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FEASIBILITY AND PROCESS SCALE-UP OF LOW COST ALUMINA FIBERS FOR ADVANCED RE-USABLE SURFACE INSULATION (RSI)

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16. Abstract

The objective of this program was to establish feasibility of a process to produce low cost aluminum oxide fibers having sufficient strength, flexibility, and thermal stability for multiple re-use at temperatures to 1480°C in advanced RSI type heat shields for re-entry vehicles. Using bench-scale processing apparatus, the Alcoa "Saphiber" process was successfully modified to produce nominally 8 μm diameter polycrystalline alpha-alumina fiber. Thermal stability was demonstrated in vacuum reheating tests to 1371°C and in atmospheric reheating to 1483°C. Individual fiber properties of strength, modulus and flexibility were not determined because of friability and short length of the fiber.

Rigidized tile produced from fiber of nominally 8, 20 and 40 μm diameter had thermal conductivities significantly higher than those of RSI SiO_2 or mullite at relatively low temperature but became comparable above about 1000°C. Tile densities were high due to short fiber length, especially in the coarser diameter fiber. No significant effect of fiber diameter on thermal properties could be determined from the data. Mechanical properties of tiles deteriorated as fiber diameter increased. Many operating problems remain to be solved before the process to manufacture <10 μm fiber could be considered commercial.

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TABLE OF CONTENTS

	Page No.
SUMMARY	1
INTRODUCTION	2
RESULTS AND DISCUSSION	4
Task I	
Raw Materials	4
Table 1 - Analysis of Alcoa A-16 and Ugine-Kuhlmann Aluminas	5
Table 2 - Analysis of Cabot Corp. Cab-O-Grip Aluminas	5 6
Screening Tests	6
Figure 1 - Slip N-24: Spinning Properties vs. Needle Size	8
Table 3 - Summary of Slip Compositions and Spinning Behavior	9-10
Table 4 - Physical Properties of Base Aluminas.	13
Task 2	
Multi-Filament Extrusion	14
Figure 2 - Extrusion Data for Filtered and Unfiltered Slips	16
Figure 3 - Cross Sectional Drawings of Spinneret Holes	17
Thermal Stability Testing	19
Figure 4 - Saphiber Thermal Stability Cycle	21
Table 5 - Summary of Fiber Properties	22
Figure 5 - Fiber Grain Size Before and After Thermal Cycling	23
Figure 6 - Composition N-103 - Green Fiber	24
Figure 7 - Composition N-103 - Fired at 1400°C	25
Figure 8 - Composition N-103 - Fired 1400°C Vacuum Reheated 25 Cycles @ 1371°C	26
Figure 9 - Composition N-103 - Fired 1500°C	27
Figure 10 - Composition N-103 - Fired 1500°C Vacuum Reheated 25 Cycles @ 1371°C	28
Figure 11 - Composition N-103 - Fired 1550°C	29
Figure 12 - Composition N-105 - Fired 1400°C	30
Figure 13 - Composition N-105 - Fired 1400°C Vacuum Reheated 25 Cycles @ 1371°C	31
Evaluation in Rigidized Tile	32
Table 6 - Comparison of Experimental Alumina Fiber Tile with LI-900 RSI	32
Task 3	
Table 7 - Thermal Conductivity of Saphibers	33

TABLE OF CONTENTS - (CONTINUED)

	Page No.
CONCLUSIONS.....	34
APPENDIX A--Exploratory Development of a Rigidized α-Alumina Composite (General Electric Co.).	35
APPENDIX B--Evaluation of Rigidized Alumina Fiber Tiles (General Electric Co.).....	36

SUMMARY

The objective of this program was to establish feasibility of a process to produce low cost aluminum oxide fibers having sufficient strength, flexibility and thermal stability for multiple re-use at temperatures to 1480°C in advanced RSI type heat shields for re-entry vehicles.

Using bench-scale processing apparatus, the Alcoa "Saphiber" process was successfully modified to produce nominally 8 μm diameter polycrystalline alpha-alumina fiber. During the sintering step of fiber manufacture, bonding occurred between fibers necessitating a screening operation to separate fiber after sintering. Significant breakdown of fiber occurred during this step leaving short fiber with less than 1 mm average length (aspect ratios of 13 to 22). Because of this, individual fiber properties of strength, modulus and flexibility could not be measured.

Bulk fiber was subjected to 25 cycles of 60 minutes each of vacuum (10 Torr) reheating to 1371°C. No change in fiber diameter, grain size, chemical or phase composition resulted from reheating, demonstrating the fiber's excellent thermal stability. To evaluate the usefulness of the 8 μm alumina fiber as a potential RSI material, small samples were rigidized and subjected to thermal and mechanical testing. Compared to SiO_2 RSI, this preliminary work showed rigidized tile to have a relatively high density of 37 pcf, good mechanical properties but high thermal conductivity of 6.5 to 5.5 x 10^{-5} BTU/ft. sec. °F over the range of 125 to 520°F. These results indicated the 8 μm alumina fiber was inferior to SiO_2 based RSI for low-temperature service, but did not eliminate its use in applications where higher temperatures would be encountered.

Larger quantities of fiber were then prepared for a more extensive evaluation in rigidized tile. In addition to 8 μm fiber, nominally 20 and 40 μm fiber lots were also evaluated. The coarser fiber was included for two reasons. First, serious problems were encountered in producing 8 μm fiber which would have to be overcome before this material could be considered commercial. Second, previously developed Alcoa data showed thermal properties of rigidized tile prepared from 60 μm alumina fiber were similar to those of 8 μm fiber. Since production of coarse fiber involves fewer processing problems and lower cost, it was of interest to compare the relative merits of these materials.

Rigidized tile produced from fiber of nominally 8, 20 and 40 μm diameter had thermal conductivities significantly higher than those of RSI SiO_2 or mullite at relatively low temperature but became comparable (about 3 x 10^{-5} BTU/ft. sec. °F) above 1000°C. However, considerable scatter exist in these data.

Thermal stability of the alumina fiber was again demonstrated during tile fabrication with no apparent change after firing to 1483°C and holding 2 hours. Surprisingly, no significant effect of fiber diameter on thermal properties could be determined from the data. Tile densities were high at 30 to 50 pcf, reflecting the short fiber length. Mechanical properties of tiles prepared from the coarser fiber were poor, apparently due to friability and shortness of the fiber.

At the present state of development, fiber produced in this program would not be competitive as an RSI material. Thermal stability is good but fiber strength and aspect ratio are not sufficient to allow formation of low density tile with good mechanical properties. Since a significant decrease in tile density would be required to reduce thermal conductivity and reduce weight for airborne applications, future development efforts should be aimed at increasing strength and length of alumina fiber.

INTRODUCTION

This investigation was part of NASA's overall program to develop a reusable surface insulation (RSI) for use on the space shuttle. When this investigation was undertaken the most promising ceramic fiber materials were silica and mullite. It was recognized that although these fibers possessed excellent insulating properties, they were limited in maximum use temperature. It was recognized that aluminum oxide with its inherent refractoriness, inertness and high strength should be an ideal insulating material if it could be produced at reasonable costs in the desired fibrous form. Previous attempts to form alpha-alumina fibers by salt decomposition techniques had been unsatisfactory due to rapid crystal growth and phase changes during the calcination process. Single crystal alumina whiskers had been formed by vapor deposition and were available in small quantity but costs were prohibitive.

At the time the NASA RSI development program was underway Alcoa Laboratories was studying high-purity polycrystalline alumina fiber ''Saphibers'' for bulk insulation applications. This material was approximately 99% Al_2O_3 but by NASA's standards was rather large in diameter at about 20 μm. The main objective of this contract work was to modify the existing proprietary Alcoa process so that finer fiber in the 5-10 μm diameter range could be produced and evaluated for use as RSI insulating material.

The Alcoa process began by preparing a slurry (slip) of finely divided alpha-alumina particles in an organic solvent by ball milling. The use of alpha-phase alumina in the initial step eliminated undesirable phase changes in later steps of the process. After a uniform dispersion was obtained, specific resins, polymers, and plasticizers were added to the system to provide the characteristics required for further processing. The slip was then extruded under pressure through a small diameter nozzle forming a continuous stream which dried very rapidly to a coherent filament. The green filament was attenuated and collected by winding on a take-up drum. Attenuation was produced by tension on the fiber which was varied by adjusting the take-up speed. The final step of the process was firing the fiber to burn out the organic material and sinter the alumina powder to form a dense, polycrystalline ceramic in fibrous form.

Before entering into the contract, it was agreed that the proprietary slip formulations previously developed by Alcoa would remain the confidential property of Alcoa. For this reason, specific formulations are not given in this report and only general features of slip composition are reported to help the reader understand the nature of the investigation. Specific details of formulations and experimental work are recorded in Alcoa Laboratories Record Books 15230, 15525, 15521 and 15228.

Work on this project was divided into 3 working tasks and a reporting task. In Task 1 raw materials were obtained, prepared and analyzed. A flexibility test apparatus was designed and constructed and a series of single filament spinning experiments were run to determine which parameters of the process could be changed to produce the fine diameter fiber desired. In Task 2 firing studies were made and larger quantities of the most promising products were produced and evaluated for microstructure and thermal stability. Preliminary tests were made to determine usefulness of the fine diameter alumina fiber in a rigidized tile configuration.

As originally planned, Task 3 was to be a scale-up to pilot plant size of the most successful process modifications found in Task 1 and 2. By the time we were ready to begin work on Task 3, however, it had become apparent from other NASA-sponsored work that fiber suitable as RSI material would need to have 1-2 μm diameter rather than 5-10μm as developed in Tasks 1 and 2. Because of this it was agreed between NASA and Alcoa that the funds originally allocated to Task 3 would be better used in a more detailed evaluation of fiber properties to determine the usefulness of polycrystalline alumina fiber in applications other than RSI for the space shuttle. Since Alcoa did not have existing in-house capability to produce rigidized test specimens and perform sophisticated thermal conductivity work, it was agreed that a sub-contract would be let to General Electric to do specimens preparations and evaluation using Alcoa produced alumina fiber in several size ranges. Copies of General Electric

fiber evaluation work are attached as appendices to this report. The reason for looking at a range of fiber diameters in the Task 3 evaluation work was that 5-10 μm fiber can be obtained only by greatly sacrificing production rate and increasing production costs. Preliminary thermal conductivity data generated both in Task 2 and before beginning this program, indicated that surprisingly fiber diameter over a range of 8 μm to 60 μm made little difference in thermal conductivity of rigidized tests specimens. Obviously, if coarser diameter fiber could be used, this would make the manufacturing process less complicated and consequently cheaper. Three lots of fiber with nominal diameters of 8, 20, and 40 μm were included in the revised Task 3 evaluation work.

This work demonstrated that polycrystalline alumina fiber with diameters below 10 μm can be produced by modification of the Alcoa Saphiber process. Individual fibers are quite weak and friable but rigid insulating tile with good mechanical properties were fabricated. Excellent thermal stability of the fiber to temperatures of 1480°C was demonstrated. Thermal conductivities of rigidized tiles prepared from alumina fiber were much higher than for fine-diameter SiO_2 and mullite fiber at low temperatures but appear to become comparable at high temperatures. Several problems need to be resolved before the process could be considered commercial. Further reduction of fiber diameter to the 1-2 μm range does not seem feasible by this process.

RESULTS AND DISCUSSION

Task I

Raw Materials - A primary objective of Task I was to identify major variables that would allow reduction of fiber diameter to below 10 μm. Without modification, the Alcoa process typically produced material in the 20-30 μm diameter range.

One important process variable is the type of alumina used to make the fiber-forming slip. The primary alumina used in Alcoa's fiber development work is Alcoa A-16 alumina. This is a highly reactive, fine particle size, high purity alpha-alumina available in commercial quantities. Analysis of the A-16 alumina used in this work is shown in Table 1. Since the goal of this program was to produce the smallest possible fiber diameter it seemed reasonable to investigate aluminas having particle size even finer than A-16 alumina as starting raw materials. Those selected were 3 calcined aluminas produced by Ugine-Kuhlman designated A.6R, A.15R and A.25R. These products all have similar very high purity but differ in degree of calcination as indicated by surface area. Analyses are also shown in Table 1. Initial work with these materials indicated

they were not completely ground so additional milling was performed on all 3 materials as will be discussed later in the report.

TABLE 1 - ANALYSIS OF ALCOA A-16 AND UGINE-KUHLMANN* ALUMINAS

Sample No.	P-1088-4	S-9052	S-9053	S-9010
Product	Alcoa A-16	Ugine A.6R	Ugine A.15R	Ugine A.25R
Analysis (%)				
SiO_2	.022	.012	.014	.012
Fe_2O_3	.013	<.003	<.003	<.003
TiO_2	.001	<.001	<.001	<.001
Na_2O	.061	<.003	<.003	<.003
CaO	.006	<.003	<.003	<.003
Ga_2O_3	.003	<.001	<.001	<.001
B_2O_3	<.001	<.001	<.001	<.001
MnO	.0007	<.0001	<.0001	.0002
Cr_2O_3	.0002	.0002	.0002	.0001
MgO	.052	<.0005	<.0005	<.0005
ZnO	<.0005	<.0005	<.0005	<.0005
CuO	<.0005	<.0005	<.0005	<.0005
V_2O_5	.0002	.0002	<.0001	<.0001
Surface Area (m^2/g)	10.6	7.2	16.3	28

*Product of Ugine-Kuhlman of America, Inc.

It was originally planned to produce alumina samples of smaller particle size by controlled calcination of Cab-O-Grip, a high purity, fine-particle size gamma phase alumina produced by Cabot Corporation. A 19-liter (5 gallon) quantity of Cab-O-Grip D was purchased for this work. Cab-O-Grip D is a 30% solids aqueous suspension of Cab-O-Grip and was purchased in this form to facilitate further processing. The material was dried at 110°C and portions calcined at 1150 and 1200°C in a gas-fired furnace. Analyses of the dried and calcined products, and analysis of a previously obtained sample are shown in Table 2. Comparison of the data shows that the sample obtained for this work (G-9046) contained an unacceptably high iron level. Because of this it was decided not to use these materials in the screening program. The three grades of Ugine-Kuhlman aluminas described above were substituted for the originally proposed Cab-O-Grip derived materials.

TABLE 2 - ANALYSIS OF CABOT CORP. CAB-O-GRIP ALUMINAS

Sample No.	S-8997	G-9046		
Product	Cab-O-Grip	Cab-O-Grip D		
Calcination Temp. (°C)	As Rec'd.	As Rec'd.	1150	1200
Analysis (%)				
SiO_2	.044	.11	.13	.13
Fe_2O_3	.005	.26	.32	.32
TiO_2	.002	.012	.012	.012
Na_2O	<.003	.004	.023	.016
CaO	.007	.024	.032	.031
Ga_2O_3	.001	.002	.003	.003
B_2O_3	<.001	<.001	.001	.001
MnO	.0005	.0016	.0024	.0020
Cr_2O_3	.0002	.0005	.0006	.0005
MgO	.0006	.010	.018	.017
ZnO	<.0005	<.0005	.005	.005
CuO	<.0005	.005	.004	.005
V_2O_5	<.0005	.0004	.0010	.0009
Surface Area (m^2/g)	105	64	10.2	7.9

Screening Tests - Thirty-five slip compositions were evaluated in a screening program to identify workable formulations which would produce fiber in the desired 5-10 μm size range. Slips were prepared on the bench scale by ball milling 3 kg batches in 4.9 liter (1.3 gal) ceramic jar mills using 6 kg charges of 2.5 cm (1 inch) diameter 96% Al_2O_3 grinding balls. All of the slips in this series consisted of Alcoa A-16 or Ugine-Kuhlman Al_2O_3 suspended in an organic solvent with several plastic ingredients added. Each of these compositions was evaluated for fiber forming characteristics using the bench scale extrusion-attenuation equipment. Using nitrogen pressure, slip was pressurized causing it to extrude or flow through short, blunt-end hypodermic needles. Various size hypodermic needles were used ranging in I.D. from 110 to 250 μm and approximately .25 cm in length. Extrusion pressures up to 6.9×10^{-5} N/m^2 (100 psi) were used. A 7.5 cm (3 inch) cylinder rotating on an axis parallel to the floor and located 1.8 meters (6 ft) below the extrusion nozzle was used to wind the fiber. For a given needle size, pressure was adjusted to produce continuous flow and take-up speed was adjusted to the maximum possible before fiber breakage became excessive. By operating at the lowest practical extrusion rate and maximum practical take-up speed, the minimum diameter fiber was produced for each composition.

Except for one test described below, all work was done at ambient room temperature of approximately 25°C. A summary of slip composition and spinning behavior is shown in Table 3.

The data in Table 3 are a highly simplified summary of results of the bench scale spinning tests. In practice, for each slip composition extrusion runs were made using a series of hypodermic needle sizes. For each needle size, pressure was adjusted to obtain a continuous flow through the needle. Fiber take-up speed was then adjusted to the maximum before fiber breakage became excessive. The objective, of course, was to find the most reasonable operating conditions for producing fiber below the 10 μm target diameter. Figure 1 shows more complete spinning data for slip No. 24 and illustrates the trends observed in the program. In general, as needle diameter was decreased, pressure necessary to obtain continuous flow increased, the minimum continuous flow rate decreased and the diameter of the resultant fiber decreased.

Slip composition N-1 was used as a starting point in this work. This composition had been developed in earlier Alcoa-sponsored work and is well suited to producing fiber in the 20-25 μm diameter range. While extruding through a 250 μm I.D. needle at a rate of approximately .15 g/min (green fiber weight basis) a maximum take-up speed of 2.5 m/sec could be used. This resulted in rather coarse fiber of approximately 20 μm diameter. An attempt was made to extrude this slip through the 110 μm I.D. needle, but continuous flow could not be attained. Slips N-2 and N-3 were identical to the N-1 composition except that the alumina content was reduced. These slips were too fluid to produce the necessary continuous flow and as a result fiber-forming conditions could not be established. Composition N-7 was the fourth member of this series and could be extruded in a continuous stream through the 110 μm needle at a flow rate of .04 to .05 g/min. Using a maximum take-up speed of approximately 6.5 m/sec, 10 μm diameter fiber was produced. This slip had the undesirable property, however, of plugging the small diameter needle within a few minutes of operation. Needle plugging was a persistent problem throughout this project and will be discussed further below.

A somewhat different composition (N-4), which had also been developed in earlier Alcoa funded Saphiber work, was used as the starting point in a second series. Extruding through the 110 μm needle at .02 to .04 g/min and take-up speed of approximately 1.5 m/sec produced fiber in the range of 10 to 15 μm diameter. Compositions N-5 and N-6 were identical to N-4 except for reduced alumina contents. Composition N-5 was extruded through the 250 μm needle at a rate of about .075 g/min and take-up speed of 6 m/sec producing green fiber in the 12-20 μm diameter range. The same slip, when extruded through a 110 μm needle at .025 g/min and take-up speed of 2.6 m/sec produced fiber approximately 10 μm in diameter. This material had good

FIGURE 1 - SLIP N-24: SPINNING PROPERTIES VS. NEEDLE SIZE

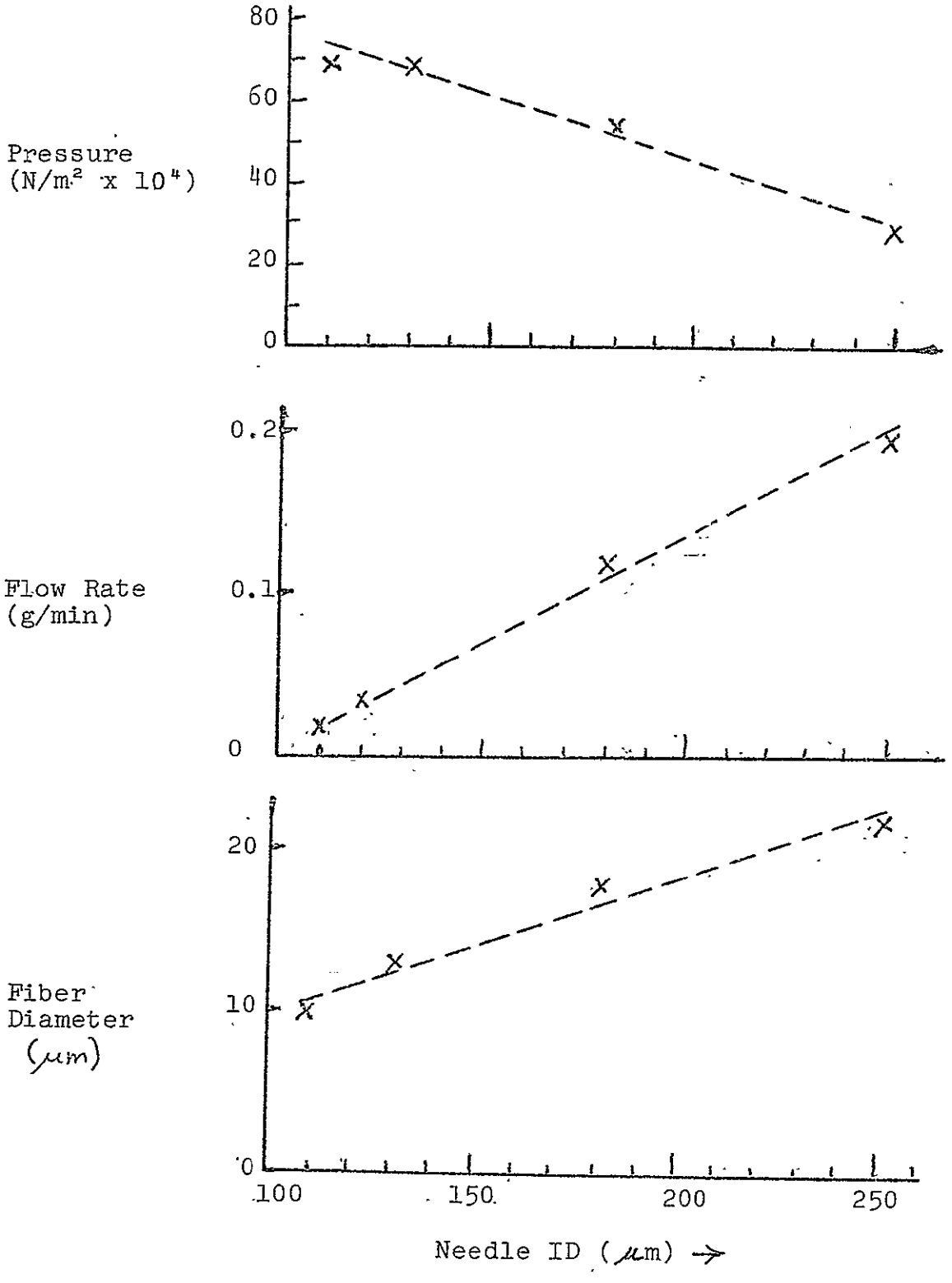


TABLE 3 - SUMMARY OF SLIP COMPOSITIONS AND SPINNING BEHAVIOR

Slip	Al_2O_3 Type	Al_2O_3 Content (Wt %-TWB)	Plastics Content (Wt %-Al_2O_3 Basis)	Viscosity[1] (cp)	Remarks
N-1	A-16	42.5	16.0	26,000	Good operation with 20-27 μm fibers
N-2	"	25.0	35.6	8,000	Too fluid, pulsating flow
N-3	"	12.5	81.8	5,800	" " " "
N-4	"	30.8	19.7	29,200	10-15 μm fiber, plugged small needles
N-5	"	25.0	26.3	21,200	8-12 μm fiber, fairly good spinning
N-6	"	12.5	61.6	11,200	5 μm fiber, good spinning
N-7	"	33.3	20.6	11,600	10 μm fiber, plugged small needles
N-8	"	25.0	22.9	17,600	9-10 μm fiber, fairly good spinning
N-9	"	12.5	38.2	28,800	Pulsating flow, poor spinning
N-10	"	12.5	38.2	34,200	" " " "
N-11	"	20.0	26.3	24,800	10-12 μm fiber, fair spinning
N-12	"	15.0	31.8	21,600	Poor green strength
N-13	"	12.5	36.3	20,800	Drip-wise flow
N-14	"	20.0	20.5	26,800	" " "
N-15	"	20.0	28.6	27,600	Fair spinning with 130 μm needle
N-16	A.6R	25.0	22.9	28,000	Poor spinning, rapid plugging
N-17	A.15R	25.0	22.9	38,800	Poor spinning, too viscous
N-18	A.25R	18.7	30.2	30,600	Poor spinning, rapid plugging
N-19	A-16	20.0	35.0	15,000	9-10 μm fiber, good spinning
N-20	A.6R	20.0	35.0	16,800	10-12 μm fiber, fair spinning
N-21	A.15R	20.0	35.0	29,200	10-12 μm fiber, fair spinning
N-22	A.6R(G)[2]	20.0	35.0	15,600	7-10 μm fiber, good spinning
N-23	A.15R(G)[2]	20.0	35.0	27,000	9-12 μm fiber, good spinning
N-24	A.6R(G)	25.0	22.9	31,600	Fair spinning, rapid plugging
N-25	A.15R(G)	21.7	27.5	33,600	Fair spinning, rapid plugging

Continued-

(1) Brookfield viscometer, spindle RVT-5, 10 rpm.
(2) Dry ball milled before use.

TABLE 3 – SUMMARY OF SLIP COMPOSITIONS AND SPINNING BEHAVIOR – (CONTINUED)

Slip	Al_2O_3 Type	Al_2O_3 Content (Wt %-TWB)	Plastics Content (Wt %-Al_2O_3 Basis)	Viscosity[1] (cp)	Remarks
N-26	A.25R(G)[2]	20.0	35.0	34,600	Fair spinning, rapid plugging
N-27	A.6R(G)[2]	25.0	21.9	29,200	Good spinning, better than N-24
N-28	A.6R(G)[2]	25.0	20.9	23,600[3]	Poor spinning, low green strength
N-101	A-16	25.0	22.9	36,400[3]	Fair spinning, rapid plugging
N-29	"	"	23.6	23,400	Fair spinning, rapid plugging
N-30	"	"	22.9	32,600	" " " "
N-31	"	"	21.6	22,600	Fair spinning, good flow
N-32	"	"	20.7	16,400	Low green strength, good flow
N-33	"	"	23.2	20,000	10 μm fiber, fairly good spinning
N-34	A.6R(G)[2]	"	"	23,200	Fair spinning, good flow
N-35	A.15R(G)[2]	23.3	24.9	35,200	Fair spinning, rapid plugging
N-103	A-16	25.0	23.2	20,200[5]	Multi-filament spinning
N-104	"	"	"	24,000[3]	" " "
N-105	A.6R(G)[2]	25.0	23.2	23,000[5]	Multi-filament spinning
N-19F[4]	A-16	20.0	35.0	17,200	8 μm fiber, v. good spinning
N-22F	A.6R(G)[2]	"	"	19,400	7 μm fiber, v. good spinning
N-23F[4]	A.15R(G)[3]	"	"	27,000	10 μm fiber, good spinning

(1) Brookfield viscometer, spindle RVT-5, 10 rpm.
(2) Dry ball milled before use.
(3) Triple-size batch containing 1.0% Pfizer Microtalc (Al_2O_3 basis).
(4) Filtered through 20 μm Nylon cloth.
(5) Triple-size batch containing 0.25% Fisher c.p. MgO (Al_2O_3 basis).

flow characteristics and less tendency to plug the small diameter needle than observed in previous slips. Composition N-6 had extremely good flow characteristics and when extruding through the 110 μm needle at .02 g/min could be wound at 4.5 m/sec producing green fiber of approximately 5 μm diameter. From both extrusion and green strength standpoint N-6 was the best composition of the series, although plastics level was later found to be excessively high at 61.6% (Al_2O_3 basis).

Composition N-8 was similar to N-5 but with a slight reduction in plastics content. By extruding this material through the 110 μm needle at a rate of about .026 g/min and using a take-up speed of 5.5 m/sec, green fiber in the range of 9-10 μm diameter was produced. To evaluate the effect of slip temperature on the spinning operation, the slip was cooled to 11°C compared with the ambient temperature of 26°C. Under these conditions, take-up speed could be increased to 8.5 m/sec and fiber in the 7 to 8 μm diameter range was produced. This showed that a slight reduction in fiber diameter can be achieved if evaporation rate near the extrusion nozzle is reduced.

Compositions N-9 through N-15 were further attempts to reduce alumina content and also reduce plastics level without sacrificing extrusion and/or winding characteristics. As indicated in Table 3 none of these compositions had properties comparable to N-5, 6 or 8.

At this point in the study the 3 Ugine-Kuhlman aluminas were substituted into the slip composition to study the effects of starting alumina particle size on the overall process. Compositions N-16, 17 and 18 were intended to be the same as N-8 except for the change in alumina type. The higher surface area A.25R Alumina did not become fluid at that solids level so the necessary solids reduction was made. None of these slips performed satisfactorily in the spinning work. Flow was erratic and resulting green fiber had low strength and could not be wound. In addition, the small diameter needle plugged rapidly on all three of these compositions. Slips N-19 through 21 were then formulated to determine if further reduction in solids level would improve extrusion characteristics. As expected, the A-16 composition (N-19) performed quite well, producing fiber in the 9-10 μm diameter range. The two Ugine products, however, produced fiber with significantly less green strength, necessitating a reduction in winding speed with a resulting coarsening of fiber diameter. Also, it was observed microscopically that fiber produced from the Ugine aluminas had much rougher surface than those produced from A-16 slips.

The poor spinning behavior and relative roughness of fiber obtained from the Ugine alumina based slips suggested that these materials were not fully ground, even though they had been wet-milled as part of the standard Saphiber slip preparation procedure.

To test this hypothesis the three Ugine products were dry milled for 8 hr in 4.9 liter (1.3 gal) ceramic jar mills using 6 kg charges of 2.5 cm (1 in) diameter 99.7% Al_2O_3 grinding balls. In these grinds the speed of rotation was 70 rpm and 300 g of alumina were charged. These grinding conditions were known from Alcoa experience to provide extremely good grinding for this type of alumina. Both ground and unground materials were analyzed for surface area (Perkin-Elmer Shell Sorptometer) and particle size (Micromeritics Sedigraph) to determine the effectiveness of the grinding operation.

Samples of these ground materials were dry pressed at 3.45×10^7 N/m^2 (5000 psi) to form cylindrical compacts 2.54 cm diameter by .5 to 1 cm thick. These specimens were then heated for 1 hr at 1500°C in a gas fired furnace and densities of the fired and green (as pressed) specimens were determined. This ''ceramic reactivity test'' is an indication of the ability of an alumina powder to densify by sintering and is a useful tool in comparing alumina powders. Those which densify to near theoretical density (3.987 g/cc) are generally much more desirable as raw materials for high purity alumina ceramics.

It can be seen from Table 4 that the ceramic reactivity of all three Ugine products was greatly enhanced by the dry milling operation. The Alcoa A-16 was not ball milled since this material had already been intensively milled in production. Fired densities of the A-16, A.6R and A.15R ground products are considered excellent under these conditions, while that of the A.25R is considerably lower, probably because of its initial lower alpha alumina content. It is interesting that surface areas of the three products were essentially unchanged by the ball milling operation, although particle sizes were reduced drastically. This was not completely unexpected and simply indicates the presence of very porous particles in the as-received product. Compositions N-22 and 23 were prepared using the ground Ugine materials and performed significantly better than their unground counterparts (compositions N-20 and 21) demonstrating that dry ball milling prior to incorporation into the composition was beneficial.

