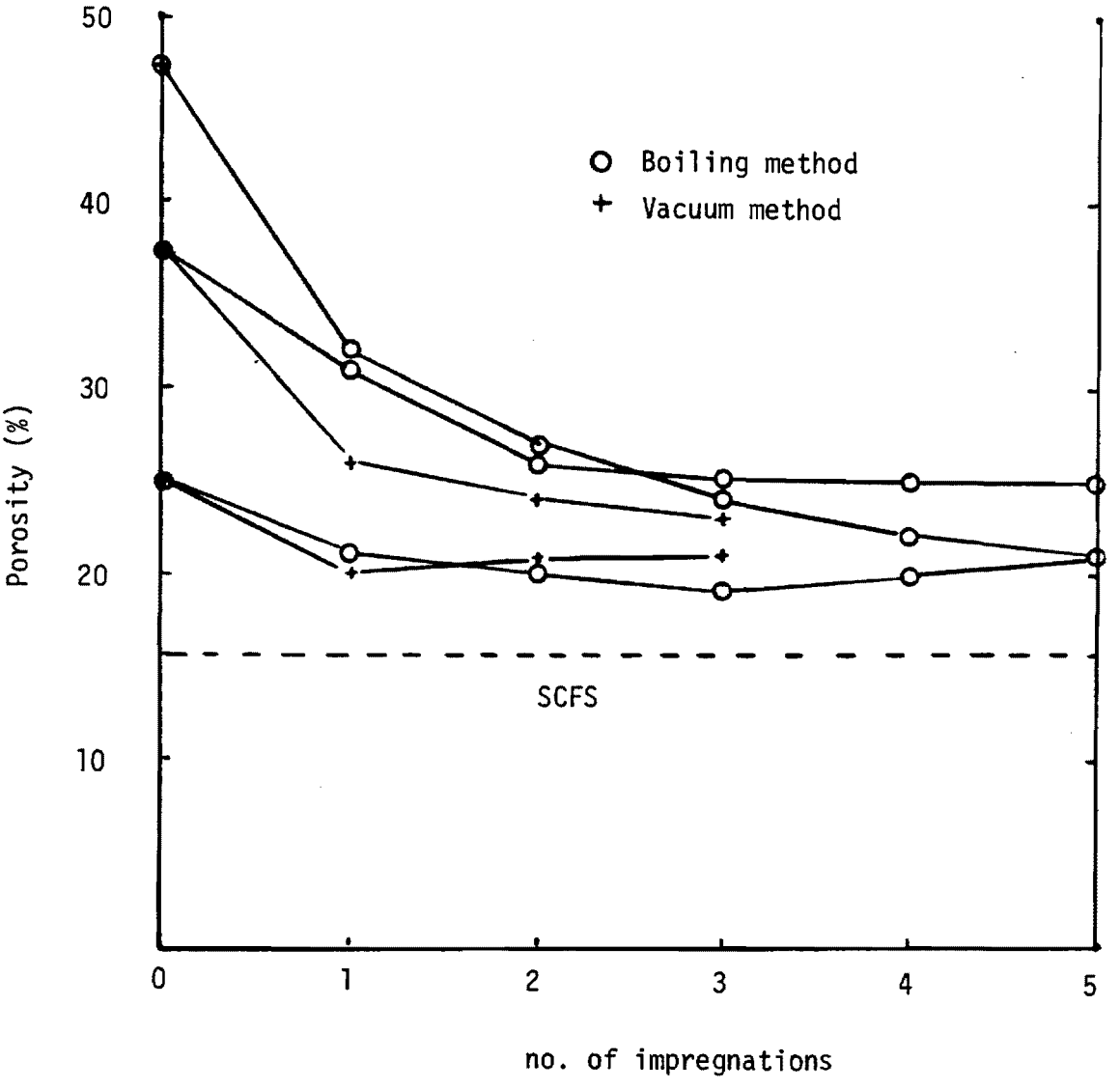

Figure 2. Impregnation of cast composites

Table 4. Fired density of SCFS composites

	Fiber loading			
	16%		27%	
Firing temperature	density	% porosity	density	% porosity
1200°C	1.93	16	1.94	17
1250°C	1.97	14	1.96	16

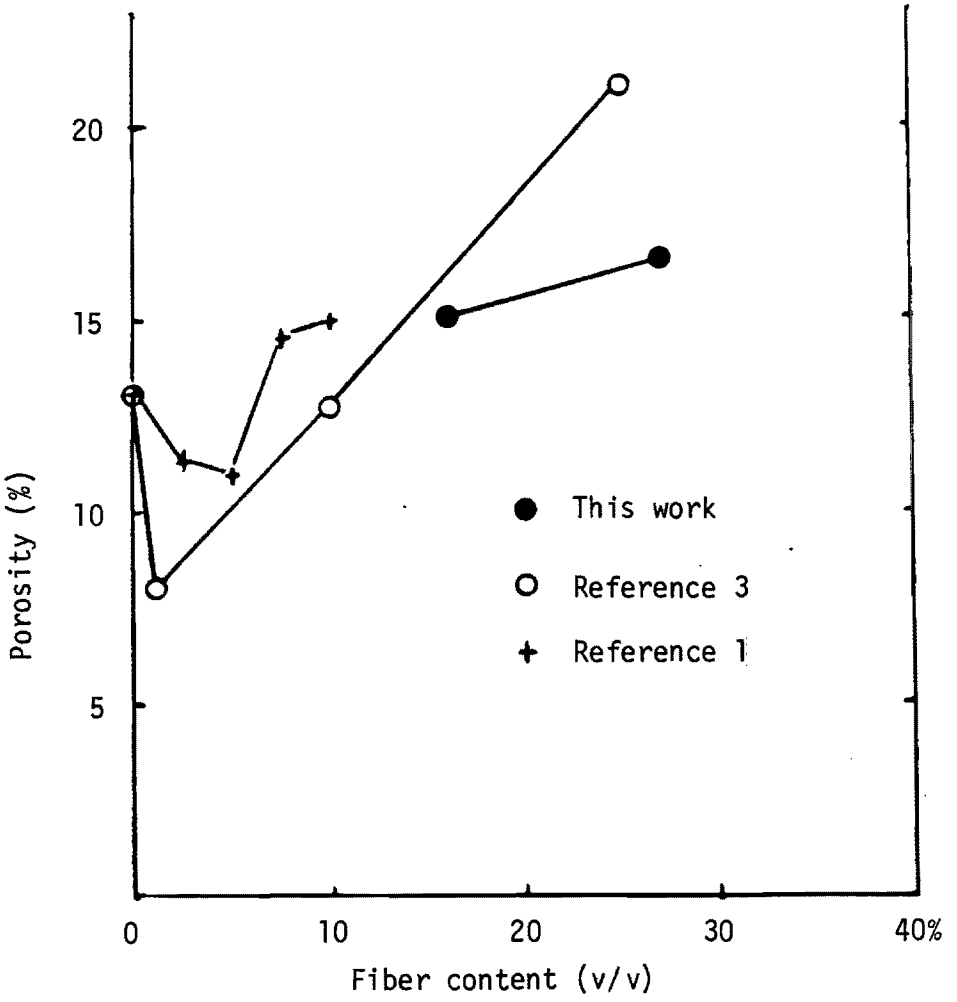

Figure 3. Fired composites

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SURFACE WEAPONS MATERIALS TECHNOLOGY (SURFMAT) PROGRAM

FIBER REINFORCEMENT OF SLIP-CAST FUSED SILICA

Thomas L. Starr and Joe N. Harris
Georgia Institute of Technology
Georgia Tech Research Institute
Atlanta, Georgia 30332

December 15, 1984

Final Report

Contract Number N60921-84-M-3992

Prepared for

NAVAL SURFACE WEAPONS CENTER DETACHMENT
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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Fiber reinforced slip-cast fused silica plates have been fabricated and tested. Impregnation of the green body with a TEOS based silica precursor resin results in higher density and strength at high fiber loadings, as compared to processing without the impregnation step. Reduced strength, as compared to unreinforced silica, appears to be due to fiber clumping which results in large surface flaws. Fracture surface morphology suggests increased toughness may be possible due to fiber pull-outs and increased fracture surface energy.