Slips N-24 through N-28 were further attempts to incorporate Ugine-Kuhlman alumina products to provide fibers with a range of starting particle sizes. Prior to use in slips these aluminas were dry ball milled as described above. None of these slips were completely satisfactory as only moderate take-up speeds could be used and rapid plugging of the small diameter needles occurred during extrusion. In one case (N-28) the binder level had been reduced to the point where a significant loss in green strength was observed. The marginal fiber forming characteristics of these slips was attributed to their abnormally high viscosities.

TABLE 4 - PHYSICAL PROPERTIES OF BASE ALUMINAS

Product	Dry Grind Time (hr)	Surface Area (m^2/g)	α-Al_2O_3 %	Med. Particle Size (μ)	Ceramic Properties Density (g/cc) As Pressed	Ceramic Properties Density (g/cc) 1h-1500°C
Alcoa A-16	-	10.6	91.4	0.43	2.19	3.89
Ugine A.6R*	0	7.2	99.2	7.0	1.44	2.89
" "	8	7.9	-	0.23	2.14	3.94
Ugine A.15R*	0	16	91.0	4.6	1.30	2.84
" "	8	15	-	0.20	2.02	3.91
Ugine A.25R*	0	28	76.1	4.0	1.26	2.87
" "	8	25		0.17	1.93	3.75

*Product of Ugine-Kuhlman of America, Inc.

At that point in the program a larger quantity of A-16 alumina based slip (N-101) was prepared for multi-filament spinning which will be described in a later section of this report. Slip N-101 had the same composition as N-8 but with the addition of 1.0% talc (alumina basis). This large batch (9 kg total wt compared to 3 kg batches used in the Task I study) was found to have an unexpectedly high viscosity of 36,400 cp compared to the 17,600 cp previously obtained for N-8. The high viscosity caused difficulty in slip handling as well as poor extrusion properties. Previous work had indicated that the 1% talc addition should have little effect on viscosity, so variability in one or more of the remaining 8 components of the system was suspected.

A short series of tests (N-29 through N-33) was then made to find a way around the high viscosity problem. Slip N-30 was a repeat of N-8 using currently available components and also exhibited the high viscosity seen in slip N-101. Since an extensive series of tests would have been necessary to determine which of the components produced the variability, it was decided not to pursue this further but to adopt composition N-33 for further scale-up work. If additional development work on this process was done, it would be necessary to identify the causes of variability in raw materials to ensure reproducibility of the process. Unfortunately, extended work in this area was beyond the scope of the present study. Slip N-34 was identical in composition to N-33 except for the substitution of A.6R alumina. N-34, like N-33, exhibited low viscosity and reasonably good spinning characteristics.

Approximately 250 samples of green fiber produced during the screening program were examined microscopically and diameters were estimated. A condensation of this data appears in Table 3. Photomicrographs of 14 selected samples were made for historical purposes.

The work in this task demonstrated that the Saphiber process could be modified to produce green fiber of less than 10 μm diameter provided substantial changes in slip formulation were made and a spinneret needle of 110 μm minimum was used. Raw materials were found to be high-purity alumina and surface areas of the Ugine-Kuhlman aluminas were approximately as expected based on product literature. Dry grinding of the U-K materials significantly reduced particle size and improved processing characteristics but surface areas were essentially unchanged by the grinding step.

Task 2

Multi-Filament Extrusion - The original concept of Task 2 was to scale up the fiber process to the extent that hundred gram quantities of several fiber compositions could be produced and evaluated for mechanical and physical properties as well as thermal stability. During the work on Task 2 several problems and conceptual changes occurred which altered the course of the investigation. The major change in approach was caused by the short, friable nature of the fired fiber which made impossible the determination of individual fiber properties of tensile strength, elastic modulus and flexibility. Because of this it was agreed between NASA and Alcoa to substitute limited testing of rigidized tiles fabricated from the experimental fiber to determine the usefulness in RSI-type applications. Also, it was decided to use microstructural examination to determine response of fiber properties to thermal cycling. Other problems encountered in Task 2 are described below.

Two problems which were investigated but not completely overcome in the Task 2 investigation were needle plugging and non-uniform flow of slip from needle to needle during multi-filament extrusion. These problems are probably related but will be discussed separately here.

One potential solution to the problem of needle plugging is to remove any particles from the slip which might be large enough to cause plugging. To test this approach, three previously evaluated slips were filtered through nylon filter cloth having 20 μm openings. Spinning tests were then carried out on these three filtered slips and results were compared to those from the unfiltered slip runs. Data for the filtered slips are shown in the lower part of Table 3. In all three cases spinning behavior was substantially improved by filtration. Longer spinning

runs could be made at faster take-up speeds resulting in slightly finer diameter fiber. Plugging still occurred, however, indicating that the problem was only reduced and not completely solved. Representative flow data for two of the slips are shown in Figure 2. Using 110 μm I.D. needles and 69 x 10^4 N/m^2 (100 psig) pressure, slip No. 23 showed a steady decrease in flow rate until it plugged after 50 minutes. The same slip after filtering through 20 μm nylon screen showed a similar decrease in flow rate, but continued to extrude for slightly over 2 hours before plugging occurred. Slip No. 19 in the unfiltered state extruded erratically through the 110 μm needle, but after filtration extruded well, plugging after 90 minutes. These data indicate that filtration through 20 μm cloth is beneficial to both extrusion and spinning behavior of slips.

Another factor probably contributing to the plugging problem is the long capillary tube length in the needles compared to the diameter. In the needles used in the Task I work, tube length was 3-5 mm or 30-50 times the diameter for a 110 μm needle. It was suspected that this long capillary length provided a good opportunity for small particles to adhere to the inner walls and gradually plug the needle.

As an example of a spinneret with a shorter capillary length, a test spinneret previously obtained from Engelhard Industries was tried. This test spinneret had a hole 100 μm in diameter drilled in a 1 mm thick stainless steel plate. The hole had a 90° entry angle, a flat bottom, and a 200 μm capillary length. Using this spinneret, filtered slip N-19 was extruded. As expected, however, the slip wet the underside of the spinneret and spread out around the hole causing drop-wise rather than continuous flow. This behavior had been observed in previous Saphiber work and is the reason needle type spinnerets are used rather than flat drilled holes.

A second spinneret hole configuration was then evaluated wherein the hole was essentially the same as the flat bottomed hole described above, but a donut-shaped recess was machined on the bottom of the plate, concentric with the hole. This provided a short, tube-like protrusion from the bottom of the plate which was 200 μm in length, 100 μm I.D. with a 50 μm wall thickness. Overall capillary length was 300 μm. A spinneret containing 120 holes of this configuration was obtained from Englehard Industries. This configuration worked somewhat better than the flat bottomed hole but apparently the recess was not deep enough and slip quickly wet the area around the hole (including the recess) and caused dripping rather than continuous flow. This does appear to be a viable approach to a multihole spinneret design but capillary length, entry angle, wall thickness and depth of recess would need to be optimized. The two configurations are shown in Figure 3.

FIGURE 2 - EXTRUSION DATA FOR FILTERED AND UNFILTERED SLIPS

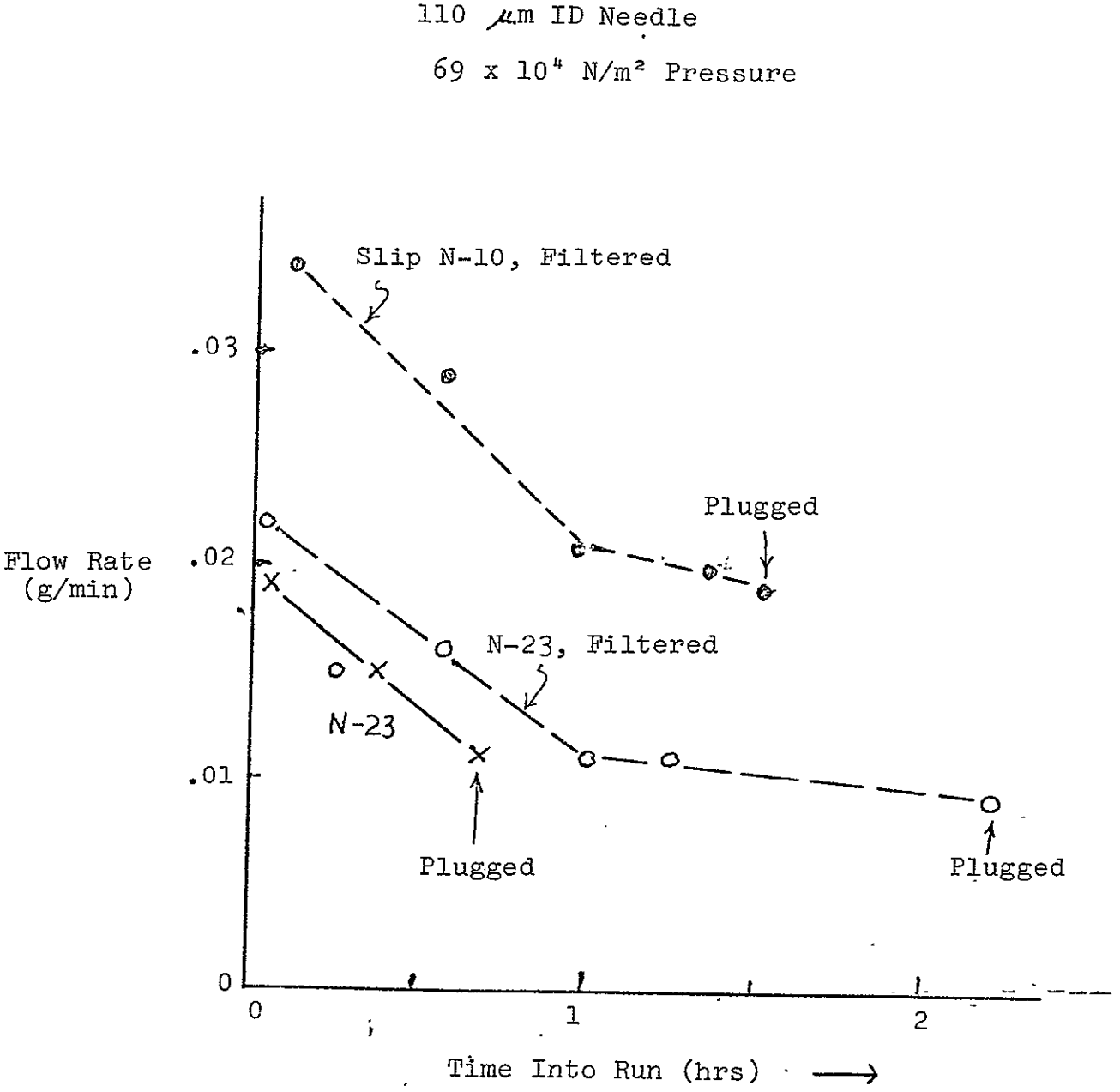
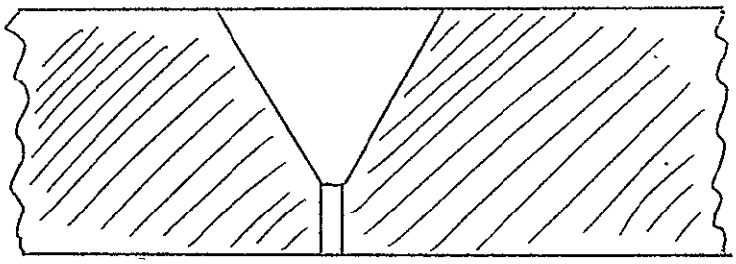
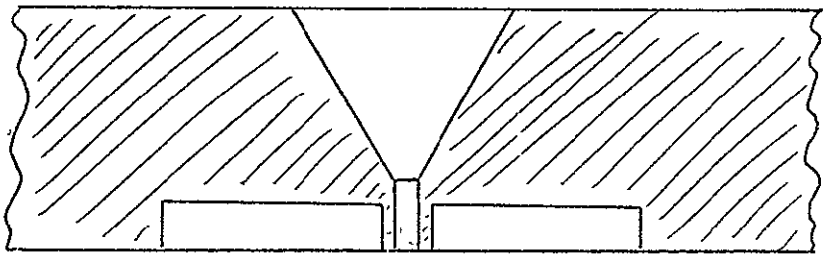


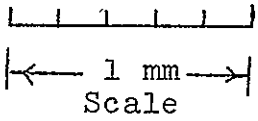
FIGURE 3 - CROSS SECTIONAL DRAWINGS OF SPINNERET HOLES



FLAT BOTTOM
SPINNERET



PROTRUDING TIP
SPINNERET



Because of the long delivery times (approx. 3 months) associated with these custom-made spinnerets, a crude spinneret was constructed on site to allow production of larger quantities of fiber for Task 2. Ninety-seven holes spaced 0.63 cm (.25 inches) apart were drilled in a stainless steel plate 1 mm thick by 10 cm (4 inches) in diameter. Short lengths of 110 μm I.D. hypodermic needle tubing were soldered into each of these holes and ground to a length of approximately 2.5 mm. Multi-filament winding experiments were conducted using this crude spinneret.

In the first attempt at producing larger quantities of green fiber, slip N-101 was pressure filtered through 20 μm nylon cloth and extruded at 69 x 10^4 N/m^2 pressure through the 97 tube spinneret described above. Because of the previously mentioned high viscosity of this slip, flow was very poor with many tubes exhibiting drop-wise rather than continuous flow. This caused termination of the run within a few minutes. Following the composition work described above for Task I, slip N-103 was prepared and filtered through the 20 μm cloth. When this material was extruded through the 97 tube spinneret, most of the extruding filaments stuck to one or more adjacent filaments forming rather coarse fiber which did not dry adequately before collection on the take-up drum.

To obtain wider spacing between filaments, alternate rows of tubes were intentionally plugged. With about 50 tubes extruding the operation was greatly improved and only 2 to 3 filaments appeared to be rejoining. Approximately 10 tubes were not extruding fast enough, however, resulting in dripping and accumulation of excessive non-fibrous waste. After several similar runs a record was made of which tubes did not extrude well and these were intentionally plugged. In a subsequent run, good operation was achieved with only 2 of the 25 remaining tubes plugging over a 2-hour period. During this time fiber was produced at a rate of 1 g/min (green basis). In this run all 25 filaments were wound on a single 7.5 cm diameter take-up drum located approximately 2 meters below the spinneret plate. This run demonstrated the feasibility of multi-filament production of green fiber in the 10 μm range.

Using the procedure described above, several hundred grams of green fiber were spun from each of slips N-103, N-104 and N-105 for use in firing work. Green fiber production was quite slow and was hampered by non-uniform extrusion from tube to tube. The fact that some of the tubes in the spinneret plate extruded well for long periods of time while others extruded in a drop-wise manner is attributed to non-uniformity of the needles. Future process improvement should include optimization of spinneret design.

Work in Task 2 also included development of a firing procedure to produce the finished ceramic fiber. Chronologically, portions

of the firing work were underway at the same time the Task I screening tests were being conducted. In the initial work small portions of 5 green fiber lots produced in the screening tests were fired to determine qualitatively how the higher plastics level and smaller fiber diameter would affect the firing operation. Firing time was 1 hour at 1500°C in a gas-fired furnace. Even though very small samples were fired and green fiber was carefully fluffed up before firing, the fired product was compacted and bonded together. In all cases the inter-fiber bonding was more severe than normally experienced in Saphiber production and was most severe for those samples originally containing the highest plastic levels. A sample of fiber from slip N-6 (which originally contained 61.6% plastic) was so severely bonded together that only a few small pieces of fired fiber could be separated from the main body. Fiber from slip N-8 (containing 20.6% plastic) was less severely bonded. Most of the fiber from this latter batch could be separated but resulting fiber was extremely short being only a few millimeters or less in length. This work demonstrated that compositions containing the minimum possible amount of plastic would be most desirable in the firing step.

In subsequent firing tests a fast firing technique was evaluated. Normally fired "control" samples were prepared by carefully placing fluffed green fiber in crucibles for firing by the standard procedure (about 3 hours to reach the 1450-1500°C firing range with a 1 hour soak at temperature) in a gas fired furnace. To obtain fast firing, other fiber samples were dropped directly into the furnace which had been preheated to 1000, 1400 or 1450°C and subsequently heated for 1 hour in the 1450-1500°C range. After firing, these fiber batches were evaluated for degree of inter-fiber bonding and quality of fiber after separation. It was concluded that fast firing offers no advantage. Material from all firings was bonded to about the same extent and separated fiber was quite short with average lengths of about 500 μm. The material retained its general green shape but exhibited an estimated 10 to 15% linear shrinkage upon firing. As a result of this work, the "standard" firing procedure adopted was sintering in crucibles after carefully fluffing up the green fiber. Following firing, material was hand shredded and screened through a set of vibrating screens, the finest screen opening being 44 μm (325 mesh). Using this separation method 90 to 95% of the fired fiber was recovered as product.

Thermal Stability Testing - One of the key attributes of alpha-alumina fiber is its high temperature thermal stability as compared to SiO_2 or mullite fiber. To demonstrate thermal stability under simulated re-entry conditions, a cyclic heating device was constructed and 7-10 gram samples of fiber representing compositions N-103, 104 and 105 initially fired 1 hour between 1400 and 1500°C were tested. For the reheat test,

samples were placed in an alumina boat which in turn was placed in the tip of an 8.2 cm O.D. by 1.5 m long mullite tube. The tube was automatically inserted into an electric tube furnace operating at a constant 1385°C temperature. Following a 20-minute soak at temperature (1371°C + 10°C), the tube was withdrawn. During the heat treatment the tube (and sample) were under 10 torr vacuum. Between cycles the sample was brought back to ambient atmospheric pressure while sample temperature between cycles was slightly higher than ambient at 150°C to 200°C. Each sample was subjected to 25 cycles; each cycle requiring 90 minutes to complete. Figure 4 shows sample temperature and pressure for a typical cycle. Temperature was measured by a platinum-6% rhodium, platinum-30% rhodium thermocouple inserted directly into the sample. Samples representing material before and after cyclic heating were analyzed by X-ray, spectrograph, light and scanning electron microscopes. A summary of this data is shown in Table 5. The primary indicator of thermal stability was fiber grain size. Grain size was estimated by the linear intercept technique from scanning electron micrographs of the fiber surfaces. Considerable scatter can be seen in the grain size data in Table 5. The reason for this is that only one section of a single fiber was analyzed for each firing condition. To reduce the scatter, many more fields should be examined and averaged. Because of the preliminary nature of this investigation, the increased expense necessary to reduce the scatter could not be justified.

Figure 5 graphically shows the relationship of fired grain size to initial firing temperature and 25 cycles of vacuum reheating. Scanning electron micrographs of selected samples at various stages of processing are shown in Figures 6 thru 13. It can be seen that fired grain size increases with initial firing temperature, but little or no further increase in grain size results from the vacuum reheating. Likewise, little or no change due to reheating can be inferred from the X-ray and spectrographic data. Based on these results, it is concluded that fiber of this type, initially fired to at least 1400°C, can withstand 25 cycles of reheating to 1371°C under 10 Torr vacuum with little or no change in properties.

The chemical analyses in Table 5 show that an unexpectedly high level of impurities (SiO_2 and CaO) were picked up during processing, particularly in batch N-105. This most likely occurred in the ball milling operation as the mill liner is only 50% Al_2O_3 ceramic. Another unexpectedly high impurity is CuO and this is attributed to screening the fired fiber through brass screens in order to separate it. A comparison of data from N-103 and N-104 indicates that the 0.25% MgO and 1.0% talc added to N-103 and N-104, respectively, were equivalent in retarding grain growth. Also, a comparison of N-103 and N-105 indicates little or no change in final fiber properties due to the different starting aluminas.

FIGURE 4 - SAPHIBER THERMAL STABILITY CYCLE

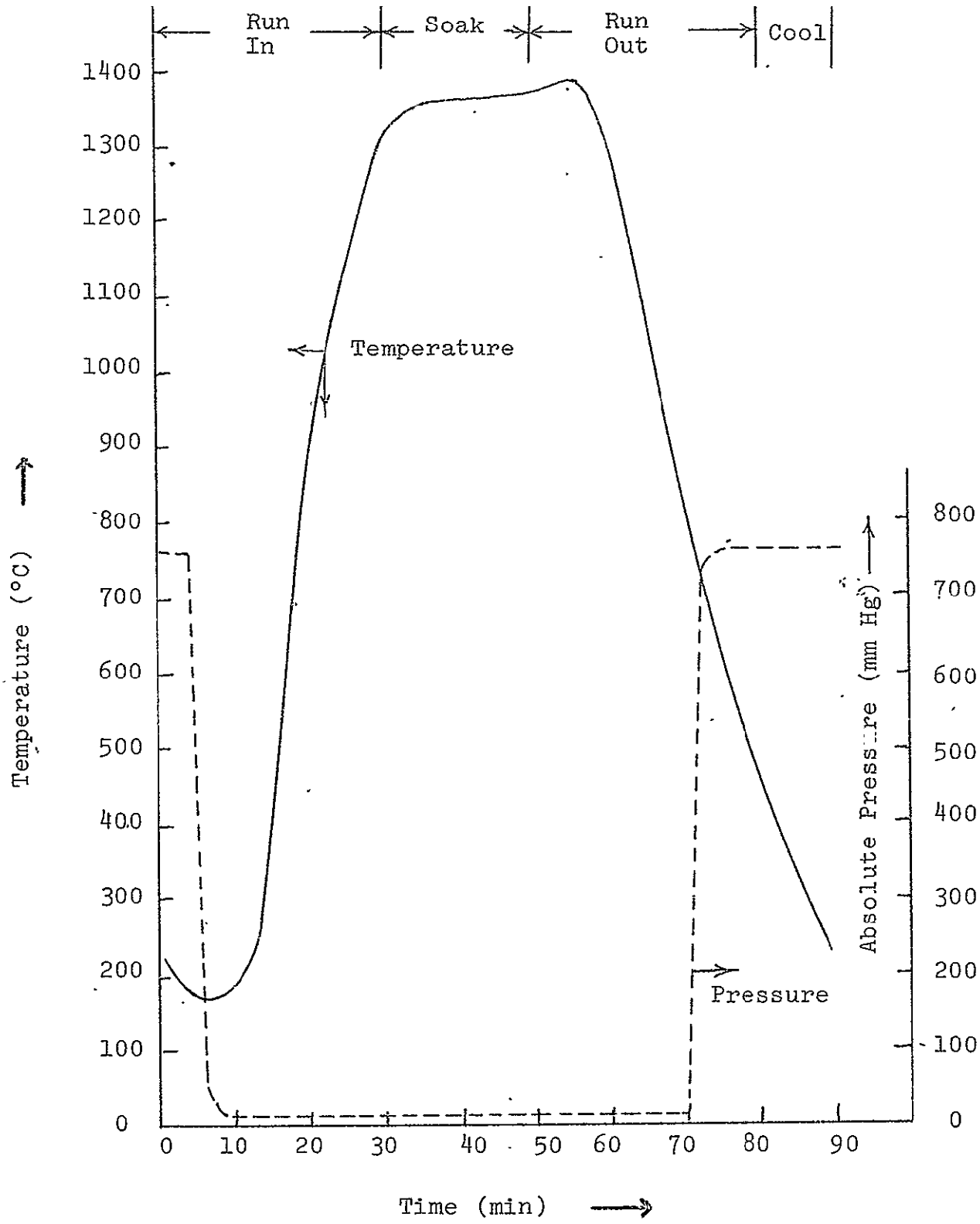
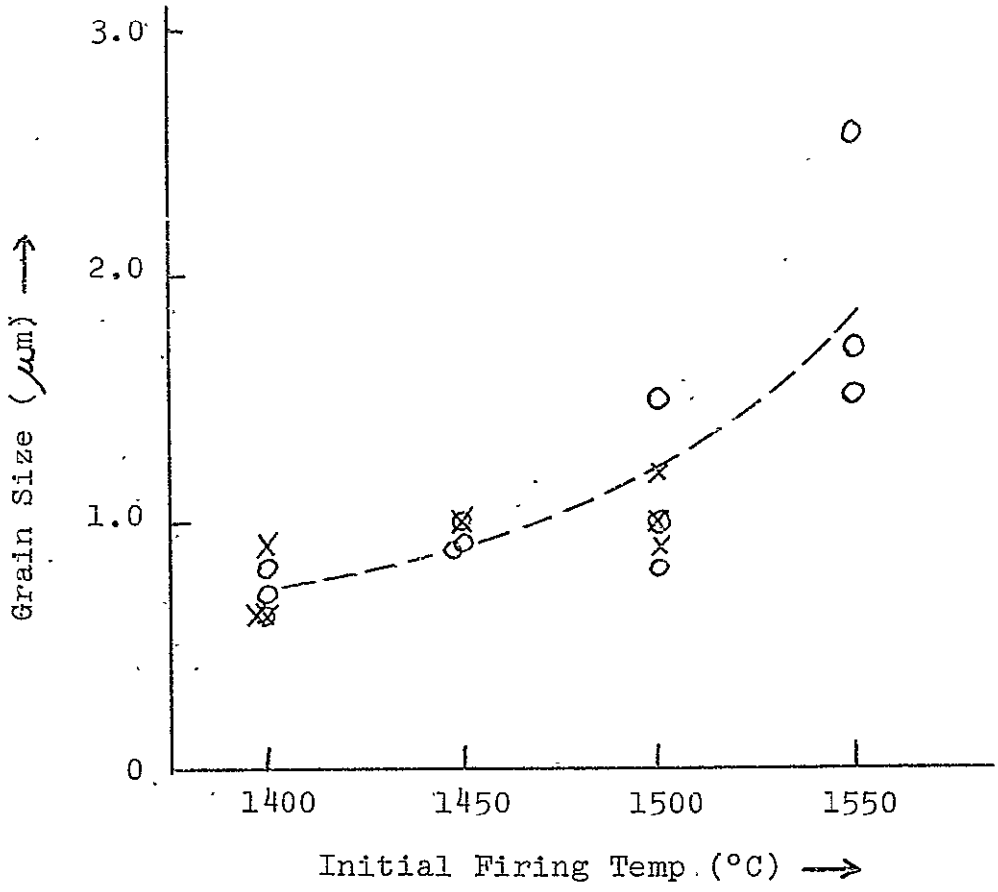


TABLE 5 - SUMMARY OF FIBER PROPERTIES

Fiber Type	Initial Firing Temp °C	No. Reheat Cycles	Grain Size (μm)	α-Al_2O_3 %	Analysis - %*					
					SiO_2	MgO	Na_2O	CaO	Fe_2O_3	CuO
N-103	1400	0	0.7	97.8	.36	.29	.089	.067	.022	.025
"	"	25	0.9	95.6	.38	.29	.017	.072	.024	.0007
"	1450	0	0.9							
"	"	25	1.0							
"	1500	0	1.0	95.6	.38	.29	.094	.074	.025	.040
"	"	25	1.2	95.8	.38	.28	.030	.070	.026	.0006
"	1550	0	1.5							
N-104	1400	0	0.8	96.5	1.10	.40	.086	.072	.021	.080
"	"	25	0.6	94.2	.98	.35	.093	.068	.028	.001
"	1450	0	1.0							
"	1500	0	0.8	94.6	1.40	.36	.12	.082	.036	.065
"	"	25	1.0	96.3	1.30	.40	.084	.080	.039	.0007
"	1550	0	1.7							
N-105	1400	0	0.6	94.2	.98	.25	.072	.096	.020	.025
"	"	25	0.6	94.3	.93	.24	.051	.11	.019	.0006
"	1450	0	0.9							
"	1500	0	1.5	94.5	1.0	.24	.080	.10	.025	.12
"	"	25	0.9	92.1	.98	.26	.059	.11	.036	.0008
"	1550	0	2.6							

*X-ray indicated all samples had minor to trace amounts of spinel.

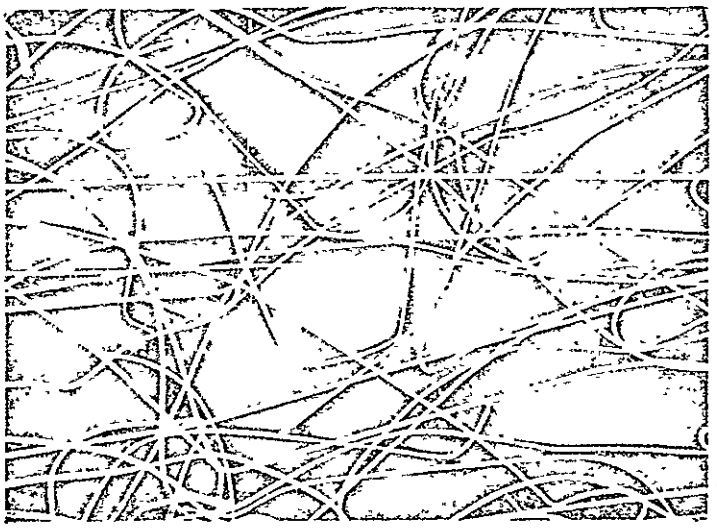
FIGURE 5 - FIBER GRAIN SIZE BEFORE AND AFTER THERMAL CYCLING



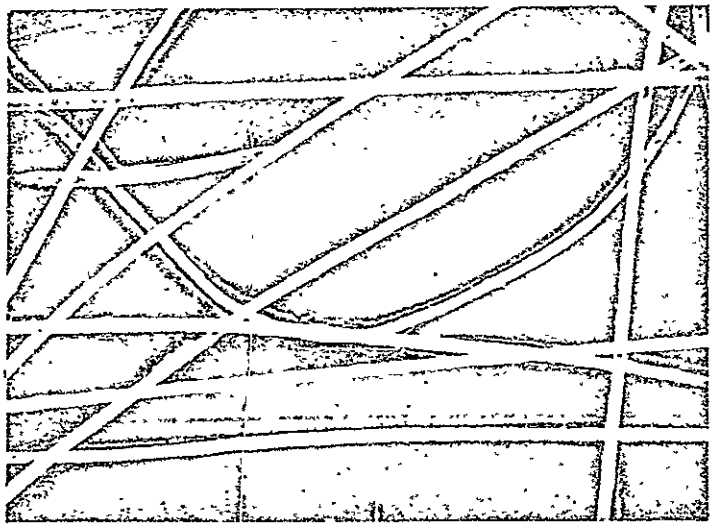
Key: O "As-Fired" material
X After 25 cycles at 1371°C

FIGURE 6 - COMPOSITION N-103 - GREEN FIBER

50 X



200 X



5000 X

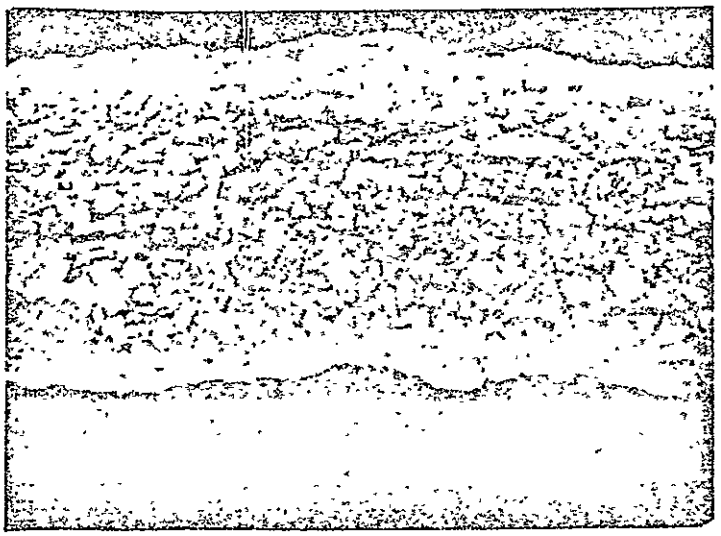
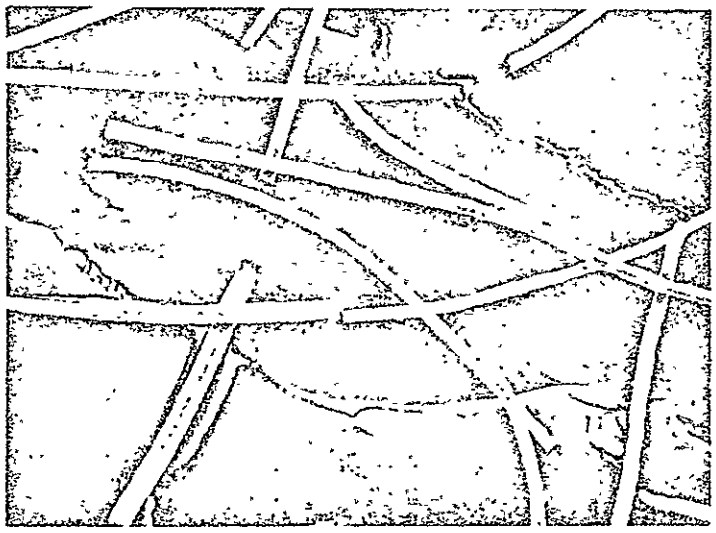


FIGURE 7 - COMPOSITION N-103 - FIRED AT 1400°C

50 X

200 X



5000 X

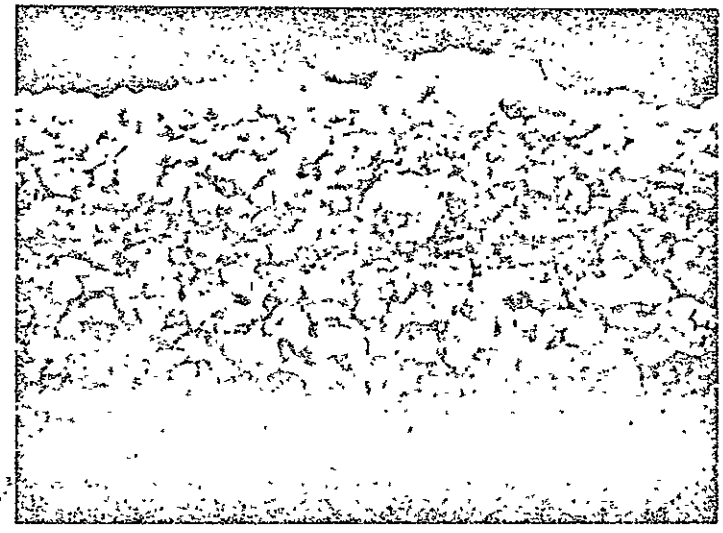
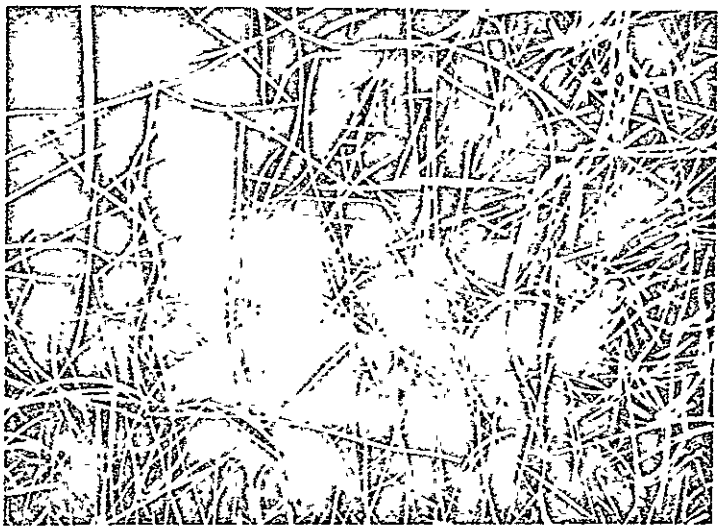
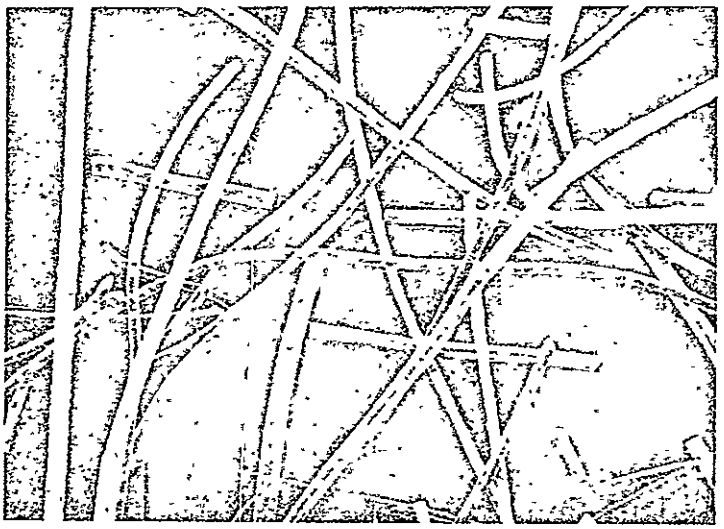


FIGURE 8 - COMPOSITION N-103 - FIRED 1400°C
VACUUM REHEATED 25 CYCLES @ 1371°C

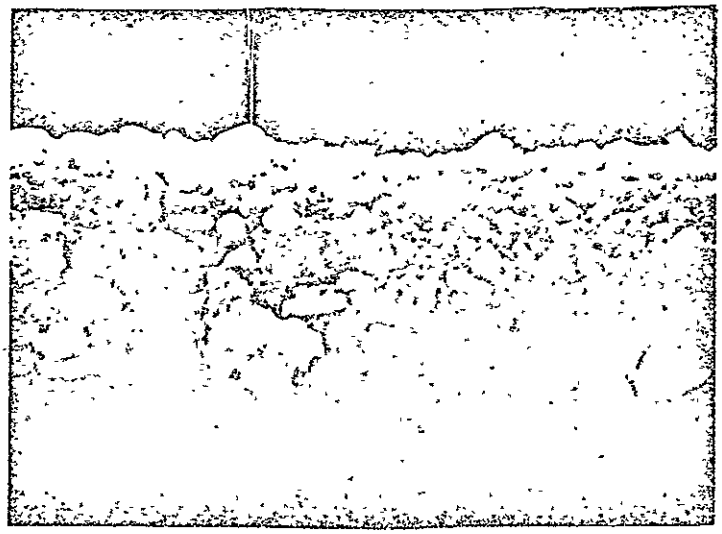
50 X



200 X

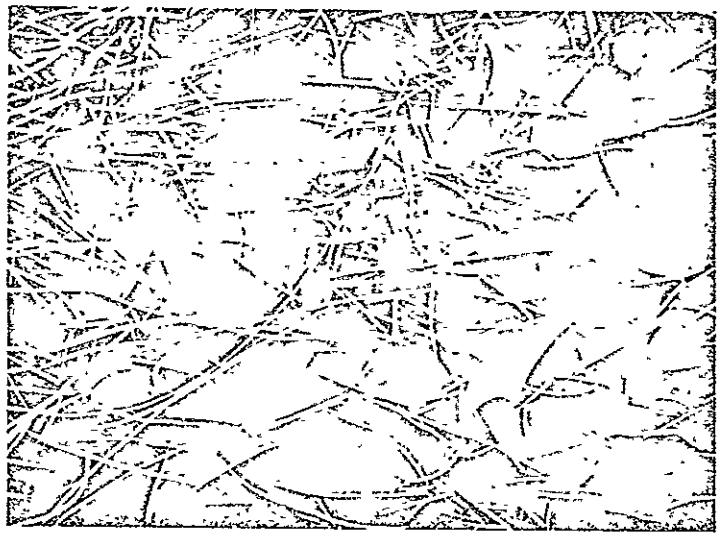


5000 X



IGURE 9 - COMPOSITION N-103 - FIRED 1500°C

50 X



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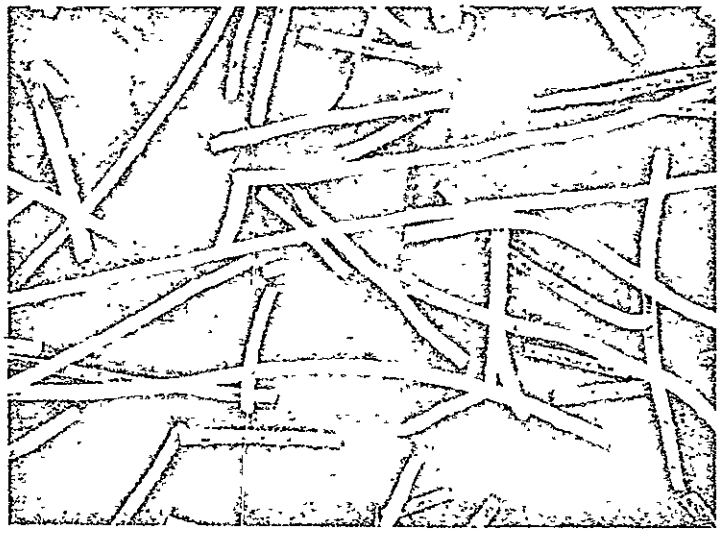
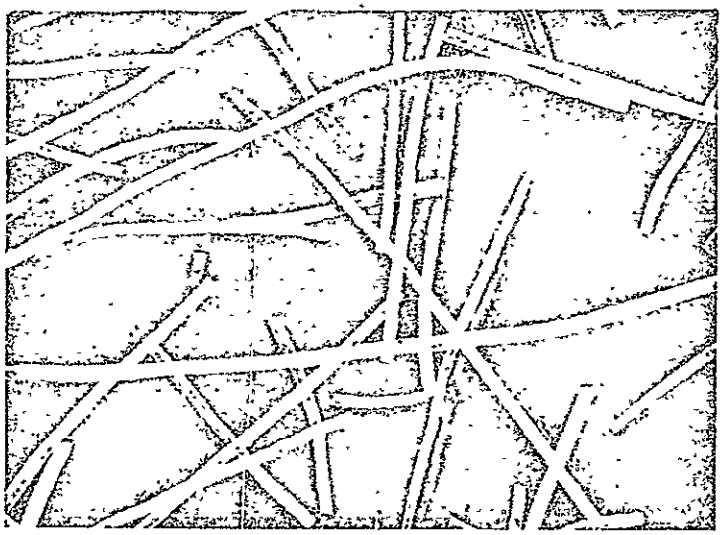


5000 X

FIGURE 10 - COMPOSITION N-103 - FIRED 1500°C
VACUUM REHEATED 25 CYCLES @ 1371°C

50 X

200 X



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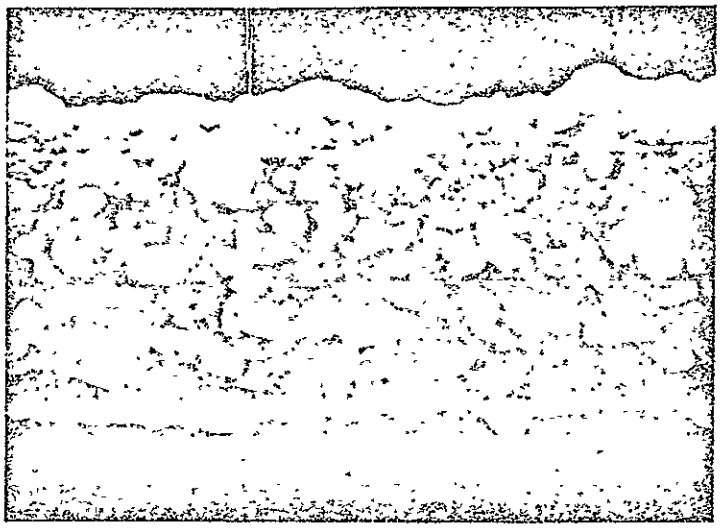

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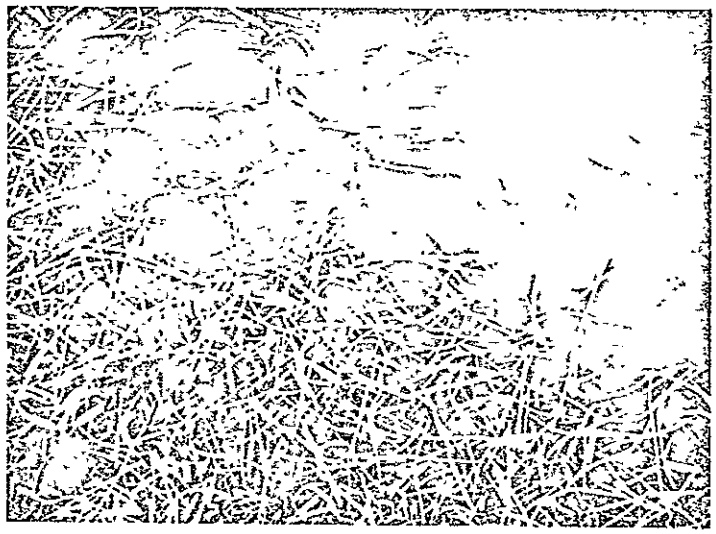

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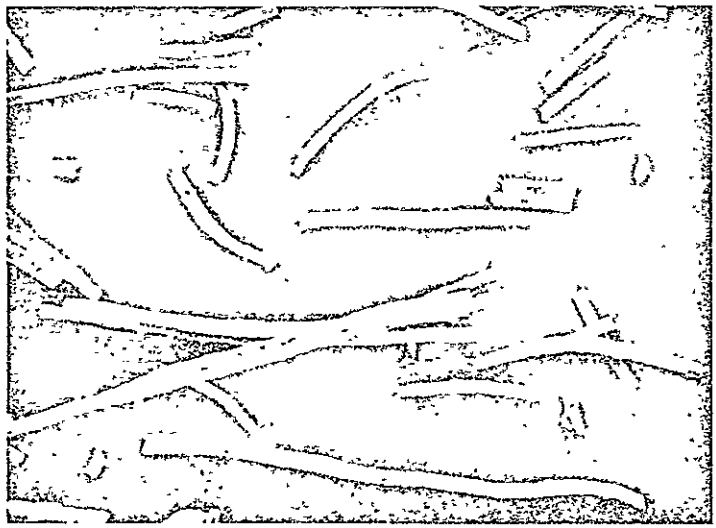


5000 X

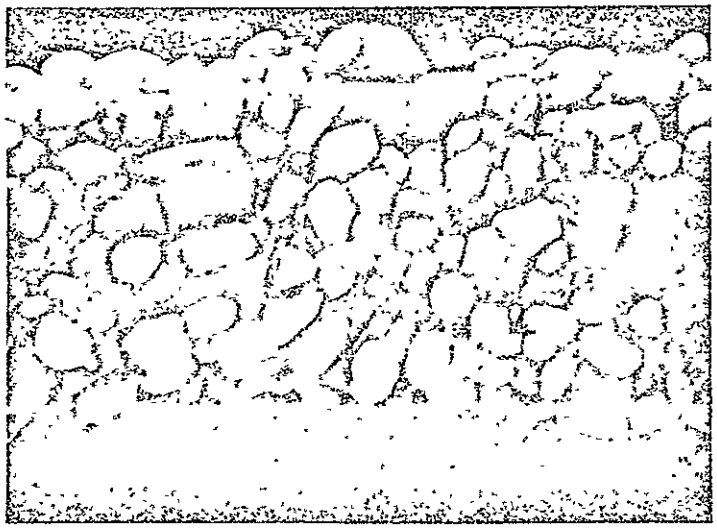
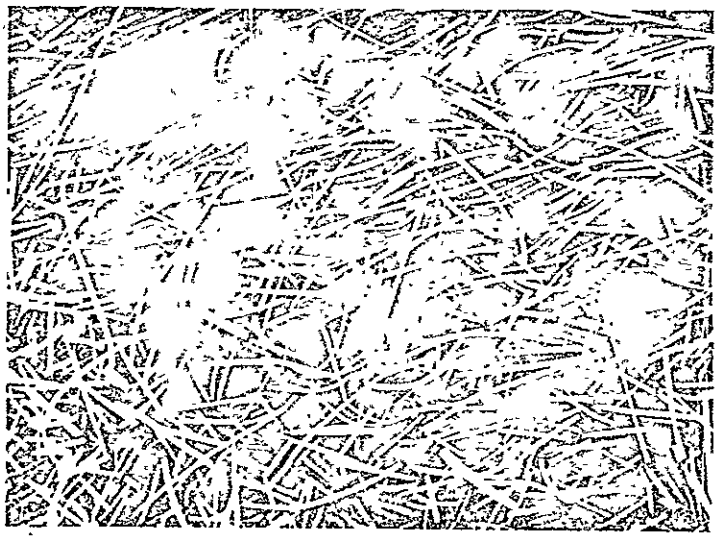
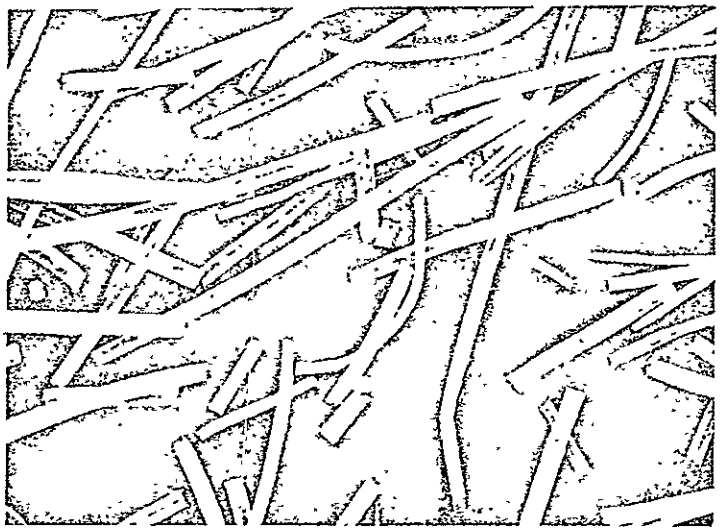


FIGURE 12 - COMPOSITION N-105 - FIRED 1400°C

50 X



200 X

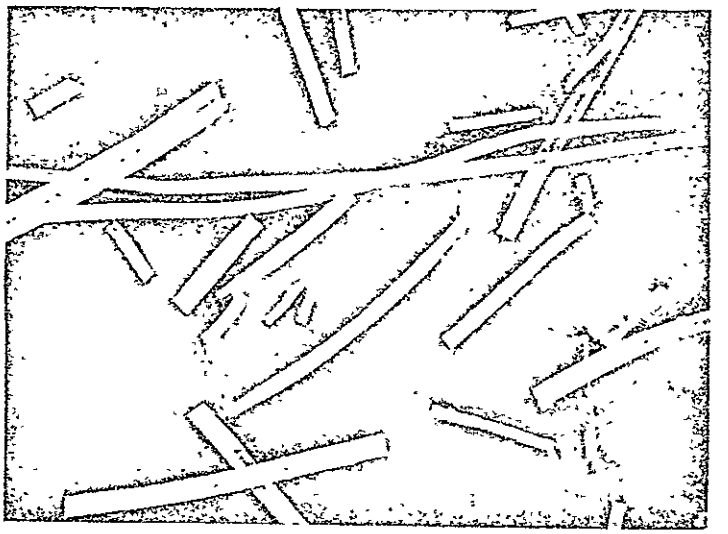


5000 X

FIGURE 13 - COMPOSITION N-105 - FIRED 1400°C
VACUUM REHEATED 25 CYCLES @ 1371°C

50 X

200 X



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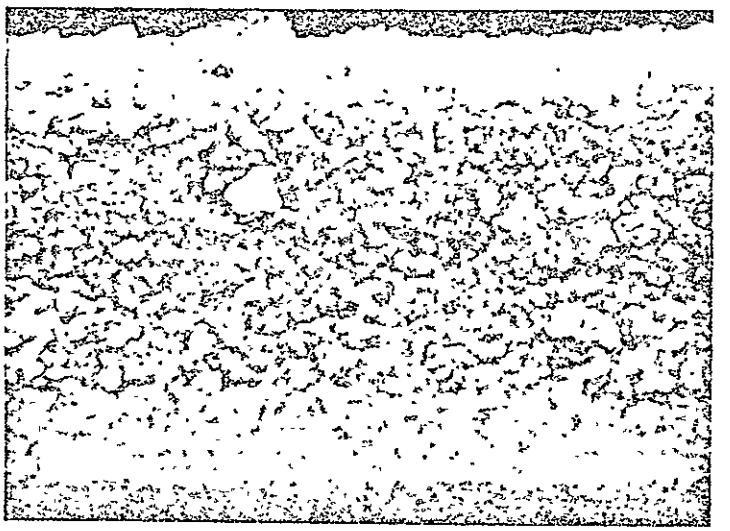

Evaluation in Rigidized Tile - Having demonstrated thermal stability of the alumina fiber, a preliminary evaluation was made to determine usefulness of this material in a rigidized RSI-type application. Since General Eelectric Co. had extensive experience and expertise in fiber and RSI evaluation, it was agreed between NASA and Alcoa that the best quick evaluation of experimental alumina fiber would be obtained by a subcontract to General Electric.

A 250 g sample of fiber (N-103, fired one hour at 1500°C) was prepared by the standard procedure and submitted to General Electric for rigidization and testing. A copy of the evaluation report is attached as Appendix A. Even though General Electric had only a small sample to work with, they successfully fabricated a rigidized tile with good mechanical integrity and reasonably good thermal conductivity. Data comparing properties of this alumina fiber with Lockheed-developed LI-900 RSI are shown in Table 6. Conductivity of the tile was significantly higher than RSI mullite or SiO_2 fiber but the combination of strength, thermal stability and thermal conductivity suggested application of this type of material in critical areas where maximum RSI temperatures would be exceeded.

TABLE 6 - COMPARISON OF EXPERIMENTAL ALUMINA FIBER TILE WITH LI-900 RSI

	Alumina(1)	LI-900(2)
Density (pcf)	37.	9
Thermal Conductivity (500°F) (BTU/ft-Sec - °F)	5.2×10^{-5}	1.1×10^{-5}
Tensile Strength (psi)	73.5	16
Modulus of Elasticity (psi)	333×10^3	5.8×10^3

(1) 8 μm alumina fiber bonded with 30% Al_2O_3 addition.
(2) Silica based RSI developed by Lockheed.

Task 3

The thermal conductivity data generated by General Electric for Task 2 were compared with other Alcoa-developed alumina fiber data and surprisingly, it appeared that fiber diameter had little influence on conductivity in the range studied. A summary of these data is shown in Table 7. Since coarser diameter fiber can be produced at significantly lower cost than fine fiber it was considered important to determine the influence of fiber diameter versus conductivity for polycrystalline alumina. With this in mind, Task 3 was re-defined.

TABLE 7 - THERMAL CONDUCTIVITY OF SAPHIBERS

Source of Data	Fiber Diam. (μ)	Specimen Density (pcf)	Conductivity Test Temp(°F)	Conductivity Test "K" BTU/ft-Sec.°F
GE (1971)	50	30	138	5.5×10^{-5}
GE (1971)	50	30	304	5.4×10^{-5}
GE (1971)	50	30	506	5.4×10^{-5}
Alcoa Labs (hot-wire)	20	11	100	4.2×10^{-5}
" "	20	28	100	5.5×10^{-5}
" "	40	27	100	6.0×10^{-5}
GE (NASA)*	8	37	130	6.5×10^{-5}
GE (NASA)*	8	37	350	5.8×10^{-5}
GE (NASA)*	8	37	520	5.2×10^{-5}

*30% Al_2O_3 added as binder (Fiber basis).

A 250 g quantity of nominally 8 μm fiber was prepared (composition N-104, fired 1 hour at 1500°C) using the standard procedure. In addition, 5 kg each of 20 and 40 μm alumina fiber were prepared using the proprietary Alcoa "Saphiber" process. These materials were sent to General Electric for rigidization and testing. The General Electric report covering this work is included as Appendix B.

The data, summarized in Figure 38 of Appendix B, show considerable scatter. It appears, however, that the fiber diameter over the range investigated does not strongly affect thermal conductivity of the rigidized tile specimens. All tile specimens were rather dense and this is attributed to short fiber length. The short length was caused by fiber degradation during the final separation following firing. In future work, process modifications will need to be made to prevent degradation by altering the firing/separation procedure and/or strengthening the fiber.

In spite of the scatter, it is quite evident that the 8 to 40 μm alumina fiber have significantly higher thermal conductivity values than lightweight RSI mullite and silica fibers at low temperatures. Above about 1000°C, however, the conductivity values appear to converge. This indicates that at high temperature, where the thermal stability of alumina fiber becomes essential, this material has excellent insulating capability. It should be emphasized that tiles prepared from nominally 8 μm fiber were pre-fired to 1483°C before evaluation (see p. 29 , Appendix B) further demonstrating the excellent thermal stability of this material. A more detailed discussion of this work is contained in Appendix B.

CONCLUSIONS

1. High purity alpha aluminum oxide fibers with diameters below 10 μm can be produced by a modification of the Alcoa ''Saphiber'' process. Many problems remain to be solved before the modified process could be considered commercial.

2. The polycrystalline alumina fiber produced by this process had excellent thermal stability and appeared unchanged by 25 cycles of vacuum reheating to 1371°C. Also, no significant change in fiber appearance was observed on heating rigidized tiles to 1483°C during tile fabrication.

3. Rigidized tile made from nominally 8 μm diameter alumina fiber had thermal conductivity significantly higher than that of RSI silica or mullite fiber at relatively low temperatures, but thermal conductivities appeared to be comparable above about 1000°C.

4. Over the range of 8 to 40 μm, fiber diameter did not strongly affect thermal conductivity of rigidized tiles. Mechanical properties of tiles deteriorated as fiber diameter was increased.

5. Strength and aspect ratio of the coarser fiber must be increased to allow reduction of weight and improve mechanical properties of rigidized tiles made from these materials.

APPENDIX A

EXPLORATORY DEVELOPMENT OF A RIGIDIZED α-ALUMINA COMPOSITE (GENERAL ELECTRIC CO.)

APPENDIX B

EVALUATION OF RIGIDIZED ALUMINA FIBER TILES
(GENERAL ELECTRIC CO.)

GENERAL ELECTRIC COMPANY
Re-Entry and Environmental Systems Division
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EXPLORATORY DEVELOPMENT

OF A

RIGIDIZED α-ALUMINA COMPOSITE

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Prepared Under Purchase Order No. TC-325816 for ALCOA

37

October 1973

FOREWORD

This report was prepared by the Re-Entry and Environmental Systems Division (RESD) of the General Electric Company, Philadelphia, Pennsylvania under Alcoa Purchase Order No. TC-325816. The report covers work conducted from August 6 through October 15, 1973 at the RESD's Advanced Materials Development Laboratory under the management of Dr. R. A. Tanzilli.

TABLE OF CONTENTS

Section		Page
1.0	Program Logic	1
2.0	Binder Screening and Panel Fabrication	1
3.0	REI-Alumina Properties	5
	3.1 Mechanical	5
	3.2 Thermal	8
	3.3 Microstructural	8
4.0	Conclusions	14
5.0	Recommendations for Future Work	14

1.0 PROGRAM LOGIC

Small diameter fibers prepared under NASA Contract 3-16779 exhibit a high degree of phase and dimensional stability at temperatures up to 1500°C. Although the fibers are friable as prepared the question arises as to whether a suitable RSI composite could be fabricated from this fiber. Previous work at GE-RESD has indicated that the incorporation of a binder at strategic locations (fiber cross-over points) could result in a rigidized composite with unusually high strength-to-weight ratios and also good insulation characteristics.

A description of the research conducted by GE-RESD (under subcontract to Alcoa) to develop an REI-Alumina composite is described in the followin subsections.

2.0 BINDER SCREENING AND PANEL FABRICATION

Binder evaluations considered precursors which upon calcining would yield an α-alumina phase. Candidate binders screened included: aluminum chloride; aluminum monohydrate; and aluminum monohydrate doped with magnesium chloride. This latter binder (which was ultimately selected) yielded a MgO second phase which had been shown in earlier work to be a grain-growth inhibitor.

Initial binder screening was performed using the B&W mullite fiber because of the limited amount of small-diameter alumina fibers ($\sim$250g) provided. Optimum rigidization was achieved with the aluminum monohydrate binder. A description of the process developed for fabrication of the rigidized REI-Alumina composite is given below.

40

A slurry was made up by adding 40 grams of Dispal(R) aluminum monohydrate to 2550 ml of distilled water. This was dispersed into a colloidal suspension by adding 180 ml of concentrated hydrochloric acid while stirring rapidly with a teflon stirring bar. Once the slurry became translucent, 110 grams of the Alcoa Saphibers (G8467) were added and stirred with just sufficient agitation to keep them suspended. To this slurry, 2.5 grams of $MgCl_2$ was added as a sintering aid and allowed to dissolve.

The slurry was then poured into a 6½ x 6½ inch casting box (shown in Figure 1) and allowed to settle about one minute. A vacuum was then applied by means of a water aspirator and all excess liquid was removed from the fiber cake. Once the initial water was removed, the cake was removed from the casting box and allowed to air dry 24 hours. The billet was then placed in a 120° oven for 70 hours, and finally in a 250° oven for 24 hours. Firing of the billet followed the schedule shown in Figure 2.

The final billet was about 3/8 inch thick with a density of about 37 lb/ft^3. Although no material balance was run on the material, it can be judged from the final weight of the panel (144 g), and the clarity of the solution leaving the bottom of the casting screen, that virtually all of the binder from the slurry remained in the billet.

Dispal(R) is a product of the Continental Oil Company. It forms colloidal aqueous dispersions which yield high purity alumina upon calcining.