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SUMMARY

Fiber reinforced slip-cast fused silica plates have been fabricated and tested. Impregnation of the green body with a silica precursor resin prepared from tetraethyl orthosilicate (TEOS) results in higher density and strength at high fiber loadings, as compared to processing without the impregnation step. Reduced strength, as compared to unreinforced silica, appears to be due to fiber clumping which results in large surface flaws. Fracture surface morphology suggests increased toughness may be possible due to fiber pull-outs and increased fracture surface energy.

PREFACE

This report was prepared by the Georgia Institute of Technology, Georgia Tech Research Institute under NSWC Contract No. N60921-84-M-3992. The Project Director was Dr. Thomas L. Starr of the Energy and Materials Sciences Laboratory.

The program was administered under the direction of Mr. Roger E. Wilson, Code R-31 of the Naval Surface Weapons Center Detachment, White Oak, 10901 New Hampshire Ave., Silver Spring, Maryland 20903-5000.

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I. INTRODUCTION

Slip-cast fused silica has sufficient thermal shock resistance and high temperature dielectric properties for hypersonic radome applications. For all-weather mission capability, however, a radome material also must exhibit good rain erosion resistance. In this respect, silica is marginal and increased impact toughness is needed.

Previous work with fiber reinforced silica glass has demonstrated the potential for achieving a substantial increase in toughness and, in some cases, an increase in strength as well (1-5). These composites all utilized continuous, unidirectionally aligned fibers and were fabricated by hot-pressing. While demonstrating the potential of fiber incorporation for improving glass toughness, this fabrication technique is unsuitable for large radome shapes.

Others have attempted to toughen silica using short, randomly oriented fibers, and normal slip casting and sintering fabrication techniques (6,7,8). Some increase in toughness was obtained but as the fiber loading increased beyond 10% the strength degraded rapidly. This is attributed to a corresponding increase in porosity, as the sintering forces are unable to densify the composite at high fiber loading.

With careful control of reaction conditions, tetraethyl orthosilicate (TEOS) can be hydrolyzed to a resin-like fluid that converts with high yield to inorganic silica upon firing (9). By impregnating a porous silica body with this resin, the effective green density can be increased and the

maximum pore size reduced, resulting in less shrinkage and greater sintering activity. Such treatment of a fiber loaded cast body should result in less porosity and greater strength.

II. OBJECTIVES

The objective of this program is to fabricate fiber reinforced slip-cast fused silica shapes using high fiber loadings while retaining the density and strength obtained with standard slip-cast fused silica.

III. APPROACH

Our approach is to:

1. Prepare a casting slip using commercially available silica slip with additions of up to 50 volume percent of chopped fiber,
2. Fabricate plates and bars using normal casting and drying techniques,
3. Impregnate the plates and bars with a specially prepared silica precursor TEOS resin to increase the pre-fired density,
4. Sinter the impregnated plates to high density with minimal devitrification, and
5. Characterize the material as to: density, porosity, modulus of rupture, degree of devitrification, and microstructure.

The results of this investigation will be used to evaluate the potential of this fabrication process and to outline plans for its further development.

IV. EXPERIMENTAL PROCEDURE

Fiber loaded casting slips were prepared from commercial radome grade silica slip* and Nextel® 312 ceramic fiber**. The silica slip was manufactured by wet milling high purity silica glass cullet in an aluminum oxide (85% Al_2O_3) lined ball mill using a similar aluminum oxide grinding media. The batch of slip (053182-B) used in this program was previously characterized during an earlier Navy program (10). Composition, rheology and particle size are shown in Tables 1 and 2, and in Figure 1.

Nextel® 312 alumina-boria-silica fiber was obtained as 1/8 inch chopped fibers. Properties of this fiber are given in Table 3. The fiber was dispersed and further reduced in length by chopping in water using an Osterizer blender. After chopping, fibers were washed with hydrochloric acid to remove metal contamination from the blades and dried.

Blending of Fibers and Slip

Chopped fiber was added to the slip using a two shaft, counter rotating mixer or a single shaft high speed stirrer. Additional water was added in order to maintain sufficient fluidity for casting. The degree of fiber dispersal was judged by visual observation and mixing was continued until no further improvement could be seen - generally 10-20

---

* Thermal Materials Corporation, Scottdale, Georgia 30079

** 3M Company, St. Paul, Minnesota

Table 1.
Chemical Composition of Thermo Materials High Purity Fused Silica Slip

	Weight percent
Al_2O_3	0.23
TiO_2	0.002
Fe_2O_3	0.003
MgO	0.007
CaO	0.001
CoO	0.001*
Cr_2O_3	0.001
SiO_2	99.76
Na_2O	10^{-5}*
K_2O	10^{-5}*
Li_2O	10^{-5}*

* Not detected. The number indicates the minimum limit of detection.

Table 2.
Properties of Thermo Materials High Purity Fused Silica Slip

Solid Contents (%)	82.7
pH @ 20°C	4.4
Viscosity @ 20°C (Pa s)	
@ 6 rpm	0.19
12 rpm	0.15
30 rpm	0.13
60 rpm	0.12
Mean particle size (μm)	7.8
% of particles <2 μm	23

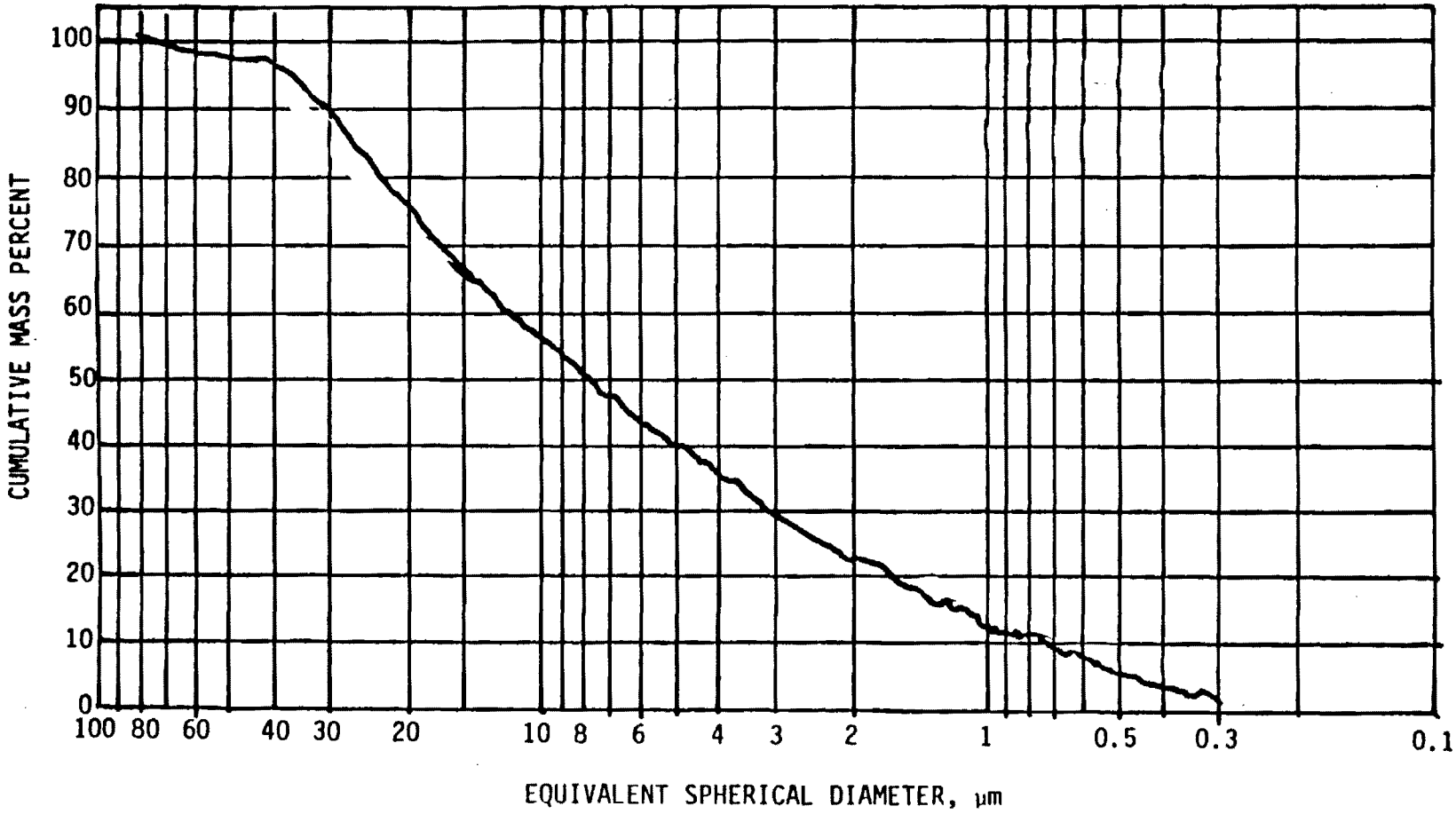


Figure 1. Particle Size Distributions of High Purity Fused Silica Slips.

Table 3.

Properties of Nextel® 312 fiber

Composition	$64Al_2O_3 \cdot 14B_2O_2 \cdot 24SiO_2$
Diameter (μm)	10-12
Forms available	continuous or chopped
Density (g/cc)	2.70
Melting point (°C)	1700
Extended use temperature (°C)	1400
Tensile Modulus (GPa)	152
Tensile Strength (MPa)	1550
Thermal expansion (10^6/°C)	3.4 (20-350°C)
	2.3 (350-465°C)
Strain to failure	1.0%

minutes.

Casting Methods

Plates and bars were cast from the slip shortly after mixing using a polymethylmethacrylate mold on a plaster base. Several fiber loadings were prepared by first blending at the highest loading, casting a portion of this, and adding additional slip to achieve a lower loading factor. Plates and bars were dried at 110°C for a minimum of 16 hours and then calcined at 980°C for 1 hour.

Silica Resin Preparation and Impregnation

Silica precursor resin was prepared by acid hydrolysis of tetraethyl orthosilicate in ethanol solution (9). As prepared, this solution contains an equivalent SiO_2 concentration of 0.1 g/cc. For impregnating the composite plates, this solution was concentrated to between 0.3 and 0.7 g/cc equivalent SiO_2 by boiling to a reduced volume. Two impregnation techniques were used: boiling and vacuum. In the boiling method, a bar or plate was placed in diluted resin solution in a beaker and heated until boiling. When the solution reached a thick, viscous state (approximately 0.7 g/cc SiO_2), the bar or plate was removed by forceps and excess resin wiped from the surface. In the vacuum method, bars or plates were placed in an airtight chamber which was then evacuated using a mechanical pump. Sufficient resin solution, pre-concentrated to 0.3 or 0.5 g/cc equivalent SiO_2 by boiling, was added to cover the specimens and air re-admitted to the chamber. After standing 5-10 minutes,

the excess resin was drained.

Calcination and Reimpregnation

After impregnation, the bars and plates were dried overnight and calcined at 450°C for 1 hour to remove residual organics. The impregnation/calcining cycle was repeated until the weight gain became insignificant.

Sintering

After casting, impregnating and calcining, the bars and plates were sintered in three separate firings with somewhat different conditions and schedules, as shown below.

Table 4.

Firing Conditions and Schedule

Firing	Set	Max. Temp (°C)	Time at Temp (hrs)	Atmosphere
1	A	1200	4	vacuum
2	A	1250	4	vacuum
3	B	1220	4	air

Evaluation of Bars and Plates

Bulk densities were obtained by measuring and weighing the individual bars and plates. The total porosity was calculated from the bulk density using the theoretical density for each composition. Modulus of rupture (MOR) was determined by the 4-point bend test according to MIL-STD-1942(MR)

using an Instron model 1331 test machine. Test bars 3 X 4 X 50 mm were cut and machined from plates using a copper-bonded diamond wheel. Microstructure and topography of the fracture surface were observed using a Cambridge Stereoscan 150. Cristobalite content was measured by x-ray diffraction.

V. RESULTS

Two sets of fiber-loaded silica plates and bars were prepared. The first set consisted of a relatively small amount of material prepared at three fiber loadings. Plates and bars were cast, impregnated and fired under various conditions in order to explore a limited range of processing variability. The second set consisted of a larger amount of material prepared at three fiber loadings. Plates were cast, calcined impregnated, and fired under identical conditions and these were used for mechanical testing.

Slip Preparation and Casting

Five grams of Nextel® 312 fiber in 250 cc water were chopped for five minutes at the speed setting "CHOP". Several batches were combined to provide a 350 g master batch for blending with slip. This chopping regimen produced compacts with a free settling density of 0.19 g/cc or 6.9% of the fiber density. This corresponds to an average length to diameter ratio (L/D) of 65:1 (11), or an average fiber length of 650-708 μm. This agrees roughly with microscopic examination although there is a wide range of individual fiber lengths, generally between 200 and 1200 μm.

Six slips were prepared and used to cast bars and plates as shown in Table 5. An attempt to prepare a slip with 50% fiber was abandoned since excessive water additions were required to maintain fluidity and since this composition was not expected to give a significantly higher loading in the cast body. (See discussion below.) Plates without fiber also were prepared for comparison.