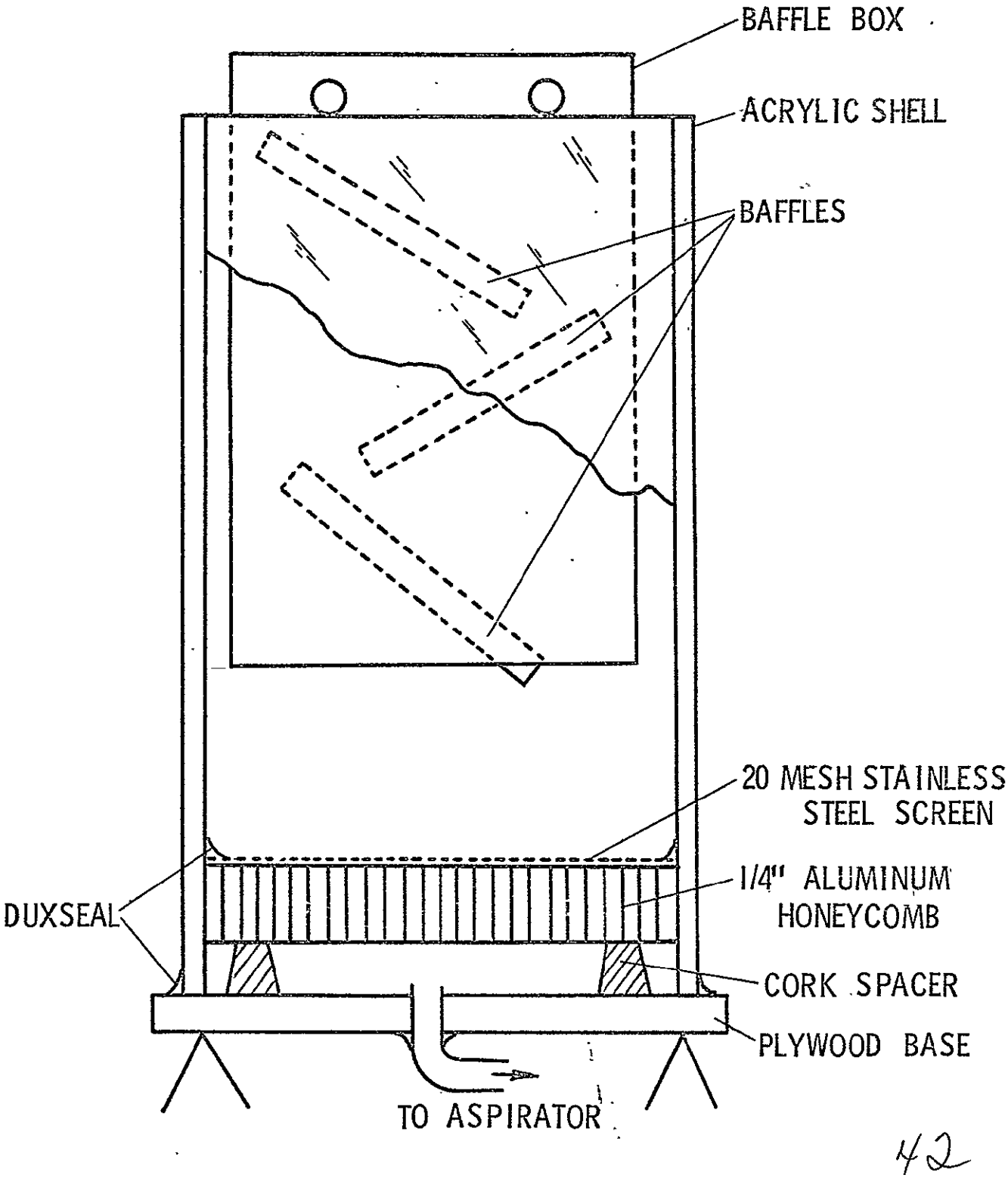


Figure 1. Schematic showing construction of Molding Fixture.

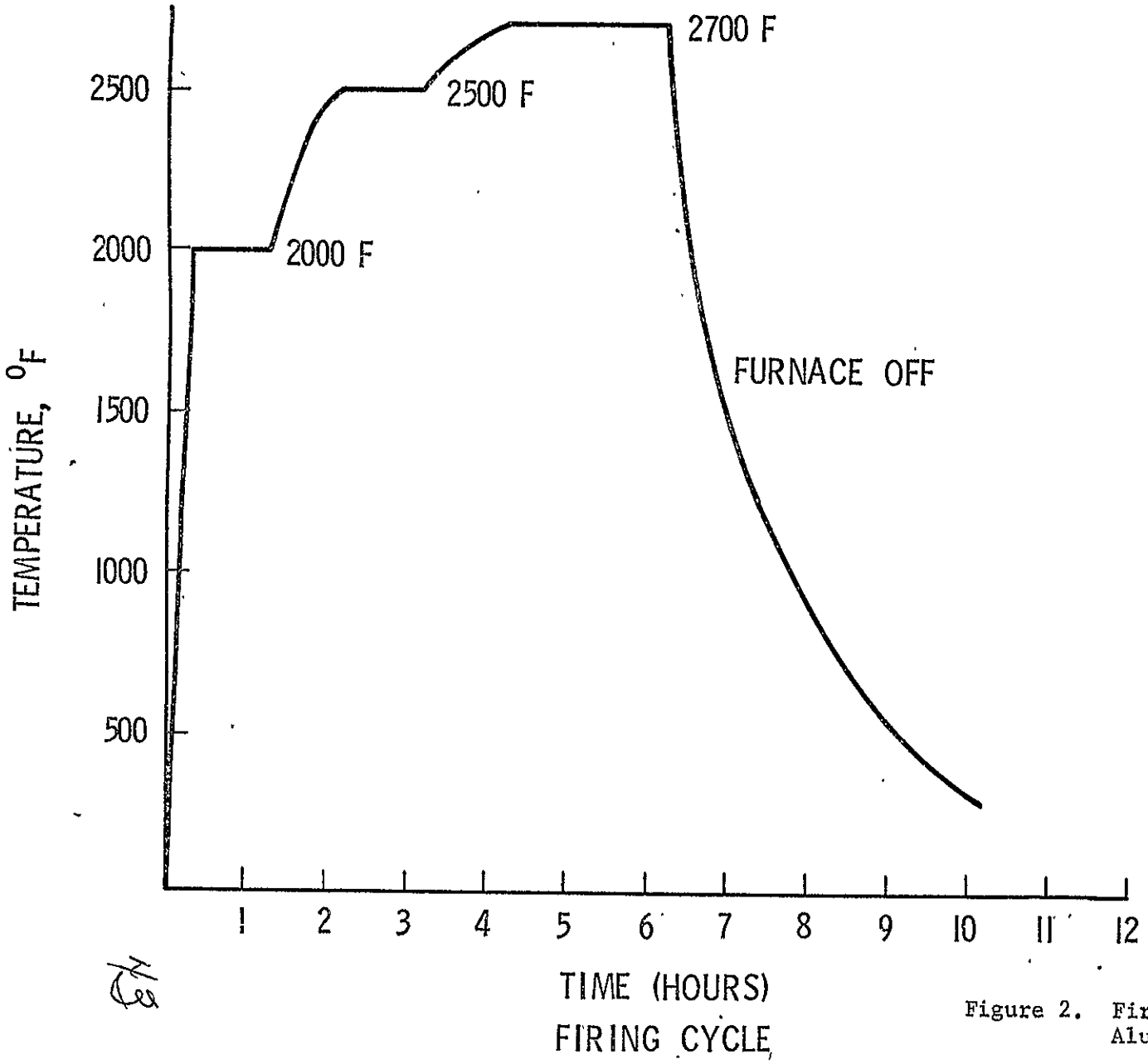


Figure 2. Firing Cycle for REI-Alumina Billet

3.0 REI-ALUMINA PROPERTIES

3.1 Mechanical

Flexure, butt tensile, and thermal expansion tests were run on the REI-Alumina billet. While not completely characterizing this material system, the results do indicate preliminary property trends.

Ten flexure specimens measuring approximately 2.7 x 0.5 x 0.2 inches were tested in four point flexure using a load span of 1.00 in. and a support span of 2.00 in. Load was plotted together with crosshead motion. Table 1 contains a listing of specimen density, modulus of rupture and bending modulus. Mean and standard deviation values are also calculated.

Through-the-thickness tensile properties were determined using a butt-tensile specimen design developed earlier for REI-Mullite testing. Test specimens consisted of four 1.0 x 1.0 x 0.3 inch REI-Alumina composites bonded to aluminum loading blocks with an epoxy cement. Loading was accomplished in a table model Instron testing machine equipped with a lightweight chain loading system and a pair of clevices into which the aluminum loading blocks were pinned. An extensometer was placed on the blocks and essentially measured deformation of both bond lines and the REI-Alumina material. In this case, deformation of the bond line was assumed to be small in comparison with deformation of the REI-Alumina. The measured elastic modulus and failure strain are considered to be representative of the material. Table 2 contains a listing of the butt tensile results plus the mean and standard deviation values.

An in-plane thermal expansion measurement was also run on the REI-Alumina billet from room temperature to approximately 2000°F. Over this

44

TABLE I

MEASURED PROPERTIES IN FLEXURE

Specimen	Density (lbs/ft^3)	Density (kg/m^3)	Modulus of Rupture (psi)	Modulus of Rupture (KN/m^2)	Bending Modulus (psi 10^{-6})	Bending Modulus (GN/m^2)
1	36.6	586	402	2770	.167	1.15
2	35.8	573	357	2460	.171	1.18
3	36.3	582	397	2740	.165	1.14
4	36.7	588	349	2400	.185	1.28
5	35.4	567	512	3530	.158	1.09
6	36.4	583	552	3800	.168	1.16
7	37.0	593	179*	1230*	.195	1.34
8	36.2	580	440	3030	.160	1.10
9	36.0	577	376	2590	.180	1.24
10	35.5	569	379	2610	.145	0.99
$\bar{X}$	36.1	579	418	2880	.169	1.16
S.D.	.519	8.30	70.4	486.	.014	.099

* Value not included in calculated mean and standard deviation on the basis of the Dixon Criterion.

4/5

TABLE 2

BUTT TENSILE TEST RESULTS - ROOM TEMPERATURE

Specimen	Ultimate Strength (psi)	Failure Strain (%)	Modulus of Elasticity (psi x 10^{-6})
1	56.1	.092	.416
2	68.4	.168	.221
3	95.7	.164	.295
4	73.9	.112	.402
$\bar{X}$	73.5	.134	.333
S.D.	16.5	.037	.092

temperature range, the coefficient of expansion varied continuously from 3.14 to 5.98 x $10^{-6}/^{o}F$ with no inflections or inversions. Figure 3 is a plot of the thermal expansion data.

3.2 Thermal

The thermal conductivity was determined on a 2.5 in square by 0.25 in. thick sample using the Dynatech TC-1000 Comparator. Three points were taken ranging from 150°F to 520°F in one atmosphere of N_2. One point was also taken at 10^{-2} atmospheres at 140°F.

Results are displayed in Figure 4 along with sample density. Comparison is also made to data for an alumina foam given in "Engineering Properties of Ceramics", AFML TR-66-52. The superior insulative effect of the virtually 2-D fibrous mat structure over the foam structure for comparable density is evident.

3.3 Microstructure

Figure 5 shows scanning electron micrographs of the as-received Saphibers (G8467) used in fabricating the REI-Alumina composite. Approximate measurements from the micrographs indicate an average fiber diameter of 8 microns and a grain size variation between ½ to 1 microns. Some porosity was noted in the microstructure.

Figures 6 & 7 are scanning electron micrographs of the rigidized REI-Alumina composite in both the in-plane and transverse directions. Rigidization appears to have been accomplished by linking bundles of fibers which have been bonded together along their length. The formation of fillets at fiber cross-over points is evident at several locations.

47

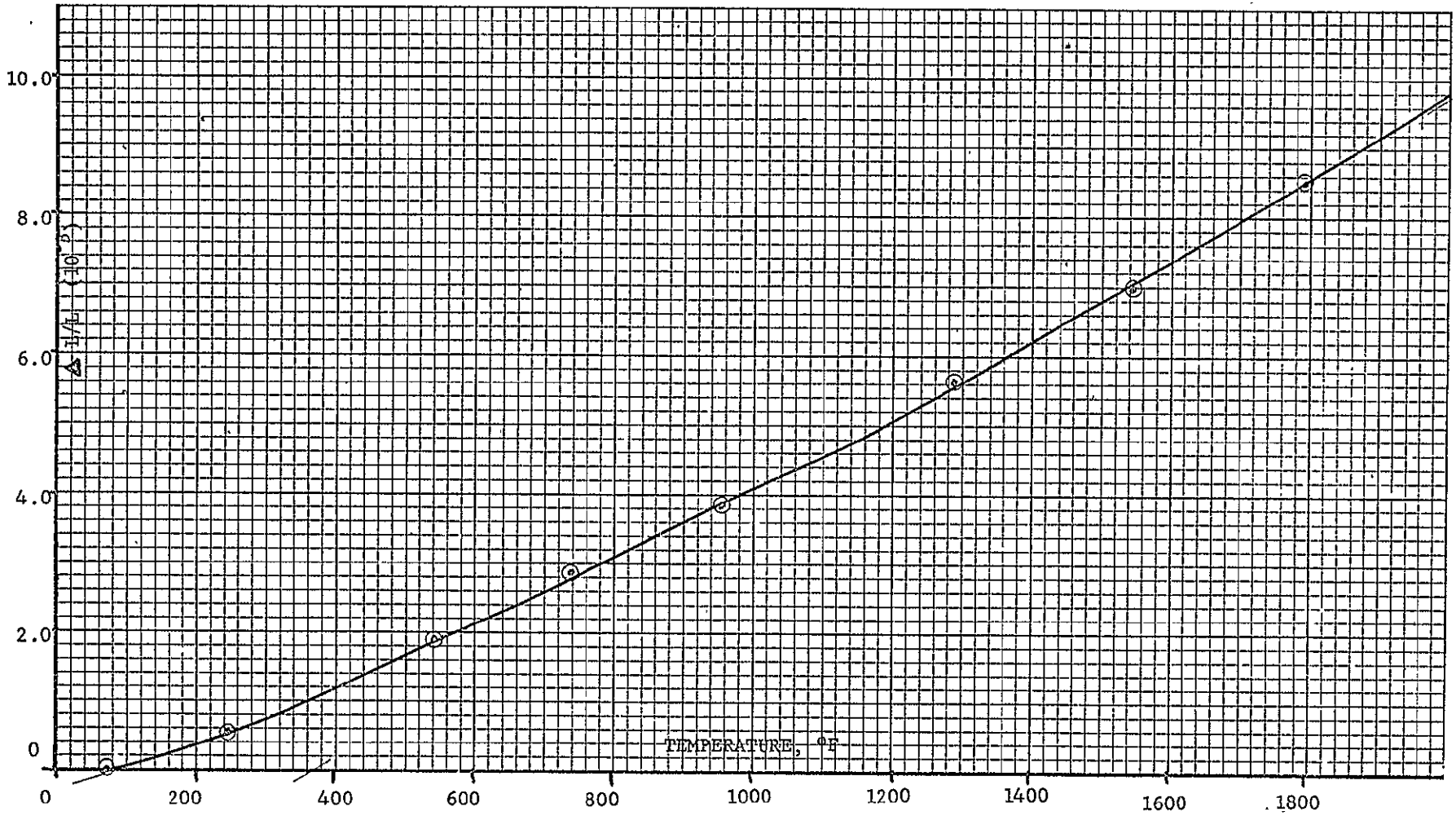
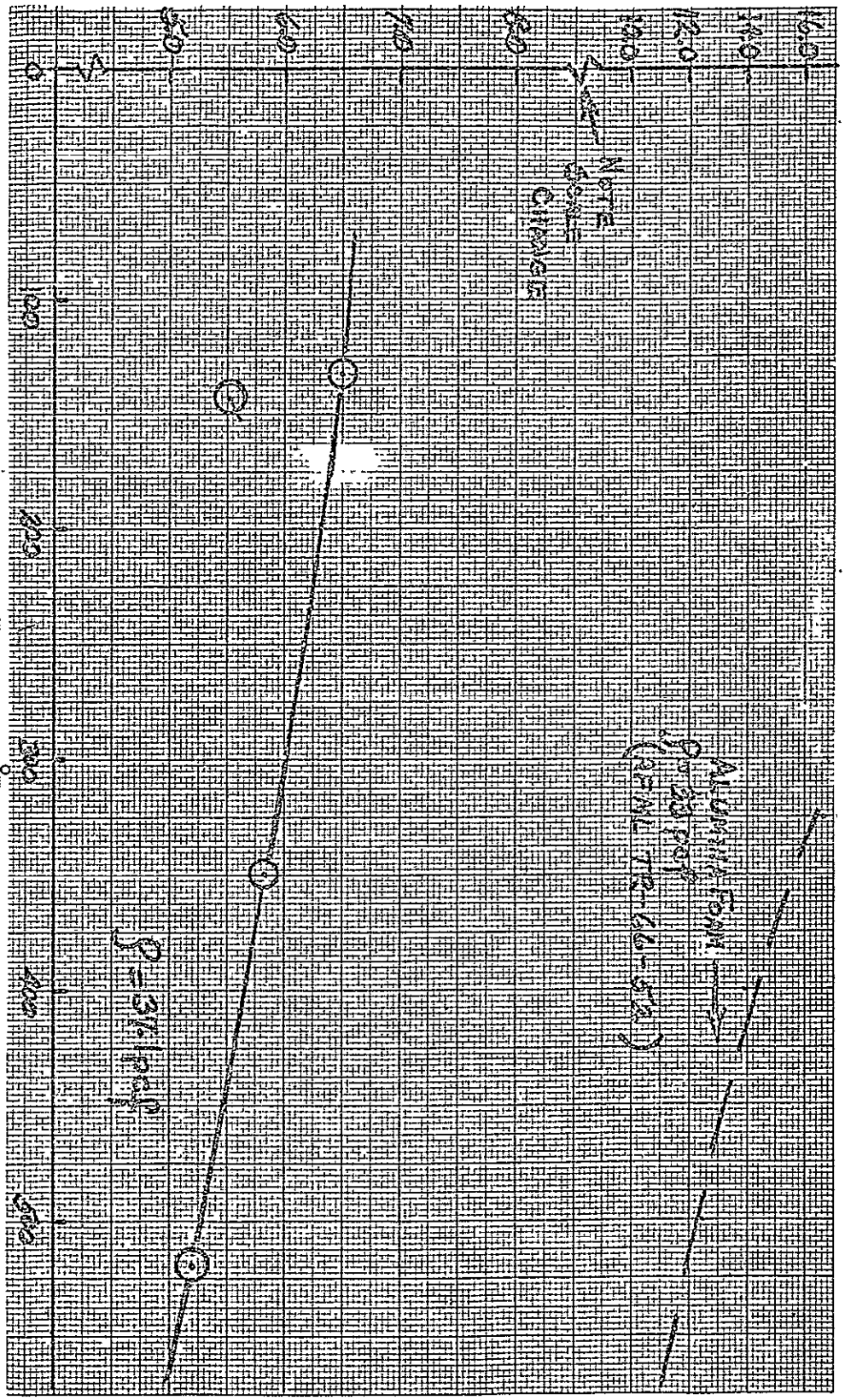


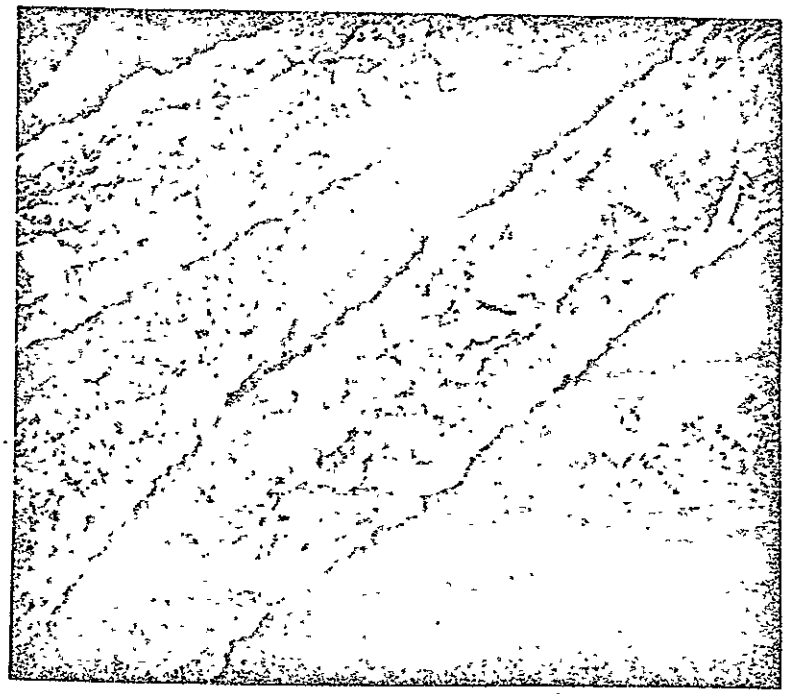
Figure 3. Thermal Expansion of REI-Alumina as a Function of Temperature

Thermal Conductivity, BTU/ ft.-sec.-^{o}F x 10^{-5}



Temperature, ^{o}F

Figure 4. Thermal Conductivity of REI- Alumina Billet



10 μm

2 μm

50

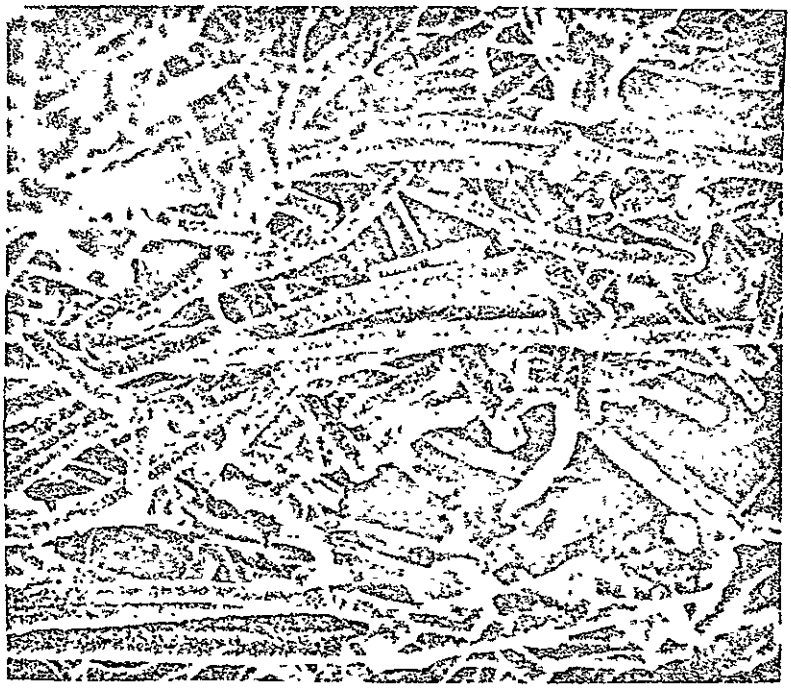
Figure 5. Scanning Electron Micrographs of Saphiber® Fibers

100 μm

10 μ

Figure 6. Scanning Electron Micrographs of REI-Alumina Composite- In-plane Surface

51



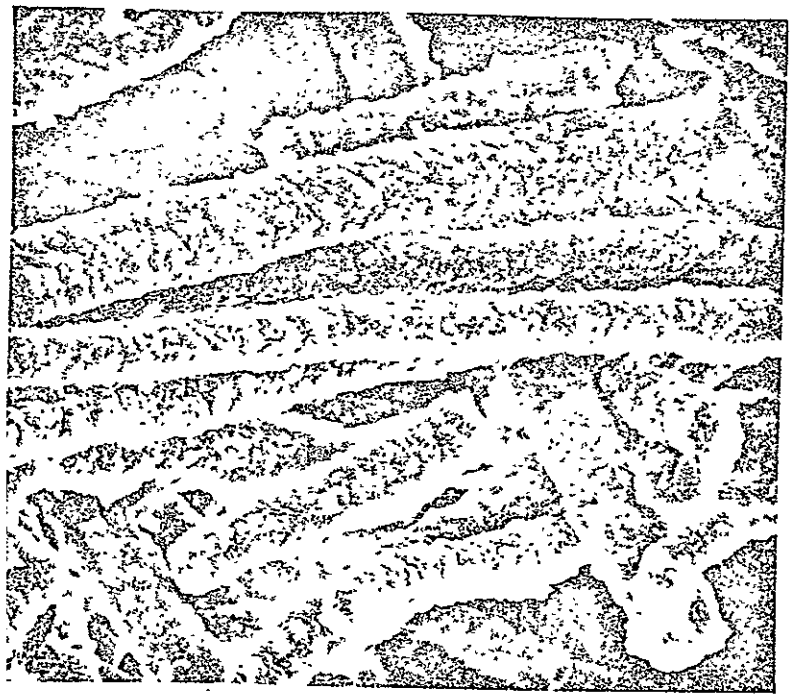


Figure 7. Scanning Electron Micrographs of REI-Alumina Composite- Transverse Section

52

4.0 CONCLUSIONS

The development program led to the following conclusions:

1. The feasibility of forming a rigidized, low-density alumina composite has been demonstrated. Optimum rigidization was achieved using an aluminum monohydrate binder (Dispal(R)) doped with magnesium chloride.

2. The rigidized REI-Alumina composite exhibited good mechanical integrity for this class of fibrous material (strength-to-weight ratio comparable to REI-Mullite), and also, superior thermal insulation characteristics compared to a foamed alumina structure of similar density.

5.0 RECOMMENDATIONS FOR FUTURE WORK

It is recommended that research be continued to fully characterize the mechanical and thermal properties of REI-Alumina as a function of density and temperature.

It is recommended that a design study (with a supporting systems test program) be initiated to assess the suitability of REI-Alumina as a potential internal insulation for the RCC leading edge regions of the Shuttle vehicle, and also, as a rigidized alumina furnace insulation with demonstrated insulation efficiencies superior to current state-of-the-art foamed alumina refractories.

EVALUATION OF RIGIDIZED TILES MADE FROM ALUMINA FIBERS

Principal Investigator - P.N. Bolinger

Thermal Conductivity Evaluations - J. Brazel

March 1975

Prepared Under Purchase Order No. TC-053689 for Aluminum Company of America; Alcoa Technical Center; Alcoa Center, Pennsylvania

54

GENERAL ELECTRIC

Re-entry & Environmental Systems Division

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TABLE OF CONTENTS

Section			Page
1	INTRODUCTION		1
2	OBJECTIVES & LOGIC		2
	2.0	Introduction	2
	2.1	Objectives	2
	2.2	Program Logic	3
3	TILE RIGIDIZED STUDIES		5
	3.1	Planned Processing Technique	5
	3.2	Fiber Evaluation	5
		3.2.1 Microscopic Techniques	5
		3.2.2 SEM Evaluation	8
		3.2.3 Crystallinity of Fibers	8
		3.2.4 Measurement of Fiber Geometry	14
	3.3	Fabrication	16
		3.3.1 Preliminary Fabrication Studies	16
		3.3.2 Small Sample Size Fabrication	22
		3.3.3 Fabrication of a Full Size Tile Using 10 Micron Diameter Fibers	29
		3.3.4 Fabrication of Tiles Using 20 μm Diameter Fibers	31
		3.3.4.1 Discussion of Individual Tile Fabrication	31
		3.3.4.2 Significant Fabrication Developments	39
		3.3.4.3 Use of 20 μm Fiber Composites	39
		3.3.5 Fabrication of Tiles Using 40 μm Diameter Fibers	39
		3.3.5.1 Fabrication Details of Individual 40 μm Tiles	39
		3.3.5.2 Significant Fabrication Development	51
		3.3.5.3 Use of 40 μm Fiber Composites	51
4	PROPERTIES		52
	4.1	Introduction	52
	4.2	Phase Stability	52
	4.3	Thermal Expansion	52
	4.4	Flexure Tests	55
	4.5	Butt Tensilte Tests	55
	4.6	Tensile Tests	55
	4.7	Thermal Conductivity	61

TABLE OF CONTENTS

Section		Page
5	DISCUSSION OF RESULTS AND CONCLUSIONS	65
	REFERENCES	70

56

LIST OF FIGURES

Figure		Pag
1	Photograph of Previously Evaluated 10 μm Fibers	7
2	Photograph of 8-10μ Diameter Fibers Evaluation in This Study	7
3	Photograph of 20 μm Fibers	9
4	Photograph of 40 μm Fibers	9
5	SEM photographs at 300X and 3000X	10
6	SEM photographs at 300X and 3000X	11
7	SEM photographs of Fiber Lot G9251	12
8	SEM photographs of 40 μm fibers	13
9	Densitometer traces prepared from portions of x-ray diffraction photographs	15
10	Fiber Length Distribution	17
11	Fiber Length Distribution	18
12	Fiber Length Distribution	19
13	Schematic showing construction of Molding Fixture	20
14	Photograph of 2-7/8" diameter specimen made from 40 μm fibers	24
15	Photograph of 2-7/8" diameter specimen made from 10 μm fibers	24
16	Photograph of 2-7/8" diameter specimen made from 20 μm fibers	26
17	Photograph of 2-7/8" diameter specimen made from 10 μm fibers	27
18	Photograph of Sample 1F	27
19	Photographs of Sample 1G	28
20	Radiographic positives of tile 20-7-3	34
21	SEM of Tile 20-7-4 at 300X and 1000X magnification	35

57

LIST OF FIGURES

Figure		Page
22	SEM of tile made from 20 μm fiber	36
23	Radiographic positive of tile 20-7-4	38
24	Photograph of Dense Portion of tile 40-7-1	42
25	SEM photographs from lower density section of tile 40-7-1.	43
26	SEM of tile 40-7-1	44
27	SEM of tile 40-7-1 from lower density portion of tile	45
28	SEM of tile 40-7-1 dense portion of tile	46
29	Montage of radiographic positive - tile 40-7-1	48
30	Photograph of tile 40-7-4 after firing	49
31	Photograph of tile 40-7-5 after third firing	49
32	Photograph of tile 40-7-6	50
33	Photograph of tile 40-7-B2 after second firing	50
34	Densitometer traces prepared from portions of x-ray diffraction photographs	53
35	Thermal expansion of alumina fibers composites	54
36	Tensile specimen for low density insulation	58
37	Photograph of In-Plane Tensile Specimen	59
38	Thermal conductivity of alumina fiber composites compared to Mod. 1A REI Silica and Mullite	63
39	Comparison of fiber length distribution as a function of slurry chopping time	66

58

LIST OF TABLES

Table		Page
I	Goals for Property Determinations	4
II	Length, Diameter and Length/Diameter Ratios of Alumina Fiber Lots	6
III	Process Set-Up Studies Using Other Type Fibers	21
IV	Preliminary Processing Studies	23
V	Standard Binder Solution	30
VI	Fabrication of 20 μm Fiber Panels	32
VII	Density of As-Cast and Fired 20 μm Fiber Tiles	33
VIII	Fabrication of 40 μm Fiber Panels	40
IX	Density of As-Fired 40 μm Fiber Panels	41
X	Flexure Test of Alumina Fiber Composites Made From 20 μm Fibers	56
XI	Flexure Tests of Alumina Fiber Composites Made From 40 μm Fibers	57
XII	Butt-Tensile Strength of Alumina Composites Made From 40 μm Fibers (40-7-1) and 20 μm Fiber (20-7-3)	57
XIII	In-Plane Tensile Stregnth of Alumina Fiber Composites Processed Using 20 μm Fibers	60
XIV	Thermal Conductivity of Alumina Fiber Composites	62
XV	Comparison of Mechanical Properties of Alumina Fiber (20 μm) Rigidized Tiles with GE's Mod. 1B REI-Mullite Tiles	68

59

SECTION I

INTRODUCTION

This report documents a three-month program which was undertaken by General Electric Company's Re-entry and Environmental Systems Division (RESD) to evaluate aluminum oxide fibers of various fiber diameters for the Aluminum Company of America, Alcoa Laboratories. The objective of the evaluation of these fibers in rigidized tile form was to determine mechanical and physical properties as a function of tile density and for thermal properties as a function of both temperature and tile density. The fibers were supplied by the Alcoa Laboratories at the beginning of this program. Three lots of fibers were supplied. One lot had a fiber diameter of ~ 10 microns. Another lot had a fiber diameter of ~ 20 microns and the third had a fiber diameter of ~ 40 microns.

60

SECTION 2

OBJECTIVES & LOGIC

2.0 INTRODUCTION

Small diameter fibers prepared under NASA Contract 3-16779 by the Alcoa Laboratories exhibit a high degree of phase stability at elevated temperatures. A previous purchase order contract from Alcoa Laboratories[1] explored the feasibility of using small diameter (8-10 μm) friable alumina fibers in a rigidized composite. The exploratory effort gave some encouraging results and demonstrated the feasibility of forming useable small samples using the 8-10 μm diameter fibers.

2.1 OBJECTIVES

The objectives of this effort were to determine if larger diameter fibers than those used in the previous exploratory study could be formed into useful tiles and if they could to determine some physical and thermal properties of these composite tiles.

The known restraints placed on this fabrication of the tiles were:

(1) The binder system should not degrade the refractoriness of the alumina fiber. If the binder is less refractory than the fiber the binder would be the controlling mechanism.

(2) The tiles fabricated had to be of sufficient size to permit removal of the "skin effect" normally associated with a casting operation. The "skin material" is created during the casting operation itself and during binder migration during subsequent drying and firing operations.

(3) The samples to be used for conductivity and tensile strength had to be 8" in diameter and 4" x 1-1/2", respectively, which required samples to be cast either as 7" x 7" panels or 9"x9" panels.

(4) The limited amount of fibers available (10# each type of the 20 μm and 40 μm fiber and 1/2# of the 10 μm fiber) severely limited the development work that could be accomplished. In an attempt to maximize the data which could be obtained from this limited supply of material each experimental tile had to be cast, dried, fired and evaluated before the next processing experiment could be determined.

(5) Scale-up studies using small samples (~25 gms of fibers) had been previously shown to have very limited usefulness in determining processing techniques for tiles of the required size.

61

2.2 PROGRAM LOGIC

The logic for this current program was, therefore, to utilize the fabrication experience gained on the limited exploratory program previously conducted for Alcoa and on extensive GE/RESD experience in fabricating refractory ceramic-fiber composites using mullite fibers, silica fibers, zirconium fibers and alumina-silicate fibers. The binder would be limited to the material used successfully on the exploratory contract (alumina monohydrate with a small amount of $MgCl_2$ added as a sintering aid Reference 1).

The goals for this effort were to fabricate tiles at two different densities in the 10 to 60 lb/ft^3 range and then to determine the properties listed in Table I.

62

TABLE I

GOALS FOR PROPERTY DETERMINATIONS

	FIBER TYPE		
	10μm	20μm	40μm
Density Type(s)	1	2	2
Tensile Strength (R.T.)	-	X	X
Strain-to-Failure (R.T.)	-	X	X
Tensile Modulus (R.T.)	-	X	X
M.O.R. (R.T.)	-	X	X
Bending Modulus (R.T.)	-	X	X
Thermal Conductivity**			
Air	X	X	X
10 Torr	X	X	X
Thermal Expansion**	X	X	X
Surface Morphology	X	X	X
Crystalline Morphology	X	X	X

* Range of 10-60 pcf
** Range of 260-1650°C

63

SECTION 3

TILE RIGIDIZED STUDIES

3.1 PLANNED PROCESSING TECHNIQUE

The original plan for fabricating the rigidized tiles to be used in the evaluation of the alumina fiber composites was to use the processes previously developed for rigidizing ceramic fiber composites. In particular the plan was to use the same general process described in Reference 1 with minor changes in slurry viscosity, screen size and aspiration time to control panel density. The process is described below.

A slurry is prepared which consists of one part of an aluminum monohydrate and 65 parts distilled water. Concentrated hydrochloric acid (4.5 parts) are added to disperse the material into a colloidal suspension. Next the fibers are added to the slurry and with sufficient agitation to keep the fibers suspended. Finally a small amount ($\sim$6% of the aluminum monohydrate) of $MgCl_2$ is added as a sintering aid.

The next step is to pour this slurry into a casting box and allowed to drain for a short period of time and finally a small suction is applied to remove the excess liquid.

Using this approach a tile was previously cast using the 8-10 μm fiber which had a fired density of $\sim$ 37 lb/ft^3 and a nominal flexure strength of 420 psi.

3.2 FIBER EVALUATION

The three sizes of fibers received from Alcoa were studied to determine the differences in the physical appearance of the fibers and to compare these fibers with the fibers previously supplied by the Alcoa Laboratories.

3.2.1 Microscopic Techniques

The alumina fibers were first evaluated using microscopic techniques. Table II lists the average diameter, average length and average length/diameter ratio for the fibers evaluated in this task. The fibers from the 10 μm fiber lot were similar to those aluminum fibers previously evaluated. Figure 1 is a black-field photograph at 100X magnification of the previously evaluated fiber (Lot G-8467) which had an 8-10 μm fiber diameter. Figure 2 is a similar photograph of the 10 μm diameter fibers evaluated on this contract (Lot G-9303). A comparison of these two photographs show the two lots to have similar diameters but the average

TABLE II

LENGTH, DIAMETER AND LENGTH/DIAMETER RATIOS OF ALUMINA FIBER LOTS

	LOT NO.			
	G8467 10μm	G9303 10μm	G9251 20μm	G9318 40μm
No. of Samples	27	50	59	65
Average Length (μm)	231.6	100.5	132	499.2
Average Diameter (μm)	9.7	7.8	27.4	58.7
Average L/D Ratio (μm)	22.0	13.4	4.8	9.2
Longest Fiber (μm)	1311	396	463	1900
Shortest Fiber (μm)	43	23	20	76
L/D Ratio				
% > 50	3.7	2.0	0	0
% > 30	18.5	6.0	0	3.0
% > 20	48.2	22.0	0	12.3
% > 10	89.0	54.0	3.4	33.9
% >10	11.0	46.0	96.6	66.1

65

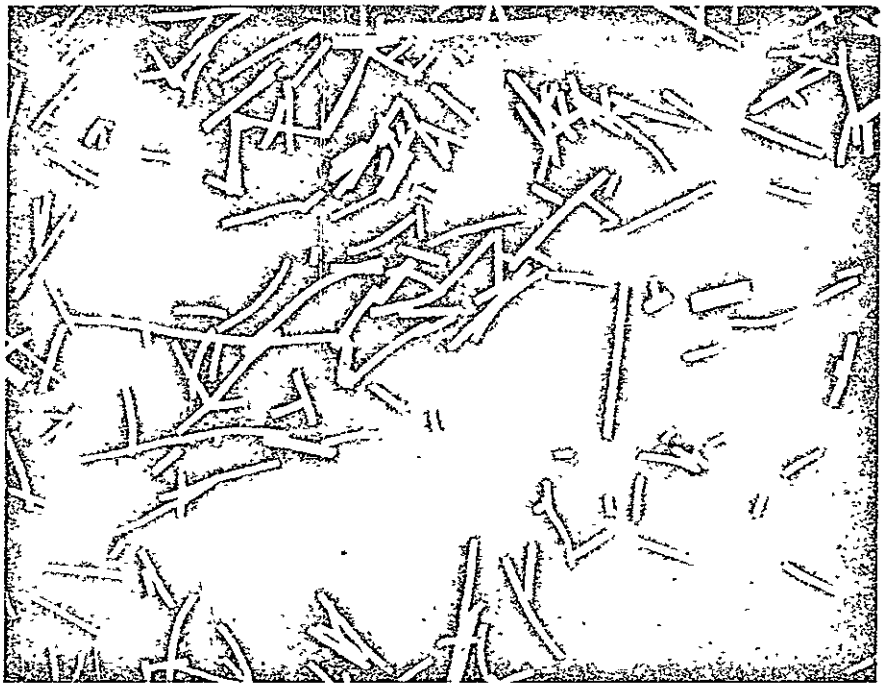


Figure 1. Photograph as previously evaluated 10μ fibers. Photograph was taken using black field techniques at a magnification of 100X. Notice the relatively short fiber lengths. (Fiber Lot 8467G).

Figure 2. Photograph of 8-10 μ diameter fibers evaluated in this study. In general the fibers appear similar to those previously evaluated.

66

length of the latter appears shorter and thus has a lower length/diameter ratio. Figure 3 is a black-field photograph of the 20 μm fibers also at 100X magnification. These 20 μm fibers (Lot G-9251) vary significantly in length as shown in this photograph but in general are quite short. The length to diameter ratios appear to be very low with a majority of the fibers having a length to diameter (L/D) ratio of less than 10. The significance of this L/D ratio will be discussed later in this section. The largest diameter fiber (40 μm) is illustrated in Figure 4 also using black-field techniques but at 72.5X magnification. These fibers vary in length and as shown in this photograph many of the fibers are only slightly longer than their diameter thus the average L/D ratio is quite low.

3.2.2 / SEM Evaluation

The fibers were also examined using scanning electron microscopy (SEM) techniques. Figures 5-8 show the surface topography of the three types of fibers evaluated in this task as well as the surface topography of the fibers previously evaluated. Each figure contains a 300X photograph which illustrates general fiber geometry and a 3000X photograph which depicts fiber surface characteristics.

Figures 5 and 6 are SEM's of the 8-10 μm fiber lots. These fibers appear to be quite similar in both geometry and surface topography. A comparison of the two fibers at 3000X does, however, show the first fiber lot evaluated to have a slightly smaller grain size in this SEM photograph than does fiber lot (G-9303).

Figure 7 are SEM photographs of the 20 μm fiber at 300X and 3000X. The 300X photograph reveals the relatively low length to diameter ratio of these fibers. Comparing the 20 μm fibers to the 10 μm fibers (Figure 7 with Figure 6) shows the average fiber lengths are much shorter for the 20 μm fiber. The 3000X photograph is interesting in that the grains in the 20 μm fiber are significantly smaller than the grains in the 10 μm fiber or the 40 μm fiber (Figure 8).

SEM photographs of the 40 μm fiber are shown in Figure 8. These photographs indicate that the fiber length and the L/D ratio for these fibers are low. The surface topography as illustrated at 3000X is similar to the 10 μm fiber but as discussed above appears different than the 20 μm fiber.

3.2.3 Crystallinity of Fibers

X-ray diffraction analyses were made on three alumina fiber samples. The samples evaluated were the 10 μm diameter fiber previously evaluated Lot G-8647, the 20 μm diameter fiber (Lot G-9251) and the 40 μm diameter fiber (Lot G-9318).

Sample preparation for x-ray diffraction analysis consisted of: pulverizing the samples: passing the powders through a 270 mesh screen;

67

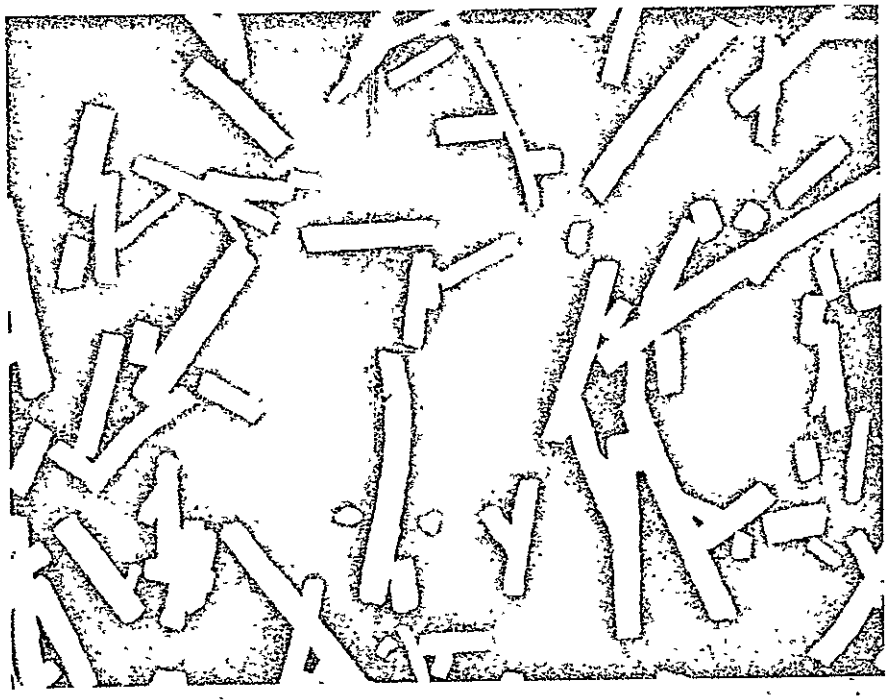


Figure 3. Photograph of 20μm fibers. This photograph shows relative geometric relationships of fiber diameter to fiber length. (Black Field - Magnification 100X).

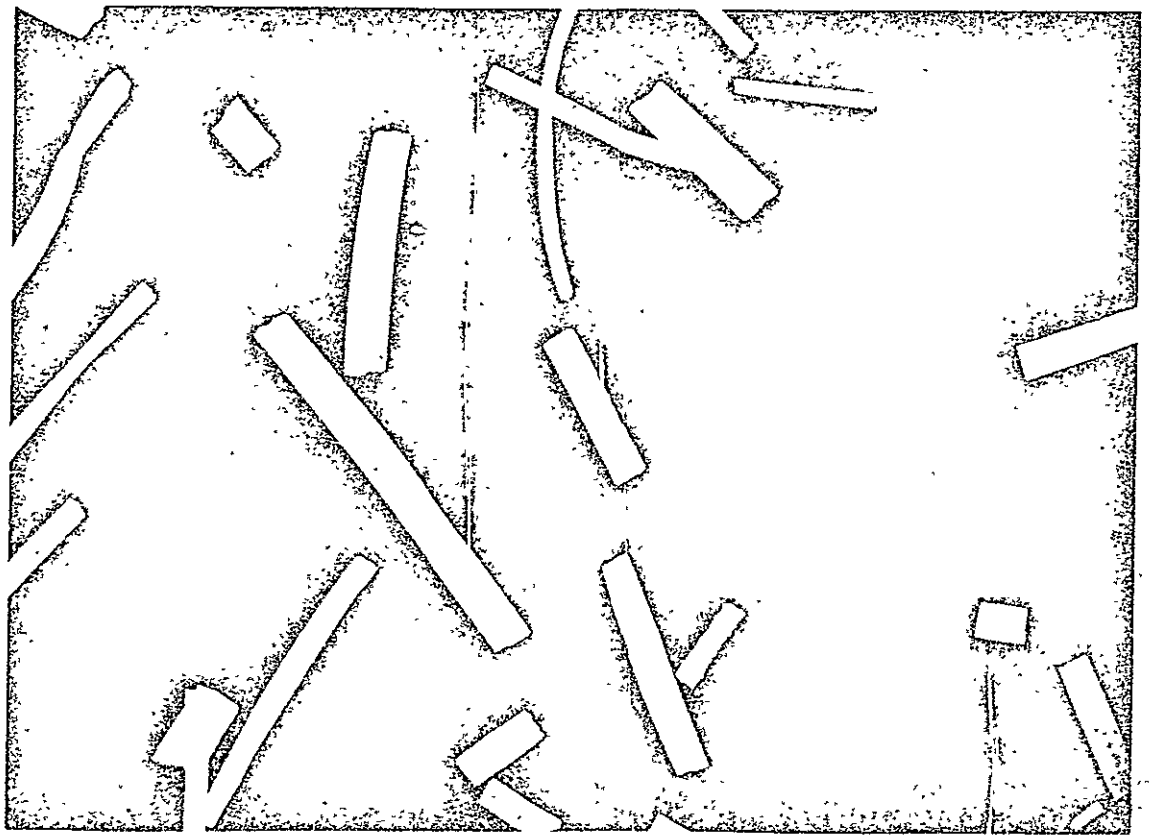


Figure 4. Photograph of 40μm fibers. Lot G9318 showing relative geometric relationships of fiber diameter to fiber length. (Black Field - 72.5X magnification).

68

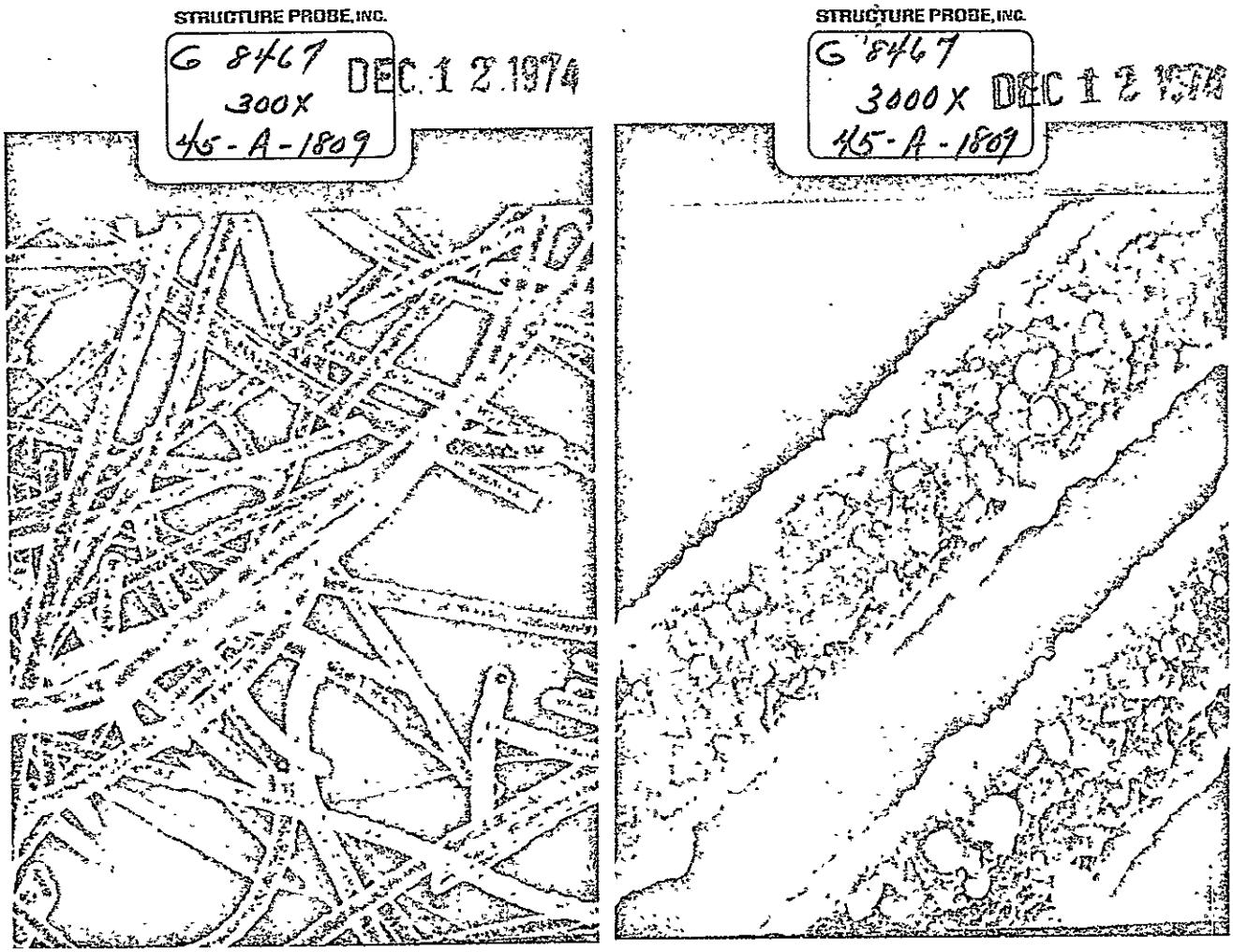


Figure 5. SEM photographs at 300X (left) and 3000X (right) of fibers used in original exploratory effort (fiber diameters 8-10μm).

69

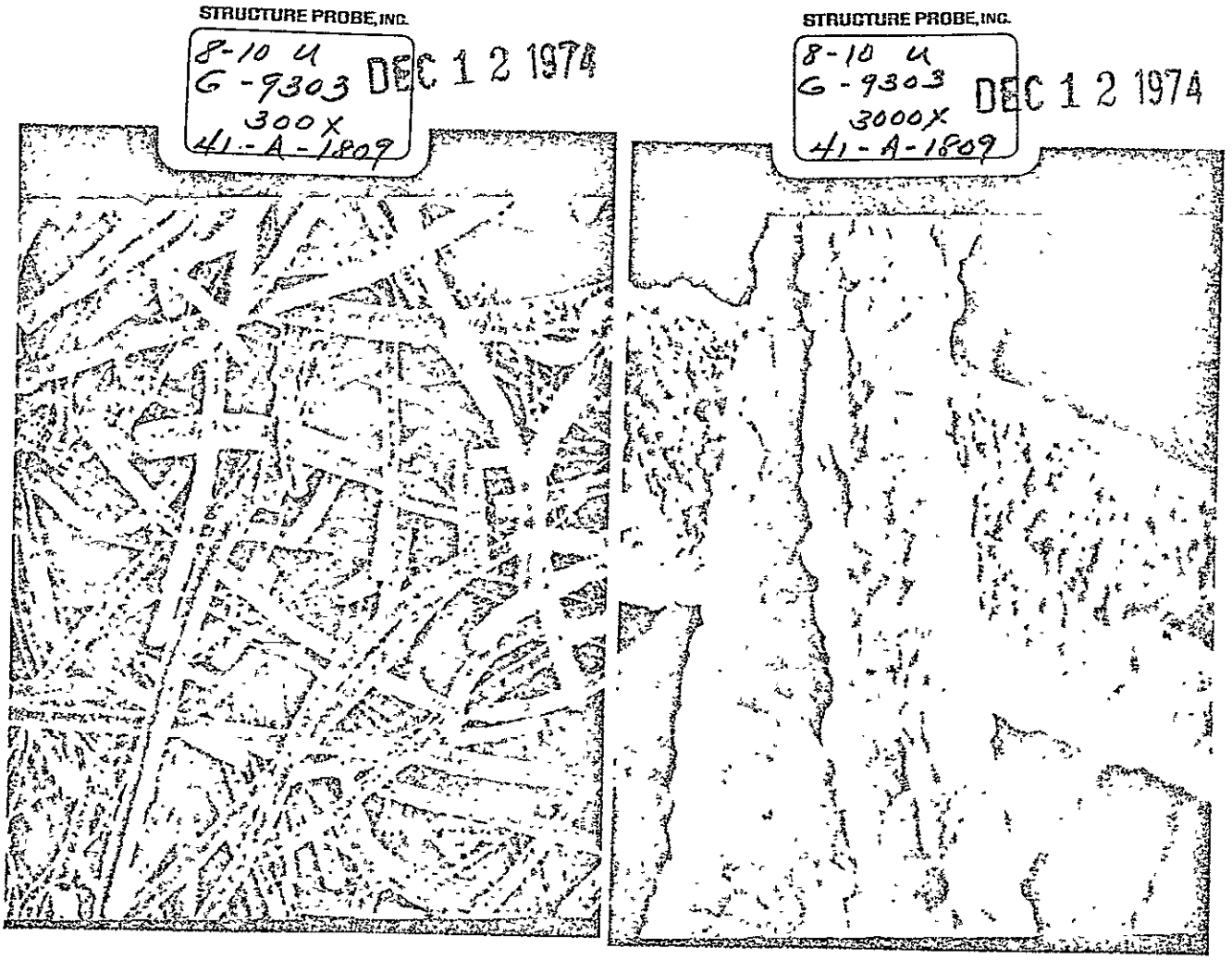


Figure 6. SEM photographs at 300X (left) and 3000X (right) of fiber lot G9303 (8-10μm). Notice the similarity of the fiber diameter, apparent fiber length, and fiber topography of these fibers to fiber used in previous effort lot G8467 (Figure 5).

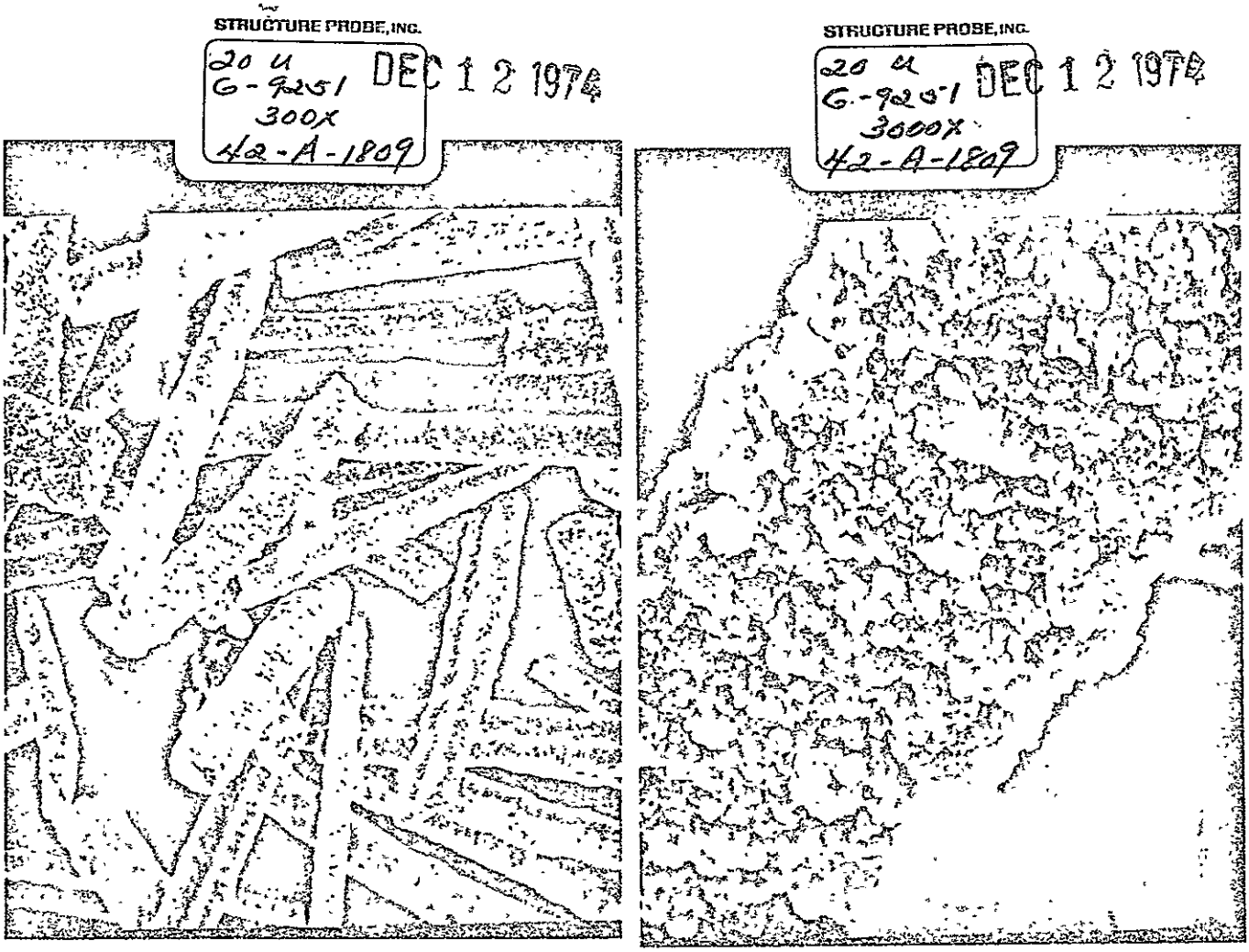


Figure 7. SEM photographs of Fiber Lot G9251. Notice the much shorter fiber lengths with smaller length to diameter ratios. The grains in the fiber at 3000X (right) appear much smaller than the grains in the 10μm fiber Lot G9303 (compared to Figure 6).

71

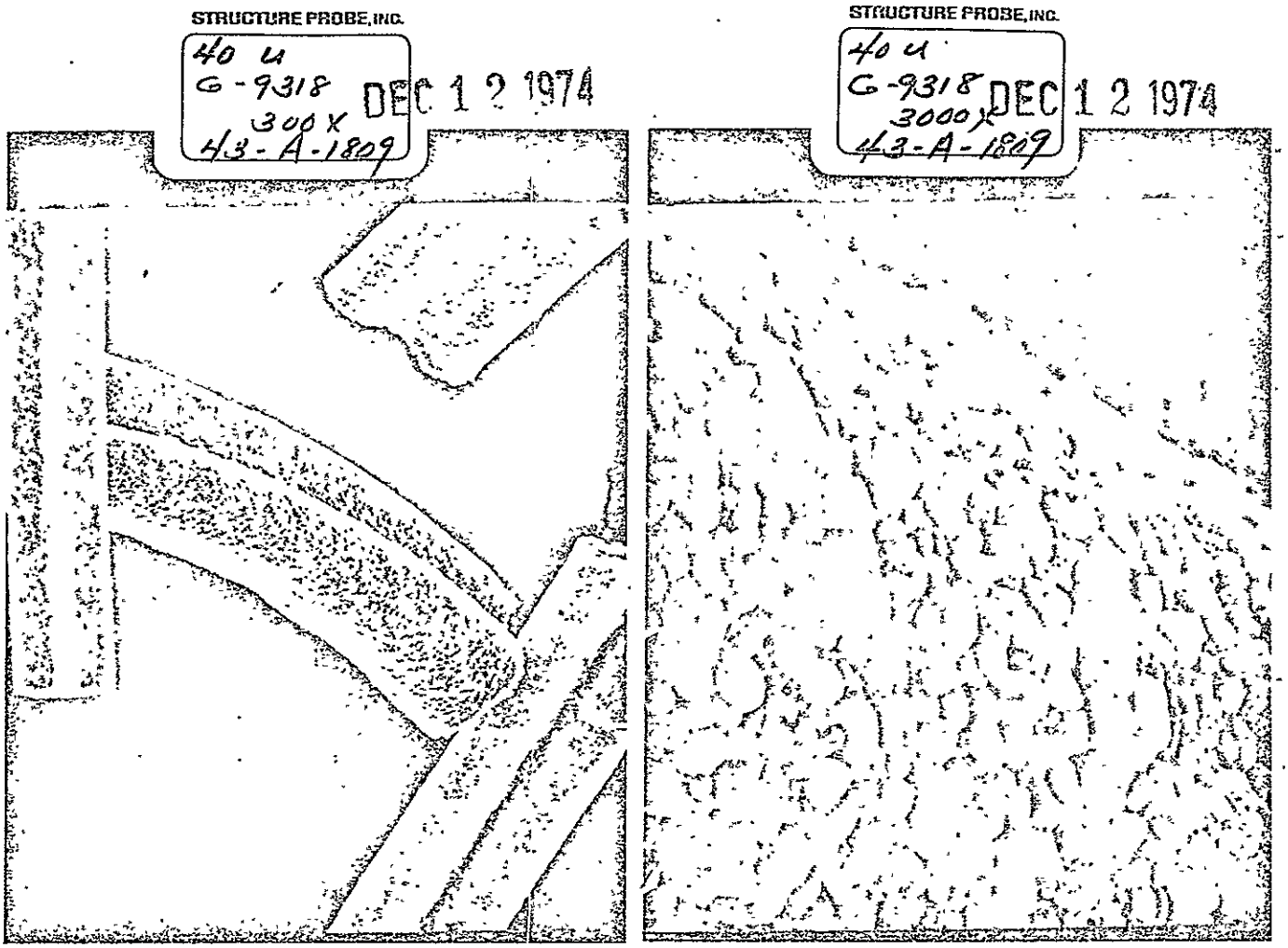


Figure 8. SEM photographs of 40μm fibers (Lot G9318). Notice the broken fiber ends and the apparent small length to diameter ratio. The grains in this fiber lot appear to be of the same general size as the 10μm fibers (Lot G9251) but smaller than the grains for the 20μm fibers (Lot 69303). Compare this figure with Figures 6 and 7.