Table 5.
Slip and Casting Characteristics

	ID	% Fiber*	% Solids**	Samples prepared	Cast Density (g/cc) Dried	Calcined
Set A						
	A-16	15.5	79.7	1 plate 10x5x0.6cm 2 plates 5x5x0.6 3 plates 5.0.6x0.6	1.71	1.70
	A-27	27.3	77.4	1 plate 10x5x0.6 2 plates 5x5x0.6 2 bars 5x0.6x0.6	1.47	1.45
	A-33	32.5	78.5	2 bars 2x0.6x0.6	1.27	1.25
Set B						
	B-11	10.6	80.8	6 plates 5x5x0.6	1.87	1.87
	B-15	15.0	79.2	8 plates 5x5x0.6	1.81	1.81
	B-25	25.0	77.2	6 plates 5x5x0.6	1.58	1.58
	B-0	0	82.8	6 plates 5x5x0.6	1.87	--

* Volume of fiber as percent of total volume of solids in slip
** Weight percent of solids in slip

Impregnation With Silica Resin

Bars and plates from each batch of slip were impregnated using the prepared silica precursor resin employing the two techniques described above. For Set A, individual bars and plates were impregnated one at a time. For Set B, a larger apparatus for vacuum impregnation was constructed and all of these plates were impregnated together. The plates with no fiber were not impregnated or calcined prior to firing.

Average density data for each different composition and impregnation technique are shown in Table 6. Reproducibility in density for different pieces of the same composition

Table 6.

Impregnation With Silica Resin

		Density after each cycle (g/cc)					
ID	technique	0	1	2	3	4	5
A-16	boiling	1.70	1.80	1.84	1.85	1.85	1.82
	vacuum	1.70	1.83	1.80	1.80	--	--
A-27	boiling	1.45	1.62	1.73	1.75	1.76	1.73
	vacuum	1.45	1.72	1.78	1.81	--	--
A-33	boiling	1.25	1.61	1.77	1.80	1.86	1.86
B-11	vacuum	1.87	1.91	1.93	1.94	1.95	1.95
B-15	vacuum	1.81	1.87	1.87	1.88	1.89	1.89
B-25	vacuum	1.58	1.72	1.76	1.77	1.78	1.79

using the same technique was better than 5% in all cases and better than 1% for Set B. The dimensions of the pieces did not change during the impregnation/calcination cycle so that it was concluded that the increase in density is a result of an increase in mass.

Sintering of Impregnated Bodies

Bars from Set A were fired for four hours at 1200°C or 1250°C in vacuum using an alumina tube furnace. All plates from Set B were sintered in a single firing for four hours in air using a bottom loading electric box furnace. Final bulk densities for these firings are given in Table 7.

Table 7.

Sintering of Impregnated Bars and Plates

ID	Temp (°C)	Atmosphere	Density (g/cc)
A-16	1200	vacuum	1.93
	1250	vacuum	1.97
A-27	1200	vacuum	1.94
	1250	vacuum	1.96
B-11	1220	air	2.05
B-15	1220	air	2.01
B-25	1220	air	1.91
B-0	1220	air	1.97

Mechanical and Microstructural Characterization

One plate of each composition from Set B was machined into test bars 50 x 4.0 x 3.0 mm. Modulus of rupture data for these bars are tabulated below. The densities measured for the machined bars were slightly different from those of the corresponding plates due to variations in density

through the thickness.

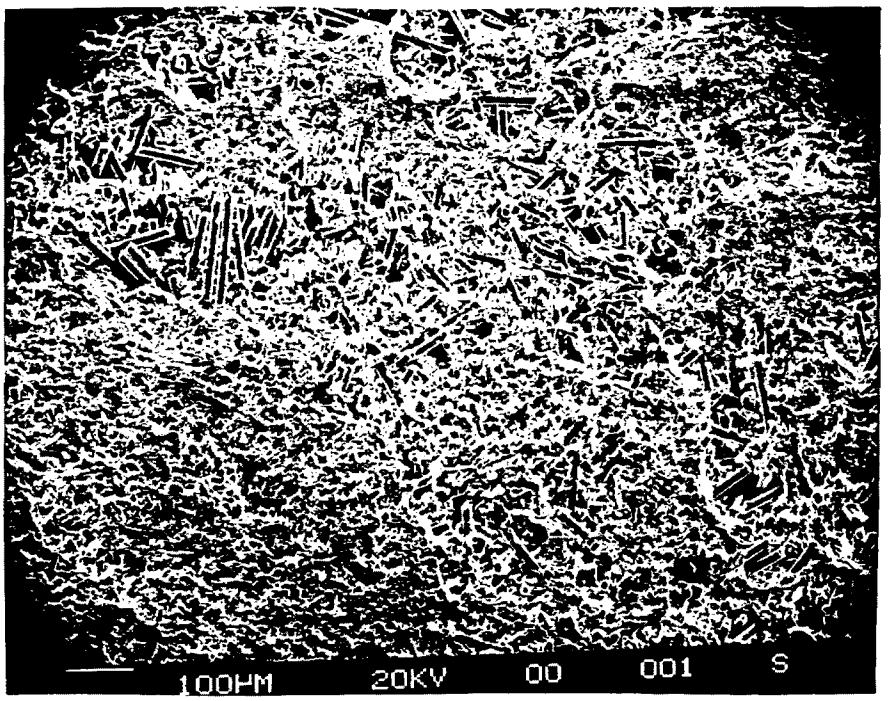
Scanning electron micrographs of the fracture surfaces and as-ground surfaces of bars from B-25 and B-0 are shown in Figures 2 and 3. X-ray analysis of these bars showed 1.3 and 0.8% cristobalite respectively.

Table 8.