42

collecting the sieved powders; packing the powders into a 0.3 mm diameter thin walled Lindemann glass capillaries. The filled capillary tubes were used as specimens in a 57.3 mm diameter Debye-Scherrer powder x-ray diffraction camera (nickel filtered copper x-radiation was used). X-ray diffraction photographs were prepared from each of the specimens.

The resulting x-ray diffraction photographs indicated that all of the specimens were similar. All diffraction lines on the photographs were those of alumina. All equivalent, same diffraction angle, diffraction lines on the various diffraction photographs were equally "sharp" (similar diffraction line profiles) thereby indicating that the crystallite sizes of the various alumina samples were similar.

We therefore conclude that each of the alumina specimens examined had similar (no marked differences) crystalline characteristics, i.e., similar composition and similar crystallite size.

Densitometer traces which were prepared in equivalent diffraction regions from each of the x-ray diffraction photographs of the three specimens are presented in Figure 9.

3.2.4 Measurement of Fiber Geometry

The fiber geometry is of extreme importance for producing light weight rigidized tiles using ceramic fibers. If one is to achieve a high strength at a low density it is imperative that numerous fiber-to-fiber contacts and bonding at these fiber contacts be attained. The longer the fiber the higher the probability of numerous fiber-to-fiber contact occurring. In addition long, small diameter fibers have been postulated as necessary if a degree of flexibility in a tile is to be achieved.

Characterization of these fibers prior to attempting to fabricate rigidized tiles including measuring a large sample of the fibers from each lot to determine the length-to-diameter ratio of the fiber. This was accomplished using a filar lens on a Zeiss microscope at 100X magnification. Slight errors in diameter measurements probably occurred due to parallax; however, these small errors in measurement do not affect the length/diameter ratios to a significant degree. The results of this evaluation are listed in Table II.

Part of the definition of a fiber (Ref. 2) is that the length-to-diameter ratio must exceed 10. As shown in Table II only a small percentage of the fibers evaluated had a L/D ratio in excess of 10. The lot of aluminum fibers previously evaluated in an exploratory study (Lot 8467G) had 89% of the fibers with a L/D ratio in excess of 10. The lots of fibers evaluated in this current effort had only 54%, 3.4% and 33.9% of the fibers with a L/D greater than 10. The very small fiber lengths compared to the fiber diameters created a situation which, within the restraints of this program at least, could not be overcome as will be discussed in the remainder of this report.

13

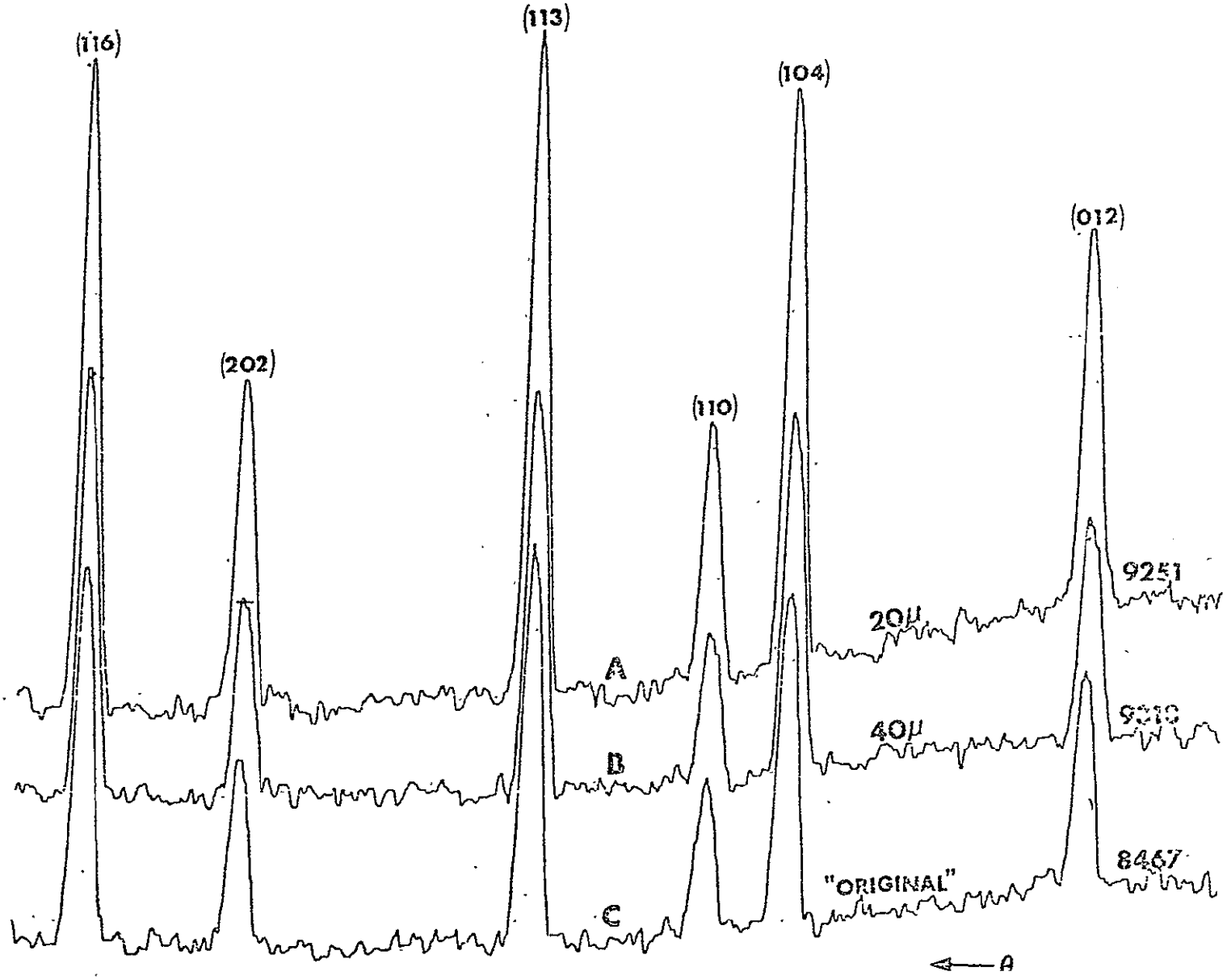


Figure 9. Densitometer traces prepared from portions of x-ray diffraction photographs. Nickel filtered copper x-radiation, diffraction range $\approx 25^\circ < 2\theta < 58^\circ$. Alumina fibers A, sample G9251, 20 μm diameter fibers. B, sample G9318, 40 μm diameter fibers. C, sample 8467G, 10 μm fibers.

Figures 10-12 are histograms showing the distribution of the fiber lengths.

3.3 FABRICATION

3.3.1 Preliminary Fabrication Studies

Because of the limited amount of fibers available on this program a series of panels were fabricated using other types of available fibers to establish casting techniques and to develop binder preparation standards. This data is of little technical use and is included only because it demonstrates the very significant part fiber geometry has on the casting and properties of lightweight rigidized tiles made from ceramic fibers.

A series of eight 7"x7" panels were cast using the standard binder and process described in Subsection 3.1 of this report. Table III lists the fibers used in these experiments and the results obtained.

The first panel was prepared as described in Reference 1. The fibers used were mullite fibers which had an average diameter of 6 μm and after chopping in a Waring Blender had an average fiber length of $\sim$270 (Reference 3). Figure 13 is a schematic diagram of the casting fixture. During fabrication of this panel leaks developed at the edges of the screen and the acrylic shell and thus the panel was of poor quality.

The second panel was made using the same type of fiber but with an improved seal. In addition a vacuum was pulled on the system instead of using the aspirator. This panel had a fairly uniform appearance and a measured density of approximately 14 lb/ft^3.

The third panel was fabricated using alumina-silicate fibers. A leak developed in the screen during the casting operation and thus no useable data was obtained.

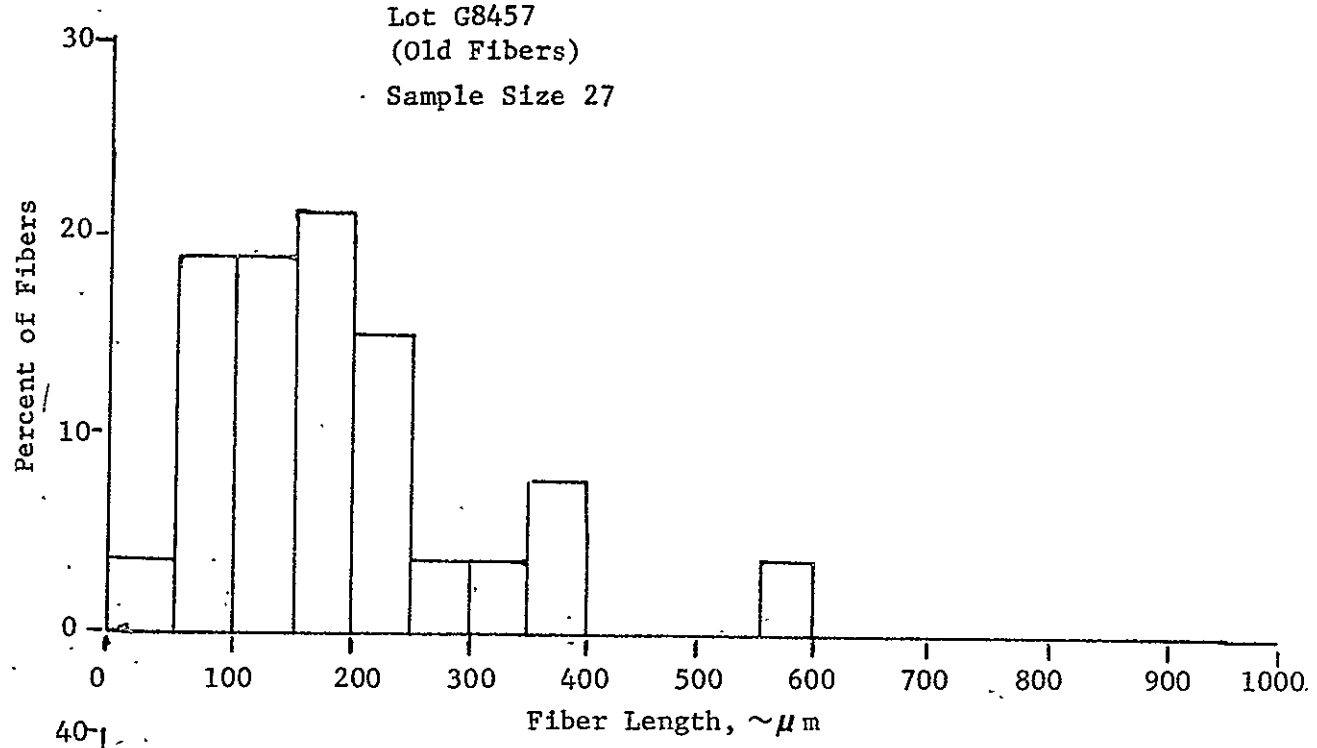
The fourth panel was fabricated using silica Microquartz® fibers from Johns-Manville. These fibers are very small in diameter and the fibers have very high length/diameter ratios. This panel looked very good after casting and drying and had a density of about 8 lb/ft^3.

The fifth panel was made using alumina-silicate fibers. This panel was allowed to drain without any applied vacuum. The panel was somewhat uneven but otherwise looked good. The density was about 20 lb/ft^3.

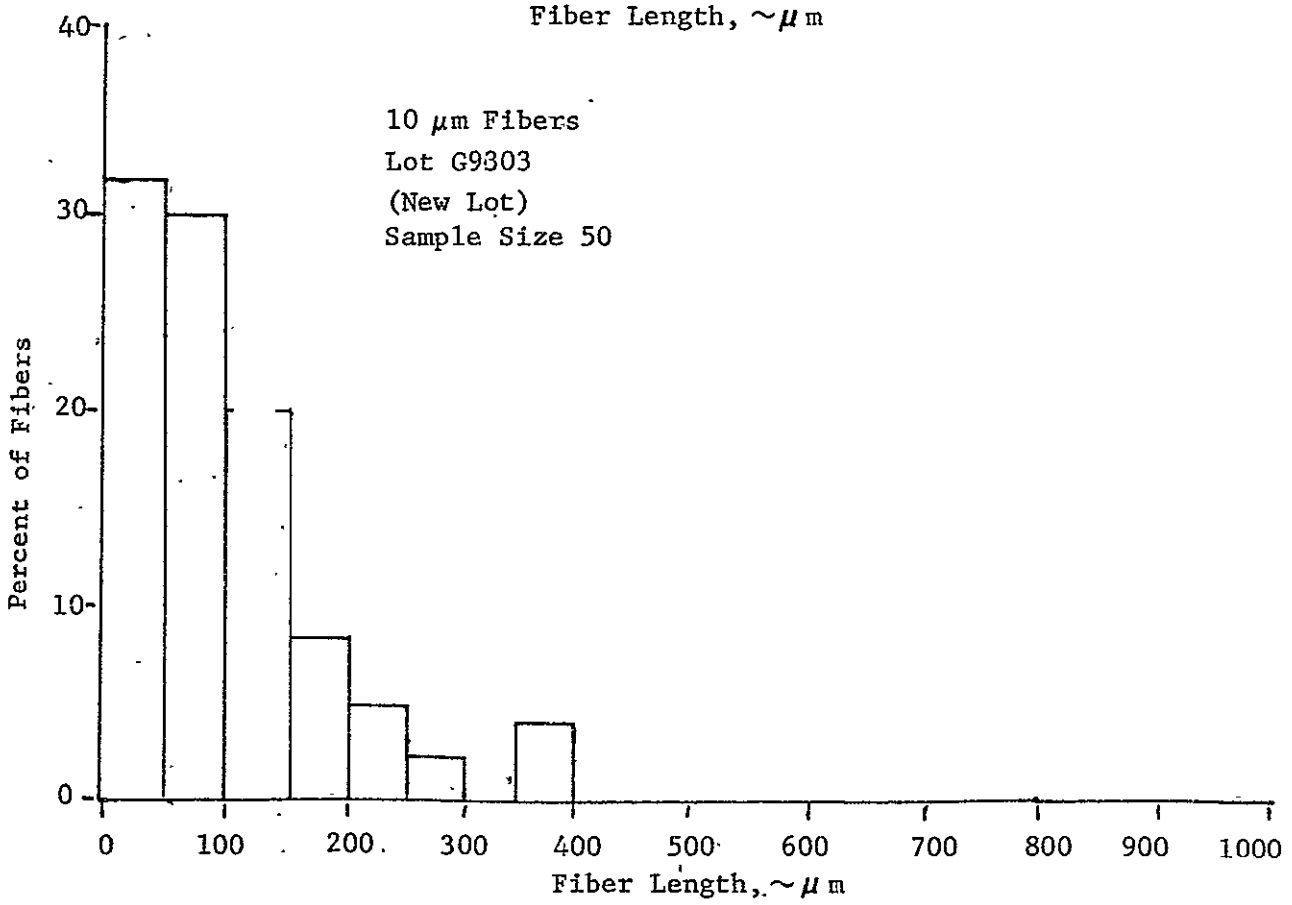
Panel 6 was made with Microquartz® fibers. In this experiment the fibers were mixed with the binder in a Waring Blender for one minute before casting. The panel was very uniform and looked good.

The first attempt to cast a panel using alumina fibers was made with the 40 μm fiber. Even though this fiber was from 5 to 20 times greater in diameter than the other fibers used in this series a very

Figure 10. Fiber Length Distribution
10 μm Fibers
Lot G8457
(Old Fibers)
Sample Size 27

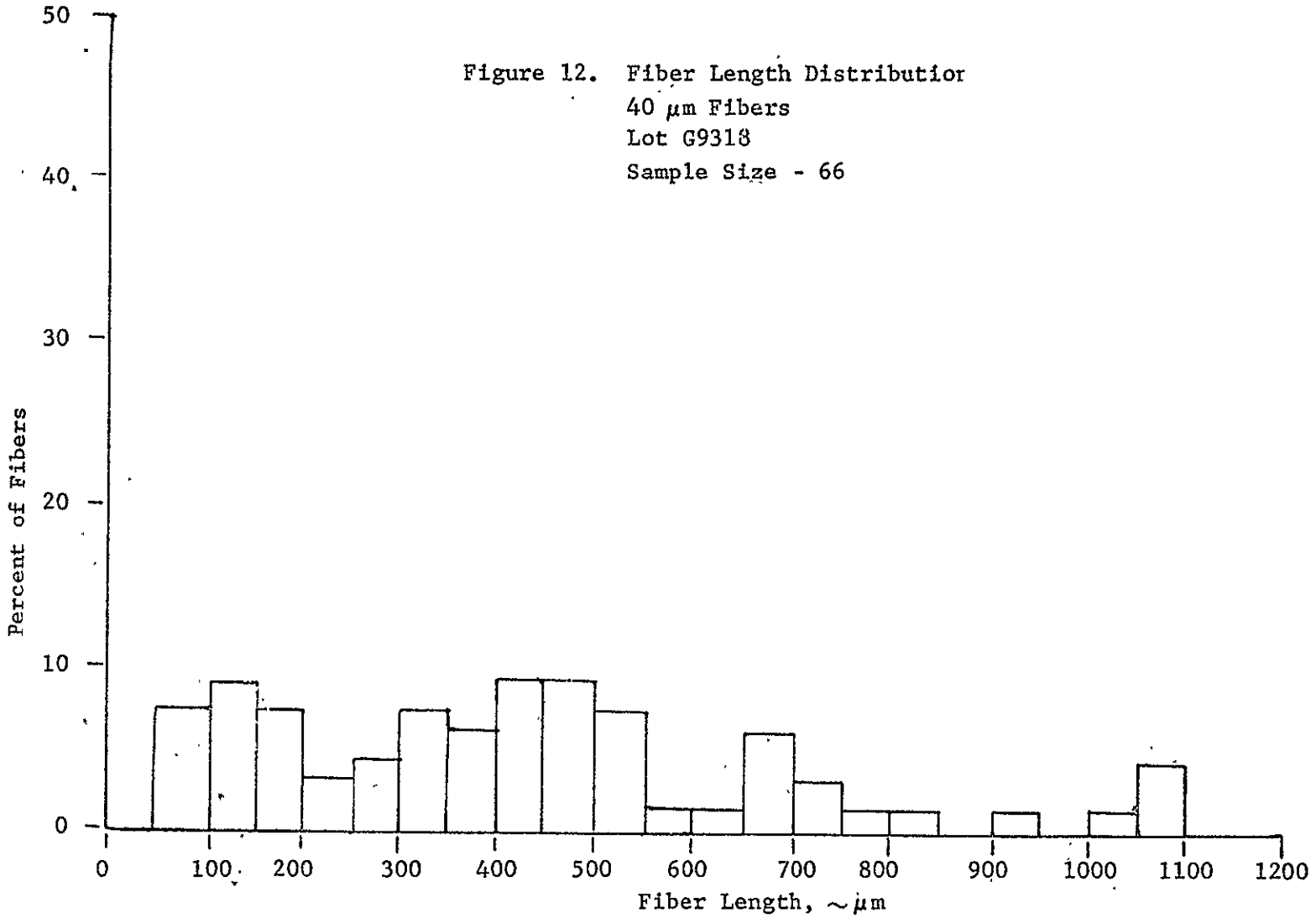


10 μm Fibers
Lot G9303
(New Lot)
Sample Size 50



76

Figure 12. Fiber Length Distribution
40 μm Fibers
Lot G9318
Sample Size - 66



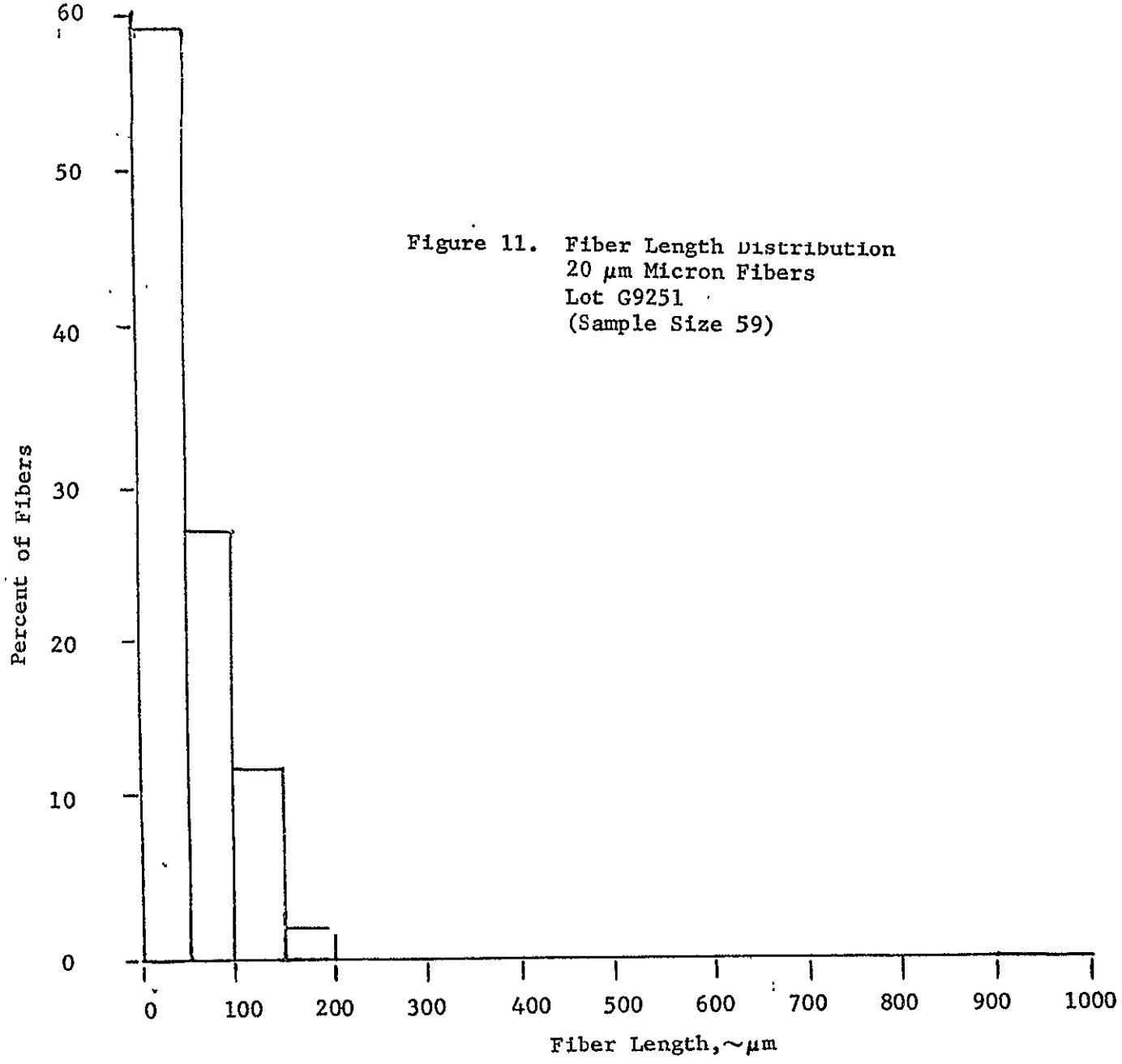


Figure 11. Fiber Length Distribution
20 µm Micron Fibers
Lot G9251
(Sample Size 59)

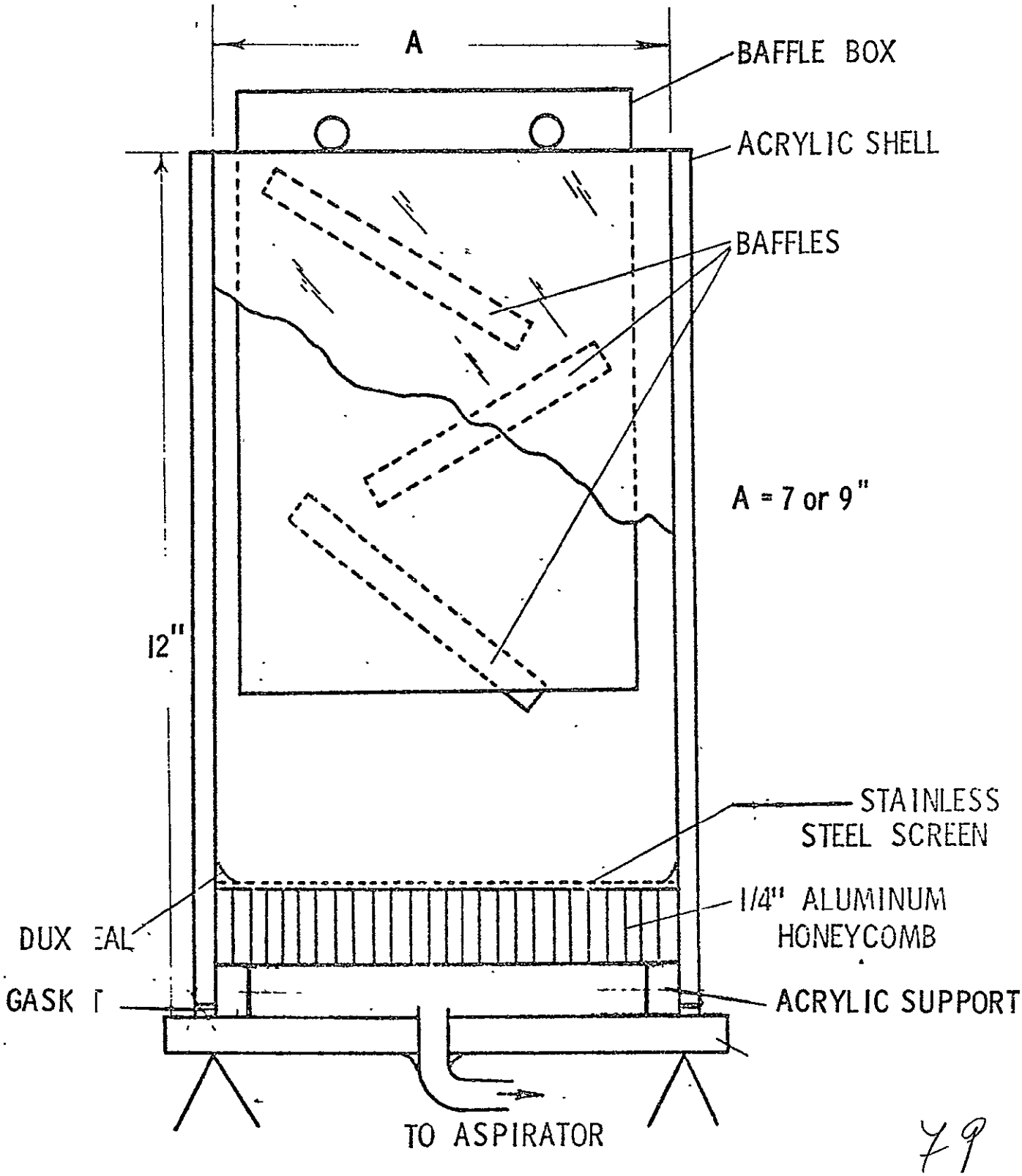


Figure 13. Schematic showing construction of Molding Fixture.

TABLE III

PROCESS SET-UP STUDIES USING OTHER TYPE FIBERS

Sample	Fiber Type	Binder	Notes and Results
1	Mullite (6 μm fibers)	(Dispal® /HCl/$MgCl_2$ standard)	Leak at edge of screen No useable data.
2	Mullite (6 μm fibers)	Same	Fair panel density ~14 lb/ft^3
3	Alumina Silicate	Same	Leak lost fibers
4	Silica Microquartz R	Same	Very good ~8 lb/ft^3
5	Fiberfrax R	Same	No vacuum was used. Good panel density ~20 lb/ft^3
6	Silica, Microquartz R	Same	Fiber mixed with binder for 1 minute. Good.
7	40 μm Lot G9318	Same with Gelatin added	Would not cast.
8	Chopped Alumina Silicate	Same	Panel looked good as-casted.

Dispal - Aluminum Monohydrate - Distributed by Philadelphia Quartz Co.

80

large percentage of the fibers simply passed directly through the stainless steel screen. This is attributed to the very short length of the fibers which resulted in little if any matting or interlocking of the fibers as they were cast. A second attempt was made using these same recovered fibers but by adding a gelatin to thicken the binder. This attempt did not cast and resulted in thick accumulation in the bottom of the casting box.

The final panel cast in this series used a gasketed seal to improve vacuum uniformity and a smaller mesh screen. Alumina-silicate fibers were used and a representative panel was obtained.

After fabricating these panels it was evident that the process, the binder solution and the equipment was capable of producing lightweight ceramic fiber composites with a relatively uniform appearance and comparable to our previous work on ceramic fiber composites.

3.3.2 Small Sample Size Fabrication

The next logical fabrication step was to fabricate some small size samples to determine what density range could be obtained and to estimate the level of strength which could be achieved at the various densities.

The same binder solution was used in these studies as used previously. A total of eight samples were fabricated and all were fired to 2700°F and soaked at this temperature for 2 hours.

The sample size was constant for all eight samples (25 grams of fibers). The fiber/binder slurries were cast into a 2-7/8" diameter by 12" long acrylic tube. A 60 mesh screen was used to support the fiber mat and the tube was designed so that a small partial pressure could be applied to help remove excess binder. Table IV lists the eight experiments and the results.

The first test specimen of this series was Sample 1A. This sample was made using the 40 μm fiber (Lot G-9318). As listed in Table IV the approximate density was 42 lb/ft^3. The sample could be handled but was friable. Figure 14 is a photograph of this sample.

Sample 1B was made with some very coarse fibers designated P522 which were in the laboratory. These fibers produced a sample which was of little value, except that the experiment shows that even a large diameter fiber can be fabricated into a relatively low density fiber composite (30 lb/ft^3) if the length/diameter ratio is relatively large.