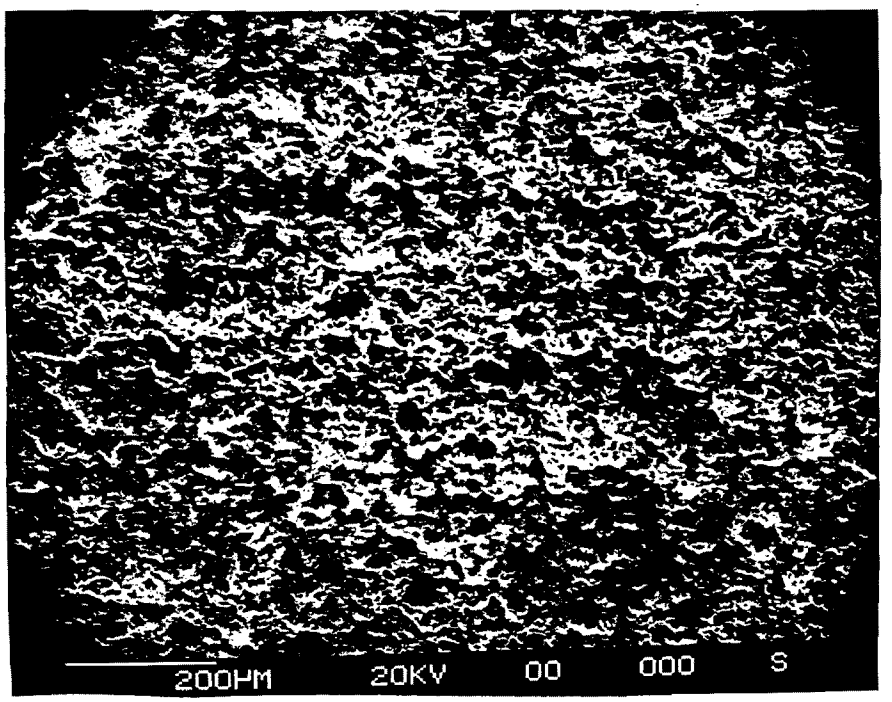
Mechanical Testing of Composite Bars

ID	MOR MPa (psi)	
B-11	22.3 (3240)	mean = 24.2 (3510)
	18.6 (2700)	s.d. = 4.8 (700)
	26.1 (3780)	density = 2.07 g/cc
	29.9 (4330)*	
B-15	33.6 (4870)	mean = 34.1 (4950)
	26.1 (3780)	s.d. = 5.5 (800)
	41.0 (5950)	density = 1.94 g/cc
	36.3 {5270)	
	33.6 (4870)	
B-25	29.9 (4330)	mean = 31.0 (4490)
	26.1 (3790)	s.d. = 5.9 (850)
	41.0 (5950)	density = 1.87 g/cc
	29.9 (4330)	
	38.0 (4060)	
B-0	61.5 (8920)	mean = 59.3 (8600)
	63.4 (9190)	s.d. = 7.3 (1060)
	67.1 (9730)	density = 1.97 g/cc
	44.7 (6490)	
	61.8 (8960)	
	55.0 (7975)	
	61.5 (8920)	

* Fractured outside of center span

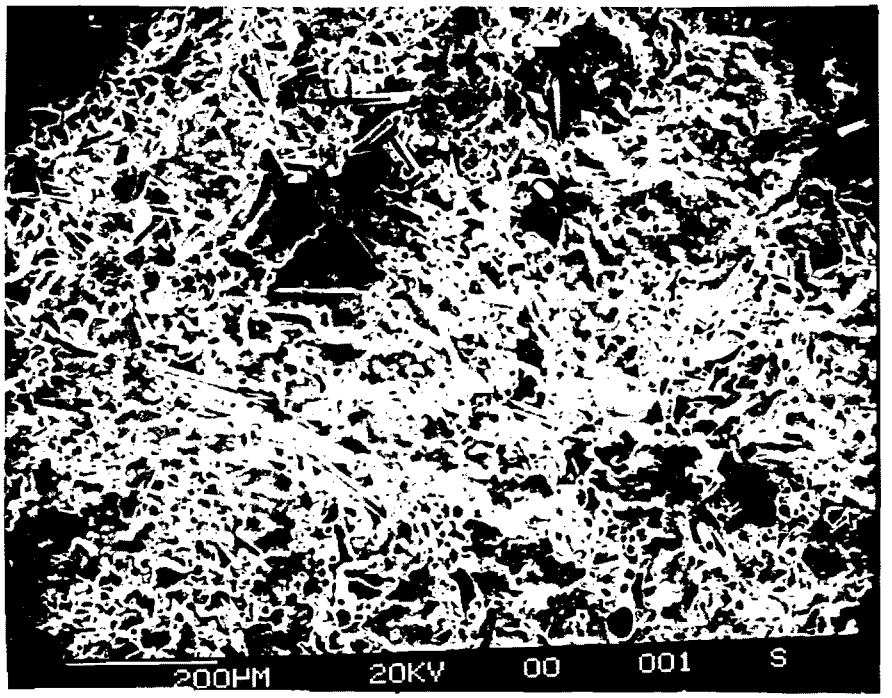


25% FIBER

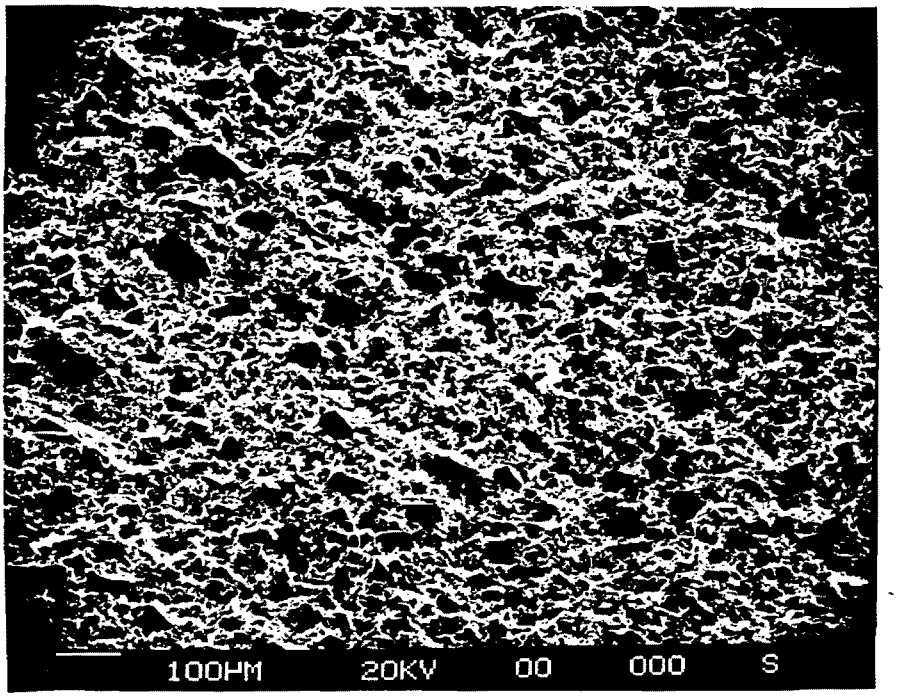


NO FIBER

Figure 2. Machined Surface Morphology (100X)



25% FIBER



NO FIBER

Figure 3. Fracture Surface Morphology (100X)

VI. DISCUSSION

The porosity of the as-cast fiber-loaded silica increases rapidly at high fiber loadings. The increase is linear in the range 10-33% as shown in Figure 4. This increase in porosity lowers the volume fraction of fiber in the cast piece at high loadings (Figure 5). Thus, increasing the fiber loading in the slip from 25 to 40% increases the fiber loading in the cast piece only from 17 up to 19%. Impregnation reduces the porosity but it, obviously, cannot increase the bulk loading factor for the fiber. Since this, likely, will determine the bulk loading factor in the fired body, no significant improvement in performance is expected beyond 25% fiber in the slip.

Note that the highest bulk loading in the cast bodies (19%) is almost three times that obtained in free settling of the fiber alone (6.9%). Thus the casting process substantially enhances the packing behavior of the fibers. This packing behavior also is strongly influenced by the L/D ratio (11), and additional chopping of the fibers could lead to even higher bulk loadings.