The next sample, 1C, was made from the new lot of 10 μm fibers (G-9303). This sample cast very well and had a density of about 22 lb/ft^3. The sample appeared to have good strength and was not friable. Figure 15 is a photograph of this sample after firing.

TABLE IV

PRELIMINARY PROCESSING STUDIES

25 grams samples - 2-7/8" diameter

Sample No.	Fiber			Filler		Fired Properties			
	Size	Lot	Amount	Type	Amount	Binder Type	Thickness (in)	Density lb/ft^3	Appearance
1A	40μ m	G9318	25 gms	None		Standard	0.34	42.0	Friable-could be handled. Very coarse
1B	~60μ m	P522	25 gms	None		Standard	0.52	30.0	Brittle
1C	10μ m	G9303	25 gms	None		Standard	0.70	22.0	Very good
1D	20μ m	G9251	25 gms	None		Standard	0.42	39.6	Good
1E	10μ m	G8467	25 gms	None		Standard	0.67	24.5	Good
1F	40μ m	G9303	25 gms	Gelatin		Standard	0.40	40.0	Bad
1G	40μ m	G9318	25 gms	30 gms chopped carbon fibers		Standard	2.40	7.0	Extremely weak
2G	40μ m	G9318	25 gms	5 gms chopped carbon fibers		Standard	0.51	22.0	Weak

82

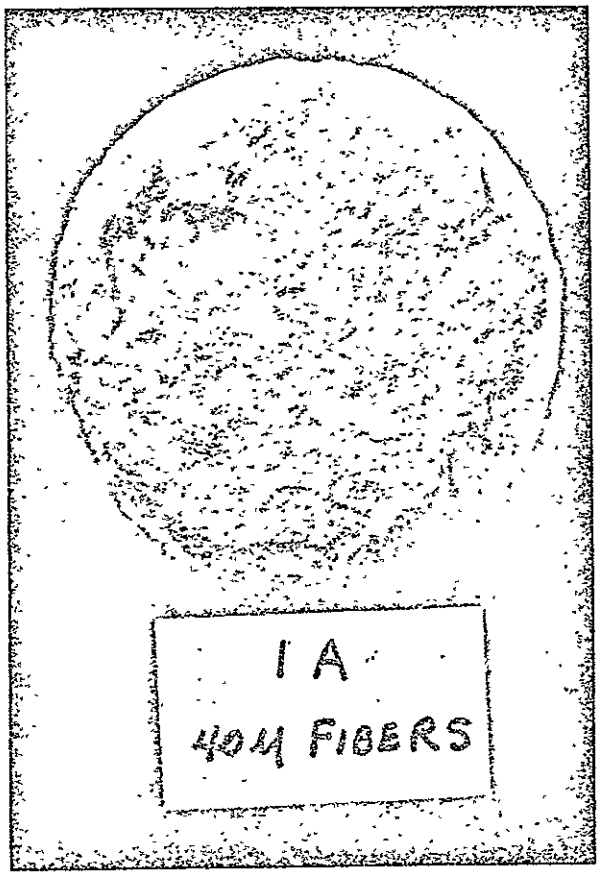


Figure 14. Photograph of 2-7/8" diameter specimen made from 40μm fibers. (Sample 1A) Fired density 42.0 lb/ft^3

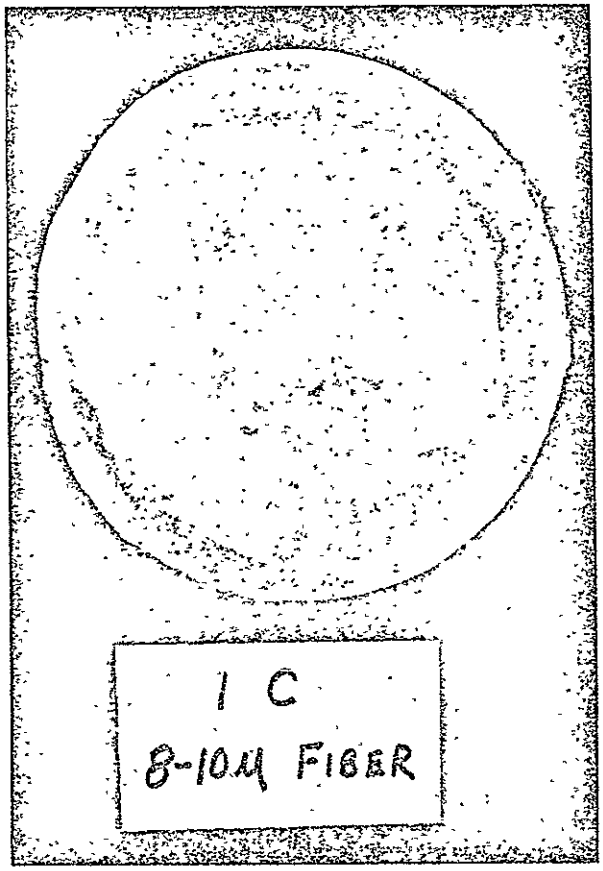


Figure 15. Photograph of 2-7/8" diameter sample made with 10μm fibers. (Sample 1C) Fired density 22.2 lb/ft^3

83

The 20 μm fiber (Lot G9251) was used in Sample 1D. Figure 16 is a photograph of this sample. The overall appearance of the sample was good and the density of this sample was about 40 lb/ft^3.

To complete this first part of this series a sample was fabricated using 10 μm fibers from the previous work (Lot 8467G). Figure 17 is a photograph of this sample which had a good appearance and appeared to be relatively strong at a density of about 24.5 lb/ft^3.

In an attempt to vary the density of the tiles three additional specimens were fabricated in this preliminary processing phase. Sample 1F (Figure 18) was made with 40 μm fibers. It was similar to specimen 1A except gelatin was added to thicken the binder slurry in an attempt to produce a lighter weight tile. The tile produced had a fired density of 40 lb/ft^3 but its appearance was poor and the sample was weak.

A second attempt was made to reduce the density of specimens fabricated with the 40 μm by using a filter which could be "burnt-out" during the firing operation. A number of consumable materials were considered. It was decided that the best approach would be to use a small diameter fiber material instead of a more conventional filler such as sawdust or phenolic microballoons. This decision was made because of the high density of the alumina fibers and the low densities of these conventional fillers would most likely lead to segregation in the slurry and would also probably result in non-uniform, weak composites. The selected filler was therefore carbon fibers. These were selected because of their high L/D ratios, small diameters, and relatively low burn-off temperatures. Another factor in this selection was that carbon does not wet readily and therefore the binder would tend to preferentially adhere to the alumina fibers. The first sample made using this technique was sample 1G. The ratio of carbon fibers to alumina fibers were 30/25 by weight. The sample produced had a very low density of about 7 lb/ft^3 and no trace of residue from the carbon fibers. However this sample, as would be expected, was extremely weak. Figure 19 is a series of photographs showing this sample before and after firing.

Another sample (2G) was made using the same techniques described above for Sample 1G except the carbon fiber/alumina fiber weight ratio was reduced from 30/25 to 5/25. This sample had a fired density of about 22 lb/ft^3 but was weak and friable.

The results of the preliminary fabrication studies discussed in this section and in Section 3.3.1 indicate that low density, relatively good strength composites can be fabricated using the casting process described with the binder system selected. There appears to be a direct relationship between fiber diameter and composite density as shown below:

10 μm fibers (G9303)	22 lb/ft^3
10 μm fibers (8467G)	24.5 lb/ft^3
20 μm fibers (G9251)	39.6 lb/ft^3
40 μm fibers (G9303)	42.0 lb/ft^3

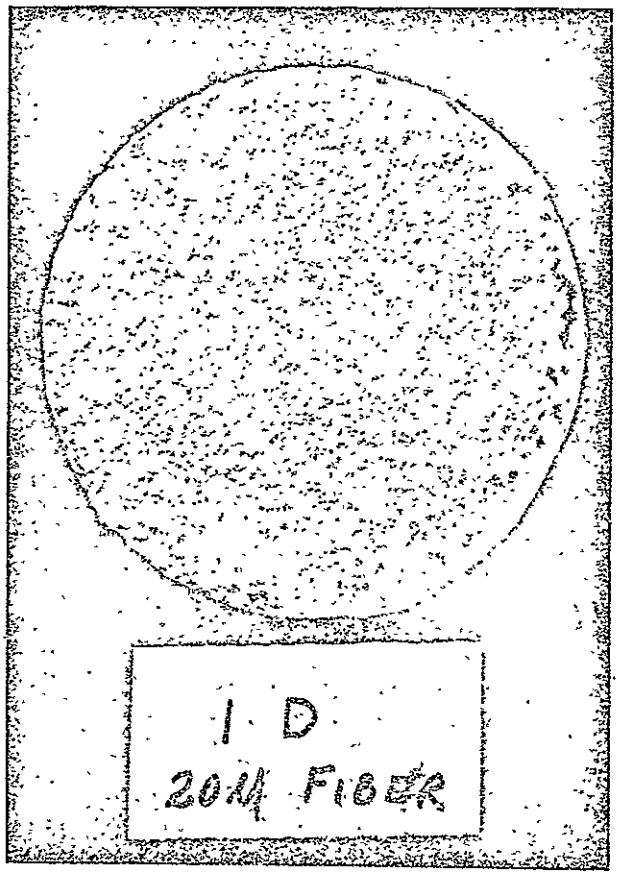


Figure 16. Photograph of 2-7/8" diameter sample made from 20 μm fiber (Lot G9251). Figure Density 39.5 lb/ft^3.

85

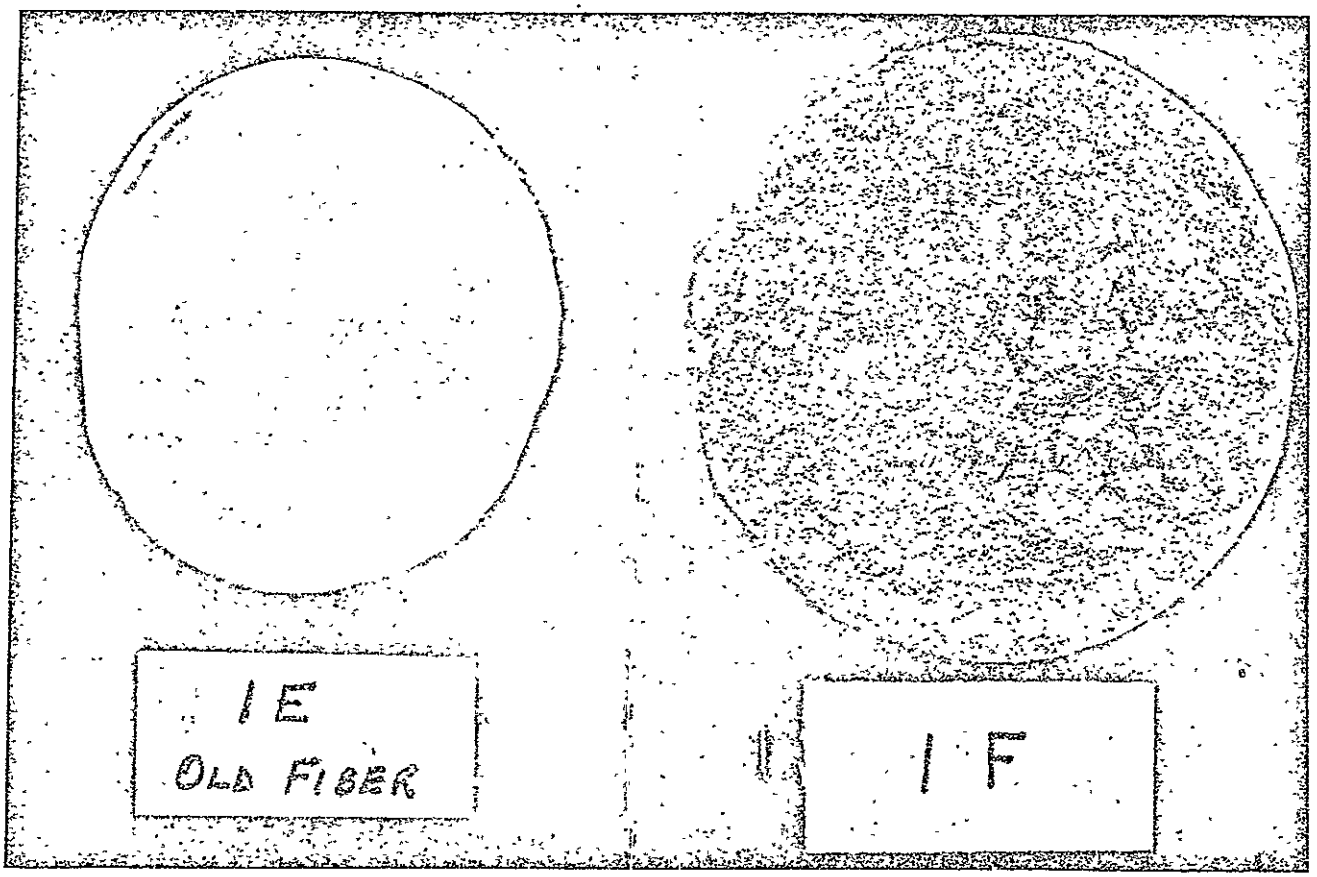
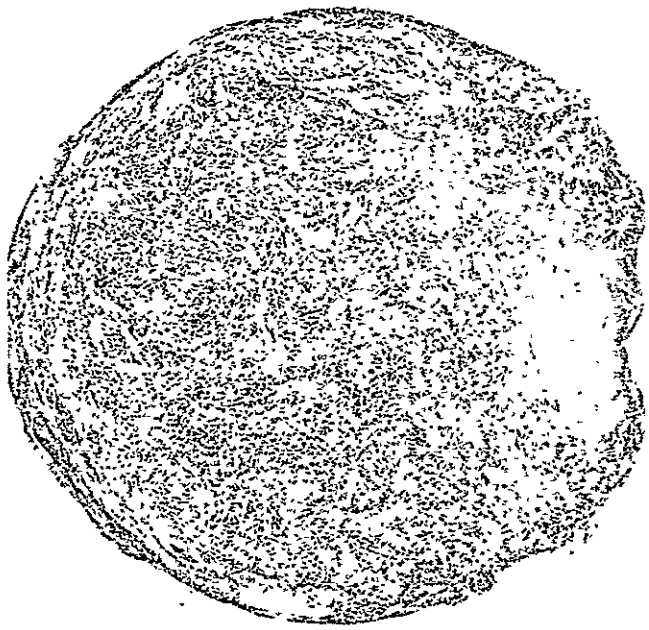
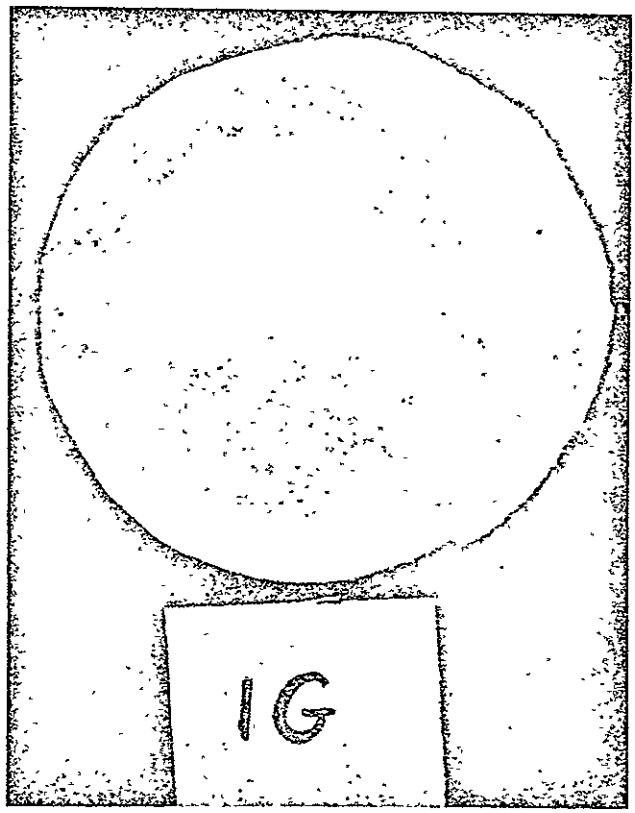


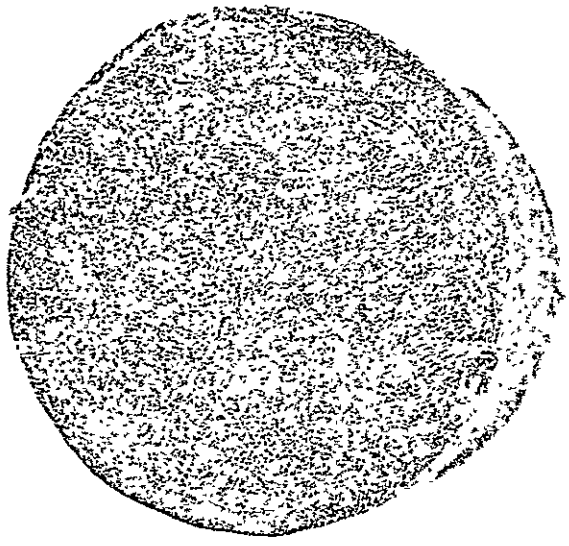
Figure 17. Photograph of 2-7/8" diameter sample made with 10 μm fibers. Sample 1E. Fired density 24.5 lb/ft^3

Figure 18. Photograph of Sample 1F. This sample was made using gelatin added to the binder solution to thicken the binder. Fired density 40.6 lb/ft^3

86







1 G

Figure 19. Photographs of Sample 1G. This sample was made with 45 w/o 40 fiber and 55 w/o chopped carbon fiber. The fired density of this sample (after burn-out of carbon fibers) was about 11 lb/ft^3.

Upper Left: Top of Sample "As Cast"

Lower Left: Bottom of Sample "As Cast"

Upper Right: Fired Sample

87

Techniques to lower the density of the larger diameter fibers by adding a fibrous "burn-out" material will produce composites with lower densities, but these composites are very weak and friable and do not appear to have sufficient strength to be considered an "Engineering Material".

It appears that larger diameter fibers will require high > 20 length/diameter ratios if low density composites with useable strengths are to be attained.

3.3.3 Fabrication of a Full Size Tile Using 10 Micron Diameter Fibers

Only 0.5 pounds of fiber Lot G9303 was supplied for evaluation. The goals for the evaluation of this material were to investigate the thermal conductivity, thermal expansion and crystalline morphology of this material at a single density. The 0.5 pounds of material limited the fabrication to a single tile. The previous results using a similar type fiber (Lot 8467G) and the results obtained using this fiber lot for a small sample (Sample 1C) indicated a good panel could be fabricated.

The panel fabricated from this fiber was designated panel 10-9-1. This first number in the series (10) indicates nominal fiber diameter, the second number (9) indicates the size of the panel fabricated (9"x9") and the third number (1) is the sequential number of this type panel. This numbering system was used for all full scale panels.

The binder system for this panel was prepared as listed in Table V. The panel cast without problems and was fired to 2700°F. The appearance of the panel was good, except for a slight and unexplained discloration. The density of the "as-fired" panel was ~ 25 lb/ft^3. During the subsequent machining operation some conglobates of fiber-binder were found in the panel. These were attributed to insufficient dispersion of the binder ingredients. It was possible to obtain good representative samples from this panel for thermal conductivity measurements and thermal expansion measurements by judicious planning during the machining operation.

The thermal properties obtained on this panel are presented in Section 4 of this report. No mechanical property measurements were possible or planned for this material because of the limited amount of fibers available. However if the appearance of the samples and the results during machining operation are considered this material is far superior in mechanical strength when compared to the tiles made with either the 20 μm fibers or the 40 μm fibers.

88

TABLE V

STANDARD BINDER SOLUTION

MATERIALS

Material	Material Description	Amount
Dispal®	Alumina Monohydrate	160 gms
HCl	Conc. Hydrochloric Acid	720 ml
$MgCl_2$	Magnesium Chloride	10 gms
Water	Distilled	10,200 ml

BINDER PREPARATION

1) Add Dispal® and HCl to distilled water and allow to mix using a magnetic stirrer for 2 hours.

2) Add $MgCl_2$ and allow to mix for 15 minutes

3) Add fibers and hand mix for 5 minutes

CASTING

1) Pour fiber/binder slurry into casting box (Figure 13)

2) Allow to drain for 1-2 minutes

3) Apply suction until visible liquid is removed

4) Remove from casting box

DRYING & FIRING

1) Air dry for 24 hours

2) Dry at 120°F for 24 hours

3) Dry at 250°F for 24 hours

4) Fire to 2700°F - hold at 2700°F for 2 hours

89

3.3.4 Fabrication of Tiles Using 20 μm Diameter Fibers

A total of ten full size tiles were fabricated using the 20 μm diameter fiber (Lot G9251). Seven of these tiles were fabricated as 7"x7" diameter tiles and the other three were 9"x9" tiles. Table VI lists the fabrication parameters for these tiles and Table VII lists the panel densities after firing and in most cases after trimming the uneven edge material. All tiles were prepared using the procedure described in Table V unless noted in the following discussion.

3.3.4.1 Discussion of Individual Tile Fabrication

Tile 20-7-1 - No useable material was obtained from this first tile. The first casting of this tile resulted in a very uneven and non-uniform tile. The fibers were recovered from this experiment and re-mixed with a 50% binder solution and then re-cast. These results were not satisfactory.

Tile 20-7-2 - The distilled water and HCl content was reduced to 50% of the water and acid used for tile 20-7-1. In addition the fibers were added to the binder and this slurry was blended for 10 seconds in a Warning blender before casting. There was difficulty in casting this material because of the short fiber length. Three attempts were made and none were successful. During these casting operations the seal at the bottom of the casting box was replaced by a rubber gasket and the screen size was reduced from 20 to 60 mesh. No useable material was obtained from these three attempts.

Tile 20-7-3 - This panel was cast using the improved casting design developed during fabrication of tile 20-7-2. That is, gasket seal on casting box and smaller mesh screen. These changes were used for all subsequent castings. This tile looked extremely good as-cast. The density of the tile was at the high range of the desired goal (52.6 lb/ft^3). After firing to 2700°F an attempt was made to machine samples from this tile. During the machining operation it was found that this sample contained lumps or conglomerations of binder slurry which appear to be well bonded masses which were not incorporated into the composite structure. Figure 20 is a radiographic positive made of tile which shows these masses within the tile. These masses were later found to be caused by insufficient homogeneity in the binder system.

Tile 20-7-4 - This tile was fabricated using the same approach as 20-7-3 except the binder was mixed for 8 hours instead of 4 before the fibers were added. This tile required 4 hours to drain to remove the excess liquid. No apparent reason was found to explain this different behavior of this tile and the other tiles in this series. The density of the tile was 49.5 lb/ft^3. The tile was distorted and no useable mechanical data could be obtained from this material.

Figures 21 and 22 are SEM photographs of sections of this tile. Notice in Figure 21 the evidence of binder coating on the fibers. Ideally one would like to have all the binder concentrated at the fiber-fiber

90

TABLE VI

FABRICATION OF 20# FIBER PANELS

Panel No.	Size (in)	Fibers (gms)	Binder					Firing		
			H_2O (liters)	Dispal (gm)	HCl (ml)	$MgCl_2$ (gm)	Special Treatments	Temp. °F	Special Cond.	
20-7-1	7x7	440	10.2	160	720	10	---	2700	---	Panel on first casting was poor. Fibers recovered. Recast with 1/2 binder solution-poor.
20-7-2	7x7	440	5.1	160	360	10	Fiber/binder chopped 10 seconds	2700	---	Recasted 3 times using same binder - results poor.
20-7-3	7x7	440	5.1	160	360	10	---	2700	---	Binder-fiber slurry developed galls of material within binder.
20-7-4	7x7	440	10.2	160	720	10	---	2700	---	Required 4 hrs to drain binder from panel.
20-7-5	7x7	440	10.2	160	720	10	Binder aged 24 hours	2700	Refired to 2800°F	
20-7-6	7x7	440	10.2	160	720	10	"	2700	---	
20-7-7	7x7	440	10.2	160	720	10	"	2700	---	
20-9-1	9x9	484	11.2	176	792	11.1	---	2700	---	
20-9-2	9x9	484	11.2	176	792	11.1	Binder aged 24 hours	2700	---	
29-9-3	9x9	484	11.2	176	792	11.1	"	2700	---	

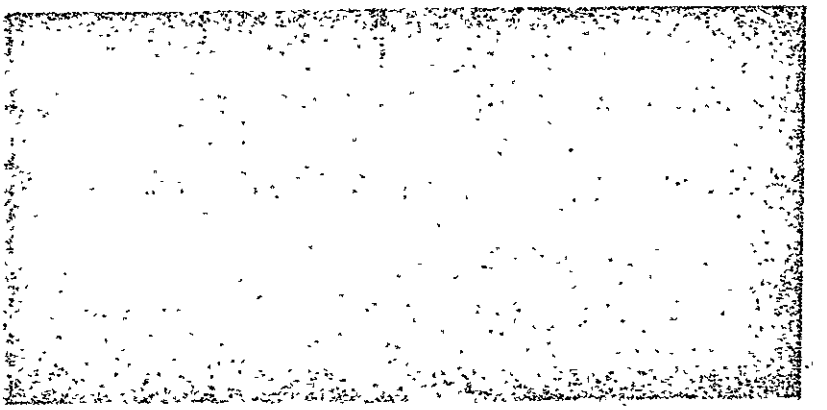
10

TABLE VII

DENSITY OF AS-CAST AND FIRED 20μm FIBER TILES

Tile No.	Final Firing Temp.	Thickness (in)	Nom. Size	Density (lb/ft^3)
20-7-1	2700°F	0.77	7" x 7"	48.1
20-7-2	2700°F	0.56	7" x 7"	55.6
20-7-3	2700°F	0.69	7" x 7"	52.6
20-7-4	2700°F	0.74	7" x 7"	49.5
20-7-5	2800°F	0.70	7" x 7"	52.9
20-7-6	2700°F	0.79	7" x 7"	46.3
20-7-7	2700°F	0.77	7" x 7"	47.03
20-9-1	2700°F	0.63	9" x 9"	52.0
20-9-2	2700°F	0.66	9" x 9"	51.5
20-9-3	2700°F	0.70	9" x 9"	48.7

92



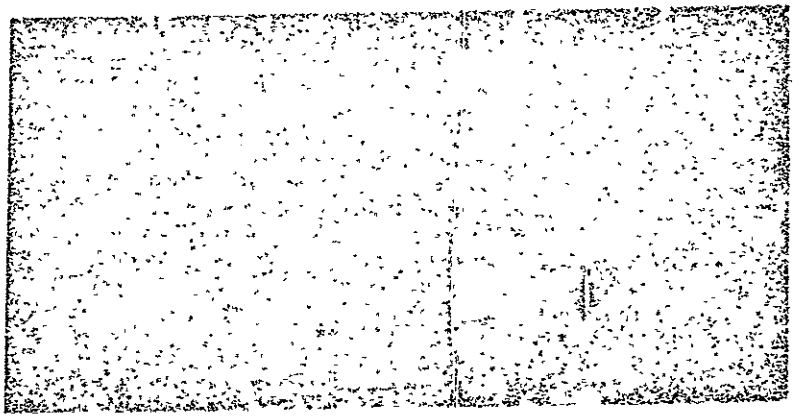


Figure 20. Radiographic positives of sections of tile 20-7-3 after machining. This radiographic positive shows some masses of binder/fiber which were not well bonded with the surface. These results were later attributed to insufficient binder homogeneity which was corrected on later tiles. (X-ray positives are at 1X magnification)

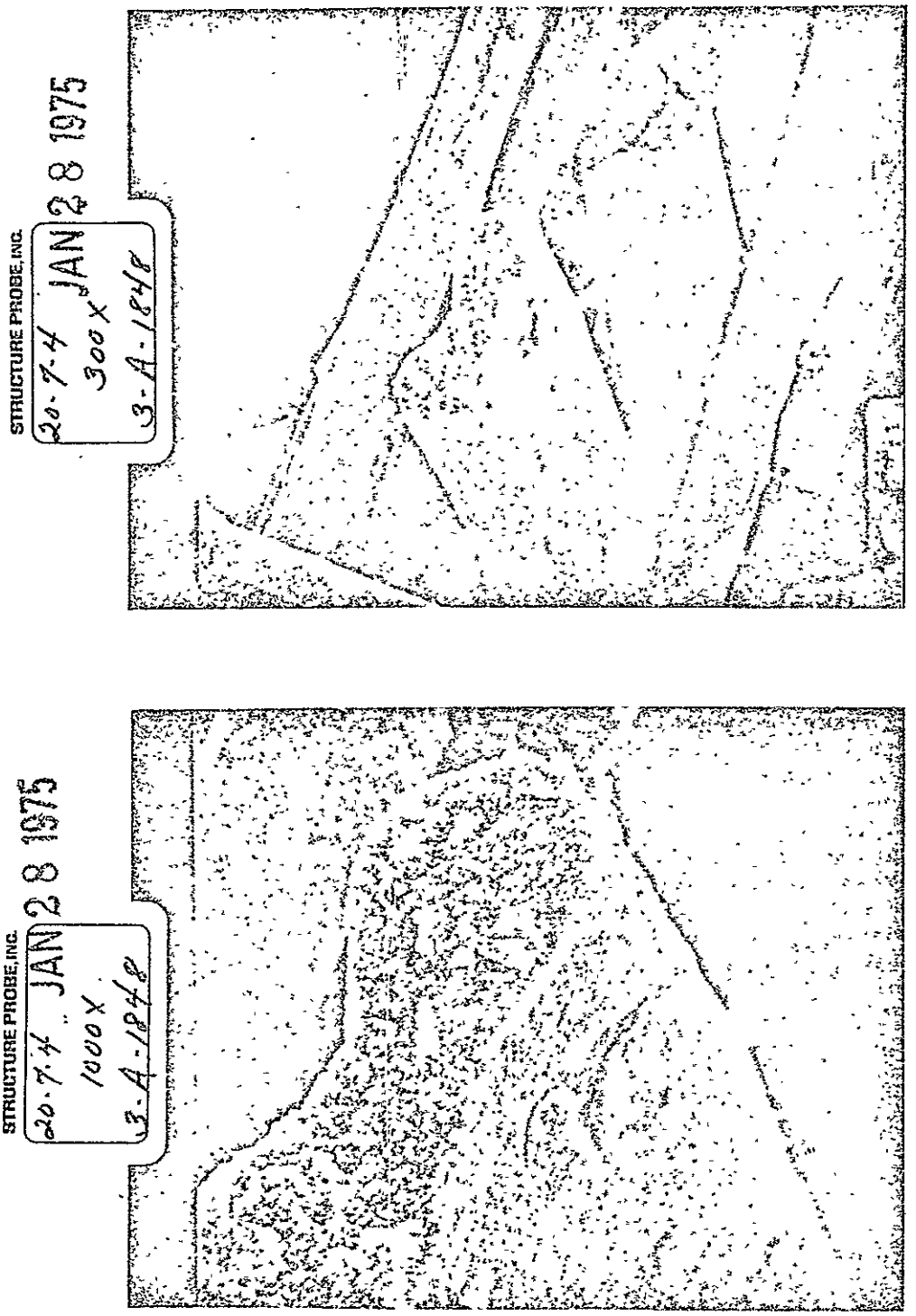


Figure 21. SEM of Tile 20-7-4 at 300X and 1000X magnification. This tile was fabricated from 20μm fibers. Notice the binder coating evident on the fibers.