The impregnation process is effective in substantially reducing the porosity of the material prior to firing. At the highest loading the porosity was reduced from 46% as-cast to 22% after impregnation. Similar improvement was obtained at lower loadings. The as-cast porosity of silica with no fiber is 15%. While not measured, it is reasonable to expect that the average pore size of the impregnated

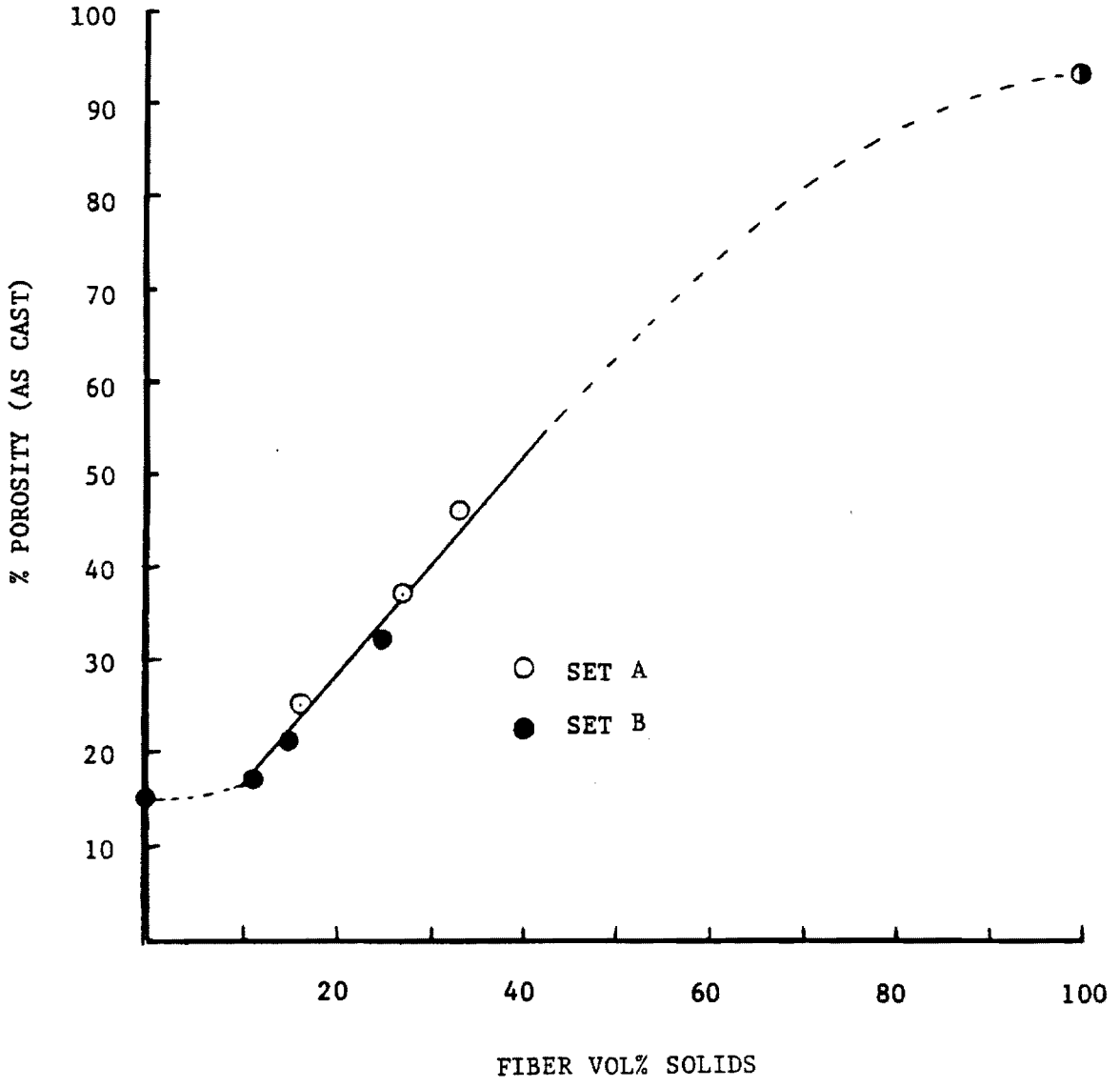


Figure 4. Porosity of as-cast plates and bars

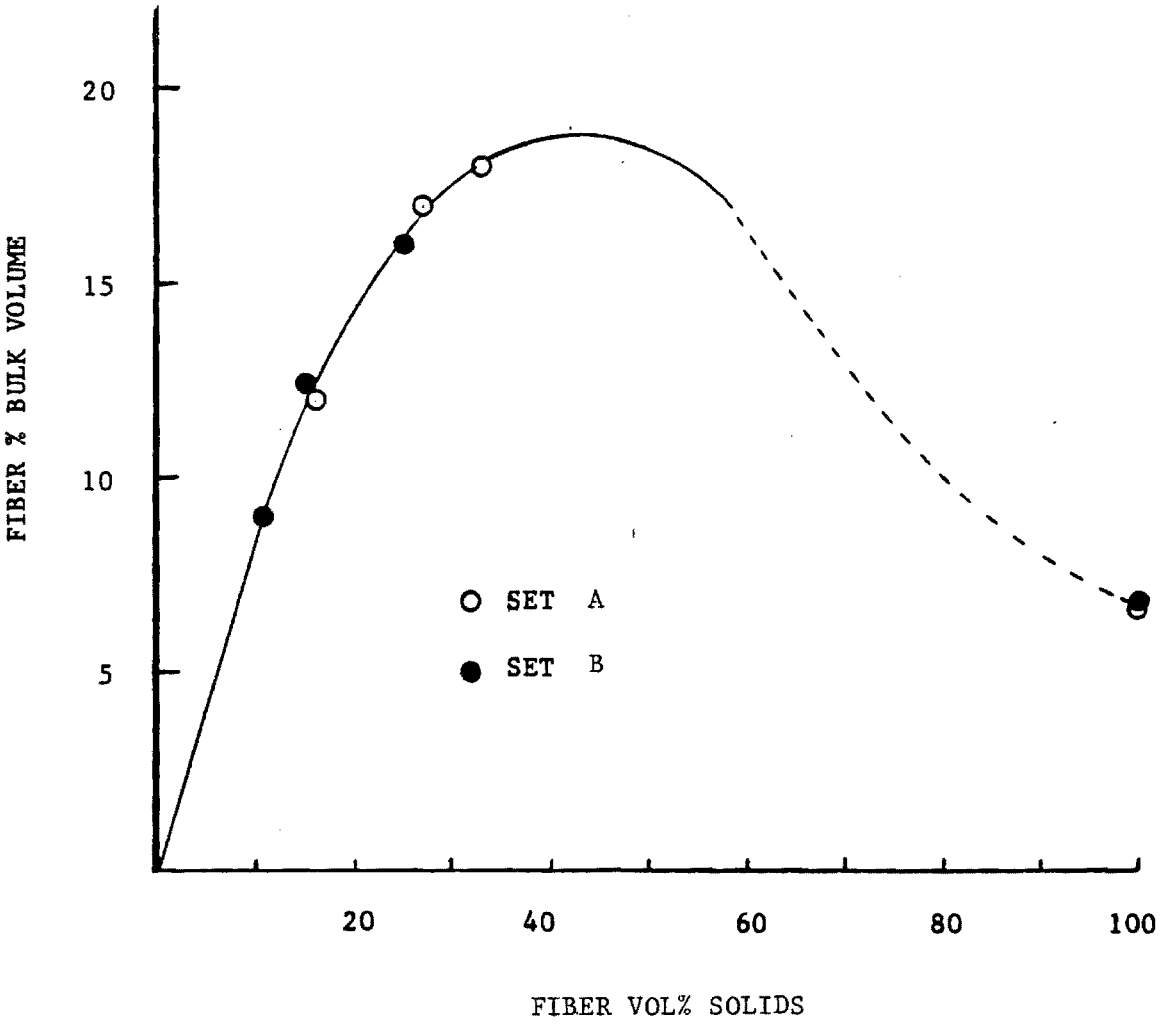


Figure 5. Loading of fiber in cast body

body is smaller than that of the as-cast body since during the impregnation process, resin will flow into all pores effectively reducing their diameters. Smaller pore size is expected to enhance sintering behavior.

Sintering schedules similar to those used for standard slip-cast fused silica produced bodies with relatively low porosity as shown in Figure 6. The plates containing 10.6 and 15.0% fiber sintered to porosities lower or equal to or lower than that of silica alone. At the higher fiber loadings, the final porosity achieved was substantially lower than that achieved without the impregnation step (6).

The higher sintering temperature (1250°C vs. 1200°C) produced a somewhat more dense bar but the improvement is not large. The effect of vacuum sintering on densification behavior is not clear but earlier work (9) indicated that it inhibits cristobalite formation which can become a problem at higher sintering temperatures. The cristobalite content of the two bars tested is well within the acceptable limit.

The modulus of rupture data for the fiber-loaded bars shows decreased strength when compared to the silica alone. However, the strength does not fall off significantly at the higher fiber loadings (Figure 7), which is contrary to what was found previously. This retention of strength is attributed to the lower porosity of these composites inspite of their higher fiber loadings. It should be noted that the MOR reported in Reference 6 for silica without fiber is

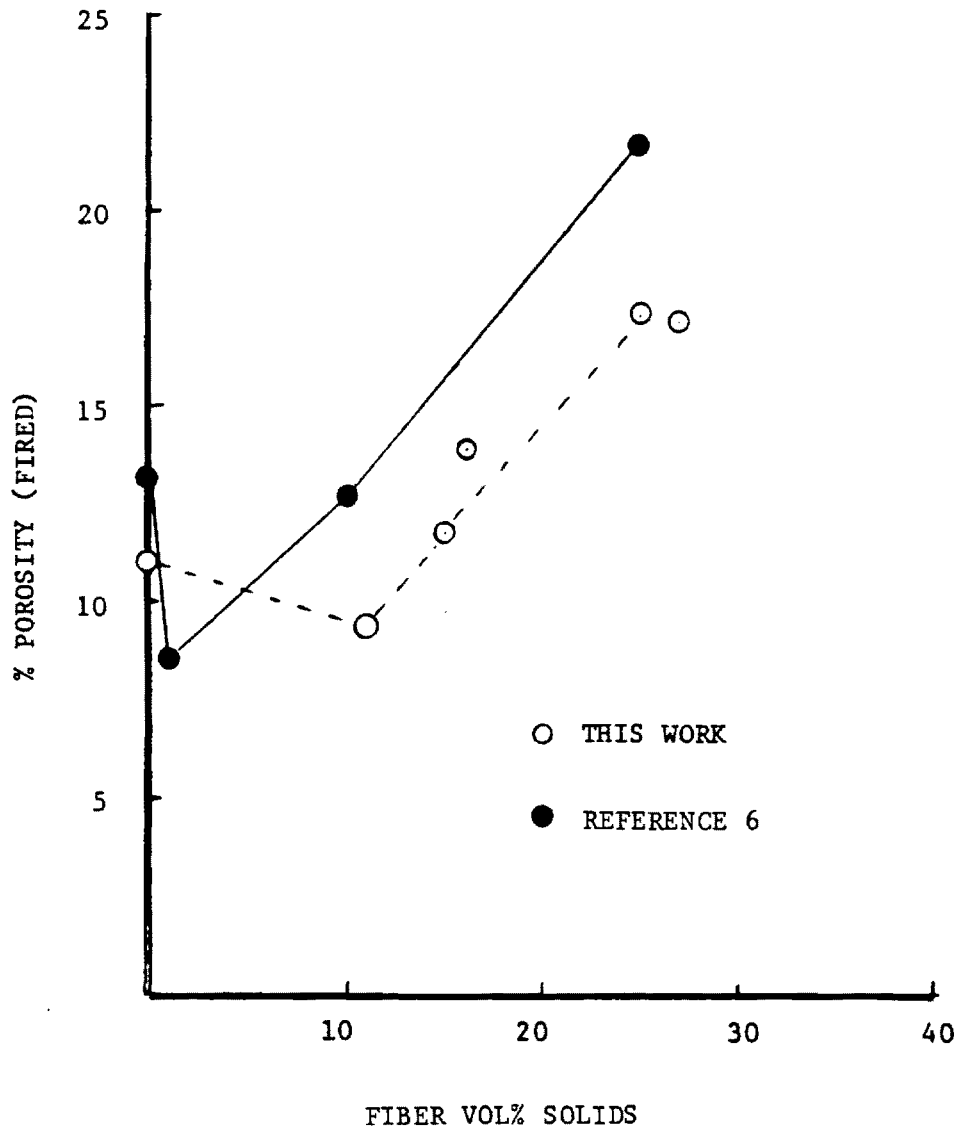


Figure 6. Porosity of Fiber-Containing Silica

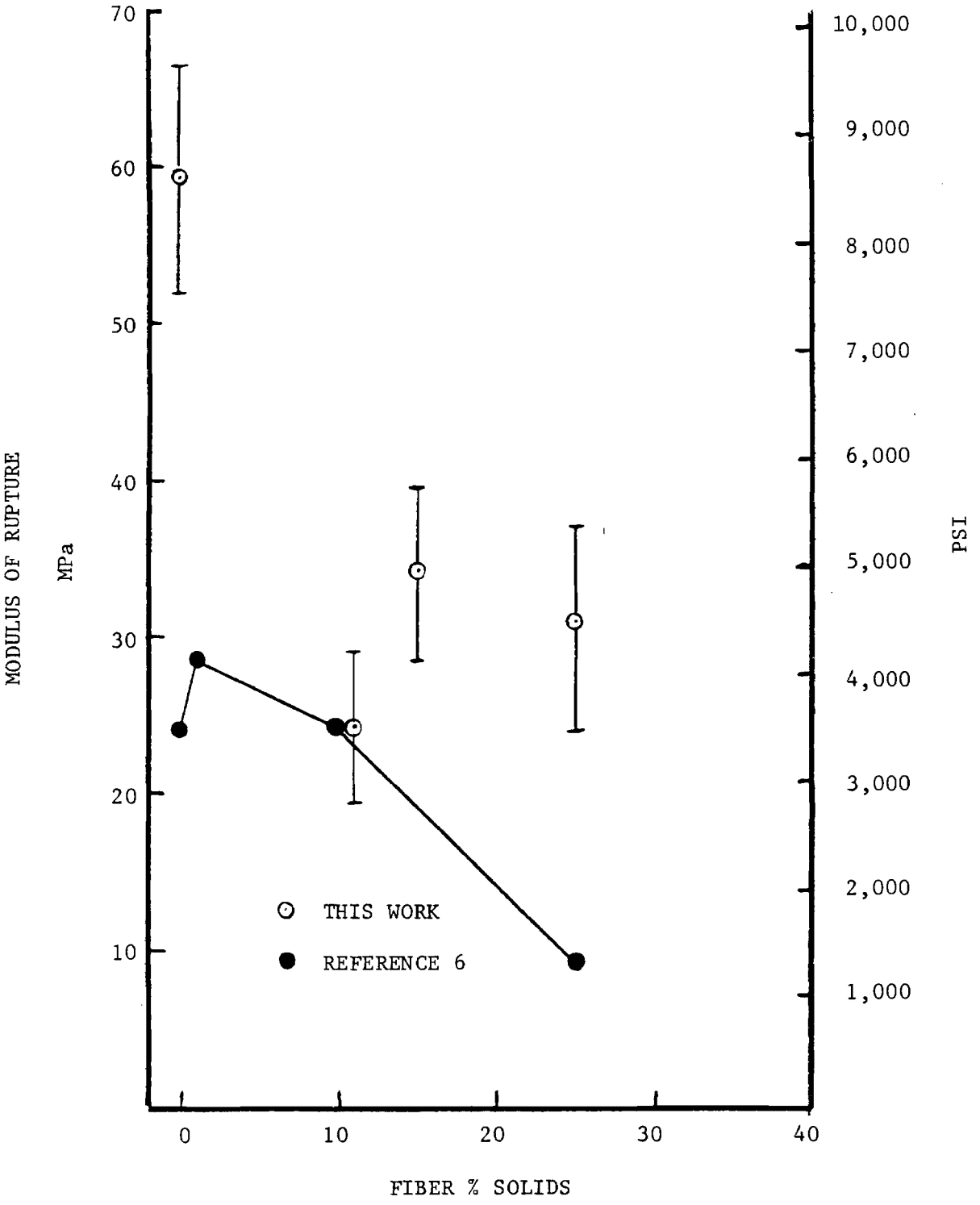


Figure 7. Flexure Strength of Fiber-Reinforced Silica

considerably lower, 24.1 MPa (3490 psi) than that reported here 59.3 MPa (8600 psi). No explanation for this discrepancy can be offered. Many determinations over several years have generally given an MOR for slip-cast fused silica of 30-40 MPa (4350-5800 psi) for as-cast bars and 60-65 MPa (8700-9400 psi) for machined bars.

Examination of the machined surface of the test bars (Figure 2) shows relatively large surface flaws for the fiber-containing bar. These appear to be fiber clumps that are not penetrated by the matrix and may be due to incomplete dispersion of the fibers during mixing with the slip. Since surface condition strongly influences MOR values, these flaws may be the cause of the lower strength for the fiber loaded bars. Comparison of the fracture surfaces (Figure 3) shows significant differences in topography. The silica (no fiber) surface is relatively smooth showing both trans-and intergranular fracture. The surface of the fiber-loaded bar is more convoluted with many fibers protruding. There are many indented regions which are a result of pull-out of material or the location of residual pores. The matrix between the fibers appears to have fractured primarily in the transgranular mode. The morphology of this fracture surface appears to imply a significant increase in work of fracture for the fiber loaded material.

VII. CONCLUSIONS AND RECOMMENDATIONS

Fabrication of fiber reinforced slip cast fused silica with high fiber loadings having increased density and strength as a result of using a TEOS based resin impregnation process has been demonstrated. However, there was no strength increase found when the Nextel® 312 fibers were added to the slip-cast fused silica. In fact, the strongest fiber loaded SCFS composite (15 v/o fiber) had only about 60% of the MOR strength of the neat SCFS specimens. Strength improvement of fiber loaded SCFS may be possible with better fiber blending technique. Although fracture toughness was not measured, fracture surface morphology suggests improved toughness may be possible due to increased fracture surface area which results from fiber pull-outs and porosity.

It is concluded from this study that fiber clumping and general lack of fiber dispersion prevented them from acting as reinforcing elements in the slip-cast fused silica composites. It is postulated that the poor dispersion or clumping observed is due to the high L/D ratio of the fibers used.

Additional investigation is recommended in the following areas:

1. Characterization. Additional mechanical characterization of the plates fabricated in this program is needed to properly evaluate the effects of fiber additions. This should include notched beam test-

ing to determine K_{IC} and work of fracture, and testing at elevated temperature.

2. Fiber processing. Additional development of fiber chopping and blending techniques is needed to better control fiber length and to eliminate localized clumping of fibers. Reduction of the maximum fiber length may allow higher fiber loadings without reducing the toughening effectiveness.
3. Sintering. Higher temperature processing may further improve the sintered density and strength. Potential deleterious effects of cristobalite formation should be monitored.

REFERENCES

1. J. F. Bacon and R. D. Veltri, "Development of Radome Material," AFML-TR-78-97, United Technologies Research Center, Final Report, July 1978.

2. K. M. Prewo and J. J. Brennan, "High Strength Silicon Carbide Fiber-Reinforced Glass Matrix Composites," Journal of Materials Science, 15 (1980), pp 463-468.

3. R. A. J. Sambrell, A. Briggs, D.C. Phillips and D.H. Bowen, "Carbon-Fiber Composites with Ceramic and Glass Matrices, Part 2. Continuous Fibers", J. of Mater. Sci., Vol. 7, pp. 676-681 (1972).

4. E. Fitzer and P. Schubert, "Fibre Reinforced SiO_2-Glass for Application at High Temperatures", Oxydes Refractaires Pour Filieres Energetiques de Haute Temperature, Odeillo, France, June 28 - July 1, 1977.

5. J. F. Bacon, K. M. Prewo and R. D. Veltri, "Glass Matrix Composites - II. Alumina Reinforced Glass", Proc. 2nd Int. Conf. on Composite Materials, Toronto, Canada, AIME, New York, pp. 752-769 (1978).

6. F.P. Meyer, "Effects of Various Additions on the Properties of Slip Cast Fused Silica", XV Symposium on EM Windows, Georgia Institute of Technology, June, 1980.

7. W. J. Corbett, A.T. Sales, and J.D. Walton, "Improving the Mechanical Properties of Slip-Cast Fused Silica by Fibrous Reinforcement", Georgia Tech Final Report, Project A-793, Contract No. 16-2092 for Sandia Corporation, August, 1965.

8. F.P. Meyer, G.C. Quinn, and J.C. Walck, "Fiber Reinforced Fused Silica for Hypersonic Radome Applications" XVII Symposium on Electromagnetic Windows, Georgia Institute of Technology, July, 1984.

9. T. L. Starr and J. D. Walton, "A Program to Improve the Strength and Toughness of Sintered Fused Silica", Georgia Tech Final Report Project A-3432 under Office of Naval Research contract N0014-83-K-0159, January, 1984.

10. J.N. Harris, "Radome Materials Fabrication", Final Report for Naval Surface Weapons Center contract no. N60921-82-C-0126, July, 1983.

11. J.V. Milewski, "How to Use Short Fiber Reinforcements Efficiently", 37th Annual Conference, Reinforced Plastics/Composites Institute, the Society of the Plastics Industry, January 11-15, 1983.