94

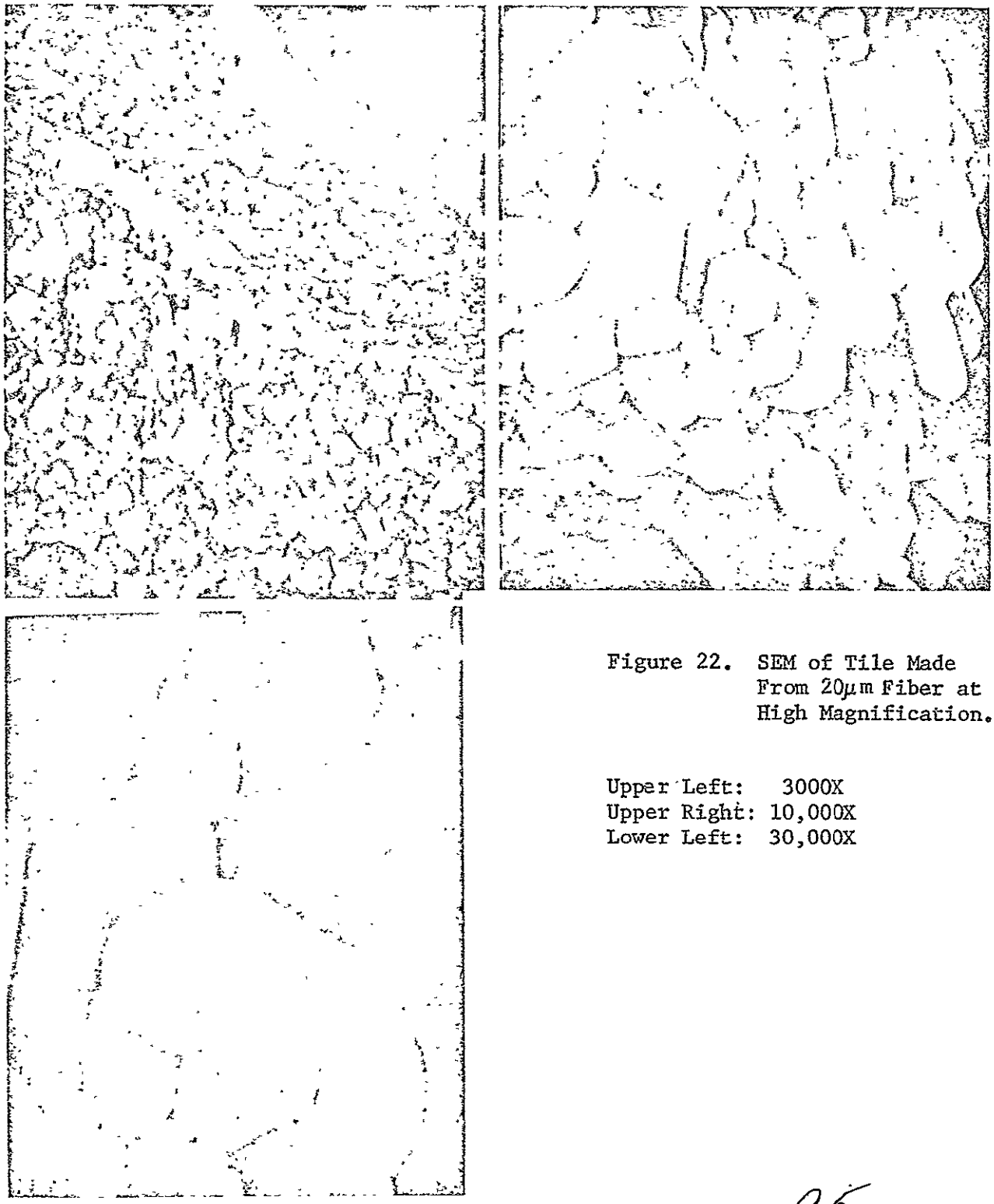


Figure 22. SEM of Tile Made From 20μm Fiber at High Magnification.

Upper Left: 3000X
Upper Right: 10,000X
Lower Left: 30,000X

95

intersections; however, if the binder is coating each fiber good bonding should occur at fibers contact points. Figure 22 are SEM photographs at higher magnification. These higher magnification photographs are interesting but do not give useful information on the composite structure.

Figure 23 is a montage radiographic positive of this tile showing variability within the tile structure.

Tile 20-7-5 - Experimentation showed that the time the Dispal, acid and water were allowed to mix had an affect on the consistency of the binder. After mixing for 8 hours and aging for 16 hours the binder solution appears to be stable and longer stirring times did not have an affect. Also after the longer stirring and aging operations the binder solution could be stored for up to a week without any apparent degradation. All remaining tiles (Tiles 20-9-1, 20-9-2 and 40-7-1 had been fabricated before these experimental data were obtained) were fabricated using a binder which had been stirred for 8 hours and allowed to age for at least 16 hours.

The tile cast extremely well with no difficulty. It was fired to 2700°F and then refired to 2800°F in an attempt to improve strength. The density after the second firing was 52.9 lb/ft^3.

Tile 20-7-6 - This tile was fabricated using the same techniques as 20-7-5 except it was not refired to 2800°F. The fired density of this tile was 46.3 lb/ft^3.

Tile 20-7-7 - This tile was fabricated exactly the same as tiles 20-7-5 and 20-7-6 except it was not refired to 2800°F and an attempt was made to compress the tile slightly before drying to enhance uniformity. The attempted compression of this sample was unsuccessful in that the tile was resilent and return to its original thickness when the pressure was released.

Tile 20-9-1 - This tile was cast before the binder aging effects were established. However there is no evidence that conglomeration in binder-fiber slurry occurred. The material cast well and produced a tile which had a uniform appearance. The density after firing was 52.0 lb/ft^3.

Tile 29-9-2 - This tile was fabricated identical to tile 20-9-1. Fired density was 51.5 lb/ft^3.

Tile 20-9-3 - This tile was fabricated identical to tiles 20-9-1 and 20-9-2 except it was fabricated at a later date and the binder was aged for 24 hours prior to use. The fired density of this panel was 48.7 lb/ft^3.

Figure 23. Radiographic Positive of Tile 20-7-4 As-Cast and Fired Showing Variability Within Tile.

97

3.3.4.2 Significant Fabrication Developments

During the fabrication of the 20 μm diameter fiber tiles several significant improvements were made. These were:

(1) When the binder solution is homogenized and aged, better panels are formed and little if any comglomerations are formed during casting.

(2) The density of the panel was slightly less when the binder was aged.

(3) A smaller mesh screen was required using the shorter length 20 μm fibers than was required using small diameter fibers (10 μm) with longer lengths and higher L/D ratios.

3.3.4.3 Use of 20 μm Fiber Composites

Tiles 20-7-5, 20-7-6, and 20-7-7 were cut-up and used to determine mechanical properties. Tiles 20-9-1, 20-9-2, and 20-9-3 were used to determine thermal properties of 20 μm fiber composites. The results of these evaluations are listed and discussed in Section 4.

3.3.5 Fabrication of Tiles Using 40 μm Diameter Fibers

A total of seven (7) full scale panels (7"x7") were fabricated using the 40 μm fibers. Table VIII lists the fabrication parameters for these tiles and Table IX lists the panel densities after firing and trimming to remove uneven edges. All tiles were prepared using the procedure listed in Table V except as noted in the following discussion.

3.3.5.1 Fabrication Details of Individual 40 μm Tiles

Tile 40-7-1 - This tile was made with the larger mesh screen. When the tile was cast it drained very rapidly at first until the fibers matted at screen surface to form a filter for the remaining slurry. This resulted in a panel with a two zone density. The bottom half of the tile was dense and appeared to have good strength. The upper half of the tile was less dense and was friable. Figure 24 is a photograph of the dense portion of the tile. Figures 25-28 are SEM photographs from the bottom and the top half of the tile.

Figure 25 are SEM's from the top part of lower density portion of the tile at 300X and 1000X magnification. The binder coating on the fibers are quite discernible. However there is little evidence of bonding between fibers at fiber content points. Figure 26 is a similar series of SEM photographs taken from the dense portion of the tile. Notice the laminar alignment of the fibers. Figures 27 and 28 are higher magnification SEM photographs which do not reveal any structural aspects of the composite.

98

TABLE VIII

FABRICATION OF 40μm FIBER PANELS

Panel No.	Size (in)	Fibers (gms)	Binder					Firing		Observations
			H_2O (liters)	Dispal (gm)	HCl (ml)	$MgCl_2$ (gm)	Special Treatments	Temp. °F	Special Cond.	
40-7-1	7x7	440	10.2	160	720	10		2700	---	Drained very rapidly resulting in a segration into a dense bottom layer and less dense upper layer.
40-7-2	7x7	440	5.1	160	360	10	Binder aged 24 hours	2700	---	Extremely friable.
40-7-3	7x7	440	5.1	160	360	10	Binder aged Fiber/binder blended for 1 minute	2700	---	Friable.
40-7-4	7x7	440	10.2	160	720	10	Binder aged 24 hours	2700	---	Friable broke into 3 pieces when removed from furnace.
40-7-5	7x7	440	10.2	160	720	10	Binder aged 24 hours	2700	Refired to 2800°F	Extremely friable-broke into 3 pieces are removed from furnace.
40-7-6	7x7	440	10.2	160	720	10	Binder aged 24 hours	2800	6-hrs @ temp.	Friable - looked good as fabricated but could not be machined into specimens.
40-7-B2	7x7	440	10.2	90	720	10	72 gms of pyrex glass added to binder. Slip ball milled 24 hrs.	2800	6 hrs @ temp.	Looked good as fired but could not be machined.

TABLE IX

DENSITY OF AS-FIRED 40μm FIBER PANELS

Tile No.	Final Firing Temp., °F	Fired Thickness	Nominal Size (in)	Density (lb/ft^3)
40-7-1	2700	.55	7 x 7	53.9
40-7-2	2700	.76	7 x 7	49.5
40-7-3	2700	.62	7 x 7	44.02
40-7-4	2700	.65	7 x 7	46.6
40-7-5	2800	.65	7 x 7	46.7
40-7-6	2700	.78	7 x 7	49.7
40-7-B2	2800	.65	7 x 7	46.1

100

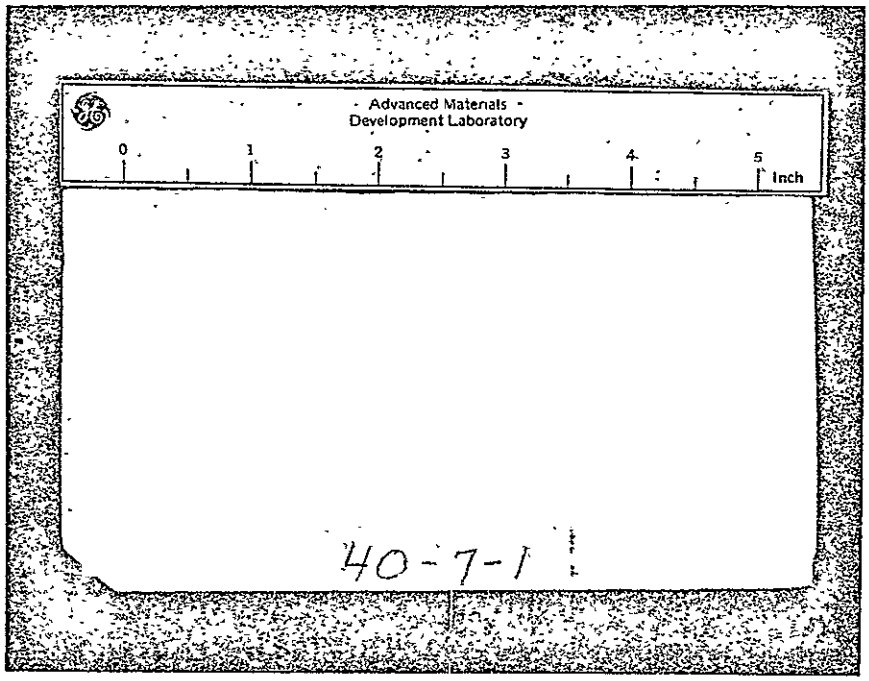


Figure 24. Photograph of Dense Portion of Tile 40-7-1.

101

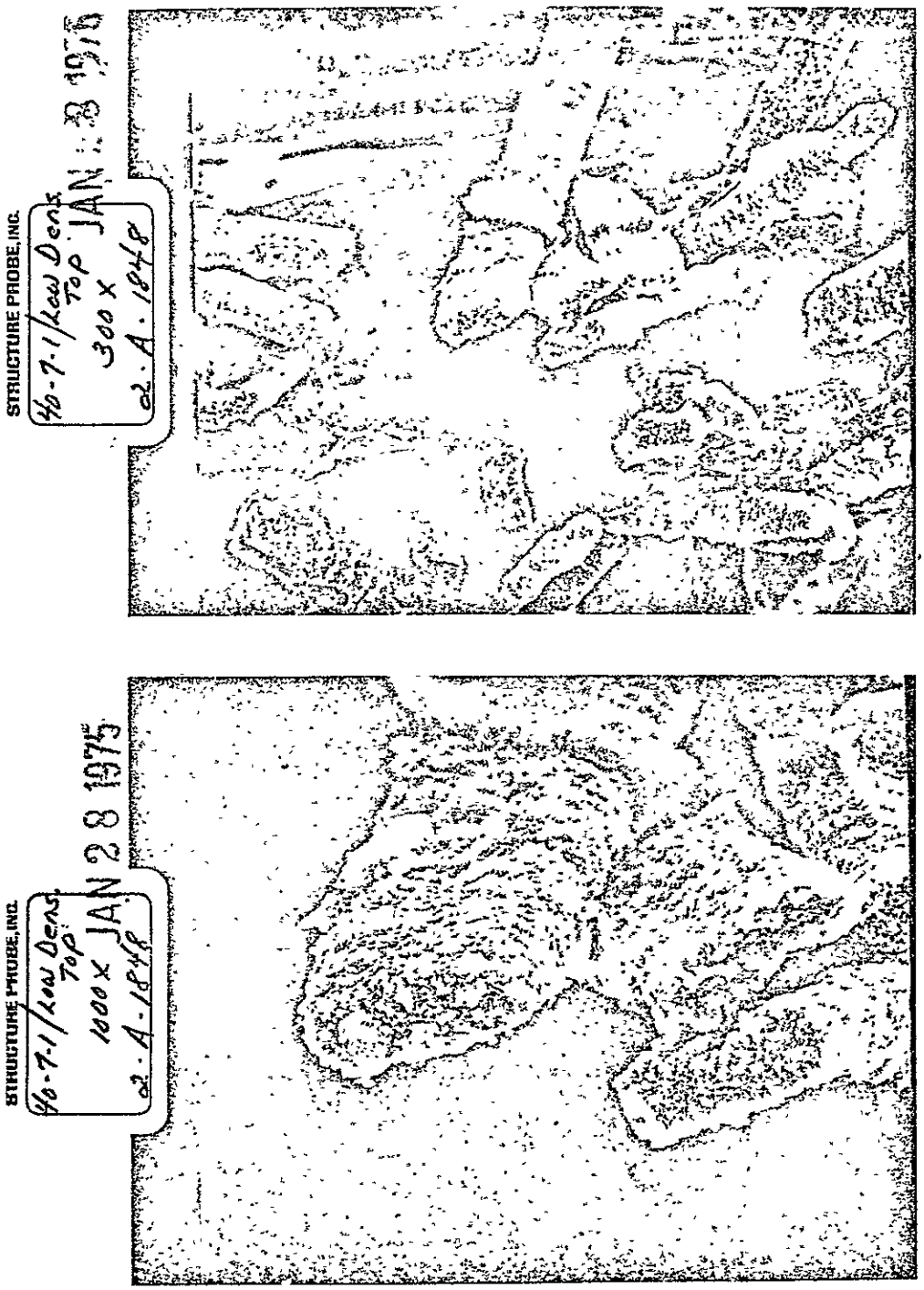


Figure 25. SEM Photographs from Lower Density Section of Tile 40-7-1. Top at 300X magnification. Lower center of top photograph at 1000X magnification. Notice binder coating on individual fibers.

10.2

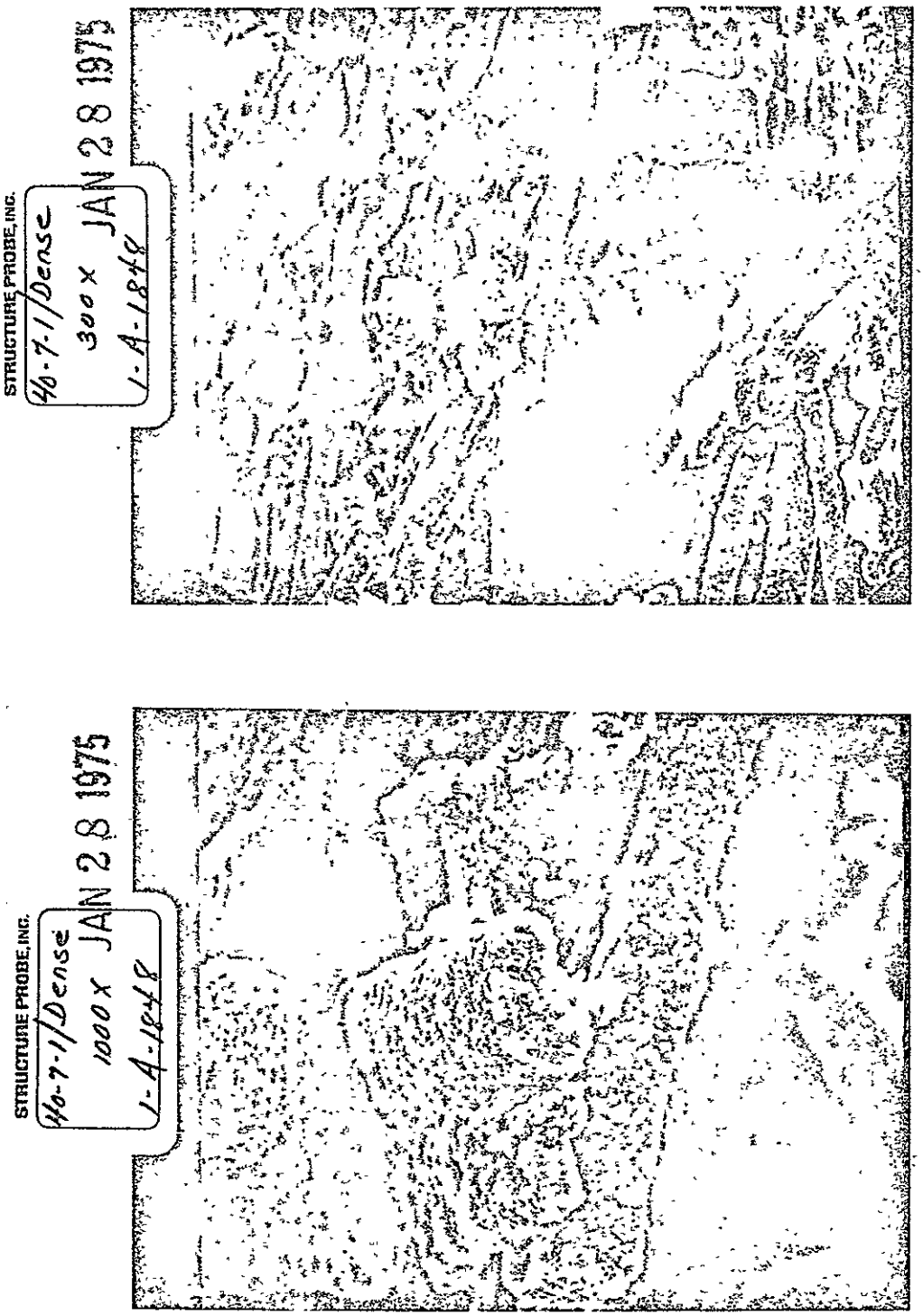
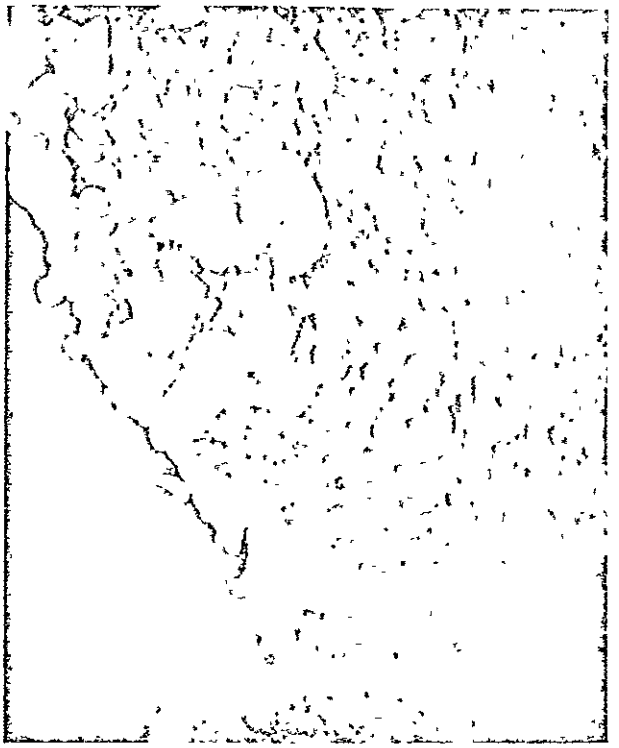
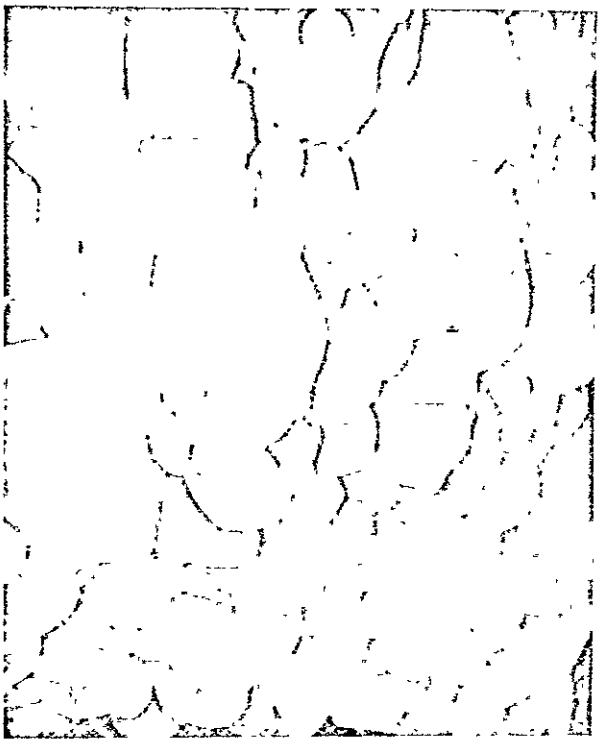


Figure 26. SEM of Tile 40-7-1. Top photograph at 300X magnification. Bottom photograph is the center section of top photograph at 1000X magnification. Notice stratification of fibers. SEM's from lower density portion of tile.

103





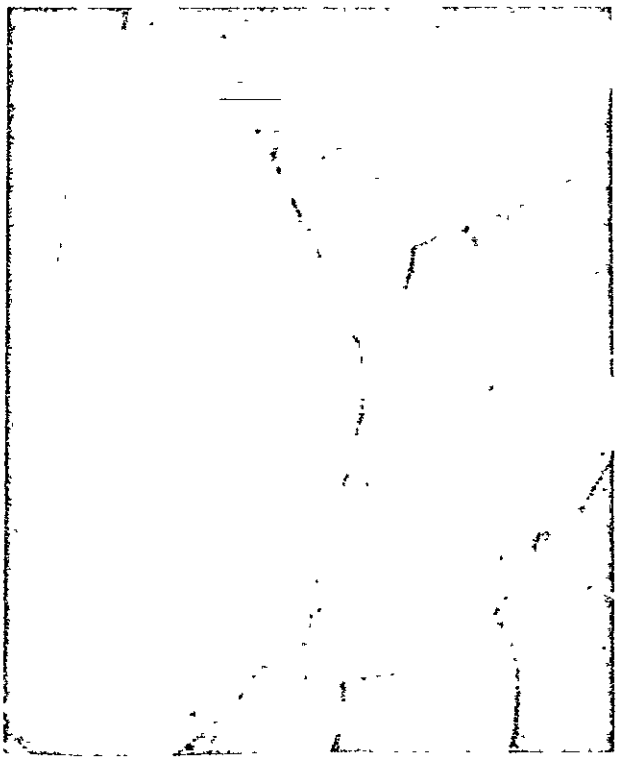


Figure 27. SEM of tile 40-7-1 from lower density portion of tile.

Upper left @ 3000X
Upper right @ 10,000X
Lower right @ 30,000X

104

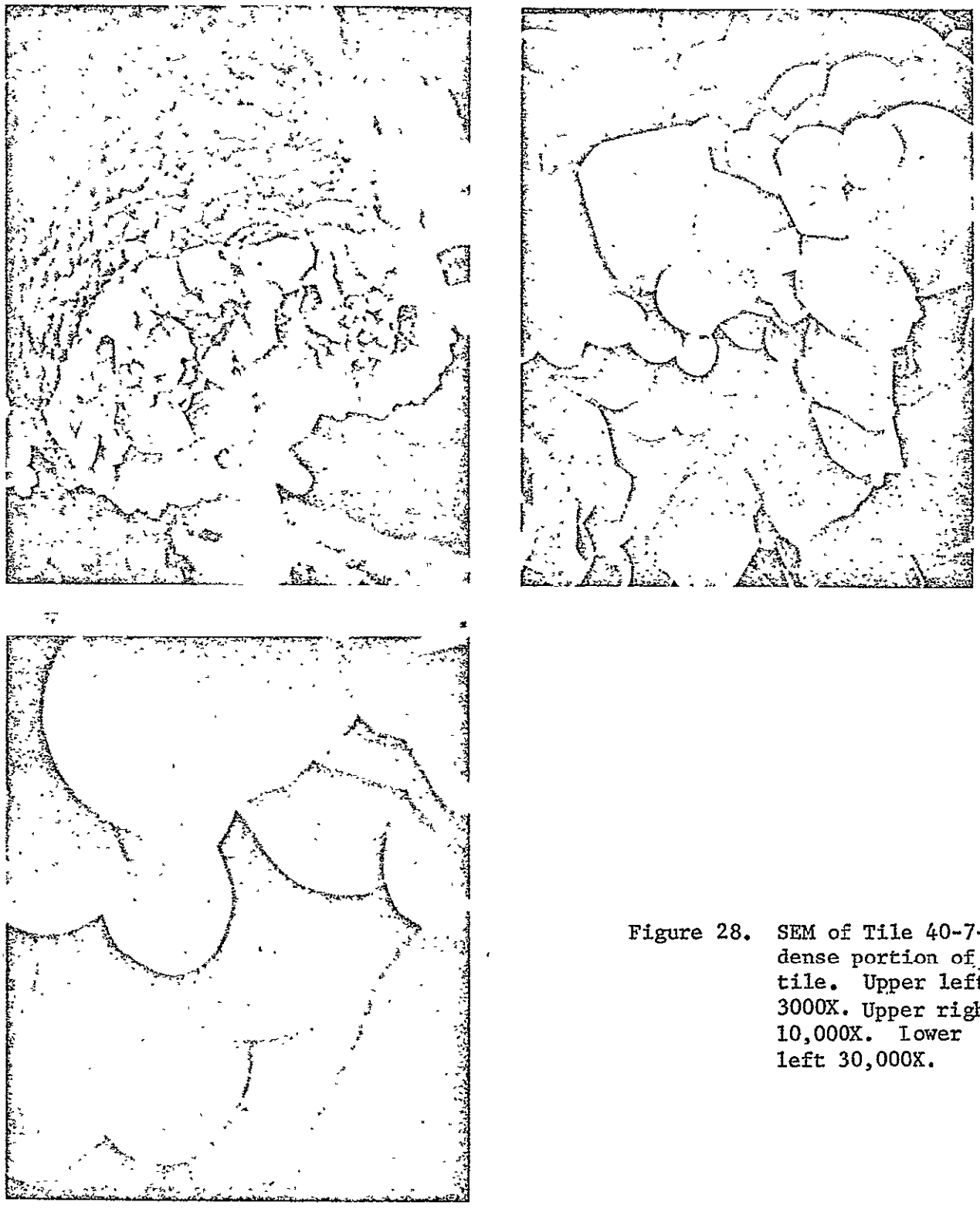


Figure 28. SEM of Tile 40-7-1 dense portion of tile. Upper left 3000X. Upper right 10,000X. Lower left 30,000X.

Figure 29 is a montage radiographic positive showing some clustering of fiber/binder conglobates within the tile.

Tile 40-7-2 - Three changes were made before casting tile 40-7-2. These were: (1) the screen size was reduced, (2) the liquid content of the binder was reduced 50%, and (3) the binder solution was allowed to age. The tile cast without difficulty. It was then fired to 2700°F and soaked at this temperature for 2 hours. After firing the tile was extremely friable. The density of this tile was about 50 lb/ft^3.

Tile 40-7-3 - This tile was processed the same as tile 40-7-2 except the fibers and slurry were blended for one minute in a Warning Blender immediately before the slurry was poured into the casting box. This panel was also extremely friable.

Tile 40-7-4 - The liquid content for this panel was increased back to the original amount and was allowed to age for 24 hours before the fibers were added. This panel appeared fairly uniform after drying. It was fired to 2700°F and allowed to soak at this temperature for two hours. After firing the tile was friable and broke into three pieces when it was removed from the furnace. Figure 30 is a photograph of this tile after firing.

Tile 40-7-5 - This tile was processed identical to Tile 40-7-4 except it was refired to 2800°F and soaked at this temperature for two hours. This tile was also very friable and broke into three pieces when removed from the furnace. Figure 31 is a photograph of this tile.

Tile 40-7-6 - This tile was processed similar to Tiles 40-7-4 and 40-7-5 except on the first firing the tile was fired to 2800°F and held at this temperature for six hours. After firing this tile had a fairly good appearance and appeared to have sufficient strength to be machined into test samples. Figure 32 is a photograph of this tile after firing. During the machining operation it was found that the interior of the tile was weak and test samples could not be obtained for this tile.

Tile 40-7-B2 - A final attempt was made to get some properties on a tile made with the 40 μm. To obtain some properties it appeared a sacrifice in refractoriness of the binder would be required. A binder was therefore prepared using a boro-silicate glass additive to the binder system. The glass containing modified binder listed in Table VIII was ball-milled for 24 hours. Tile 40-7-B2 was then cast similar to the previous tiles and after drying fired to 2800°F for six hours. This tile appeared to have some strength after firing and looked reasonably good. Figure 33 is a photograph of this tile. However acceptable samples could not be machined from this material.

Figure 29. Montage of Radiographic Positive Showing the Clustering of Fibers in Initial Casting Operations.

Tile 40-7-1

107

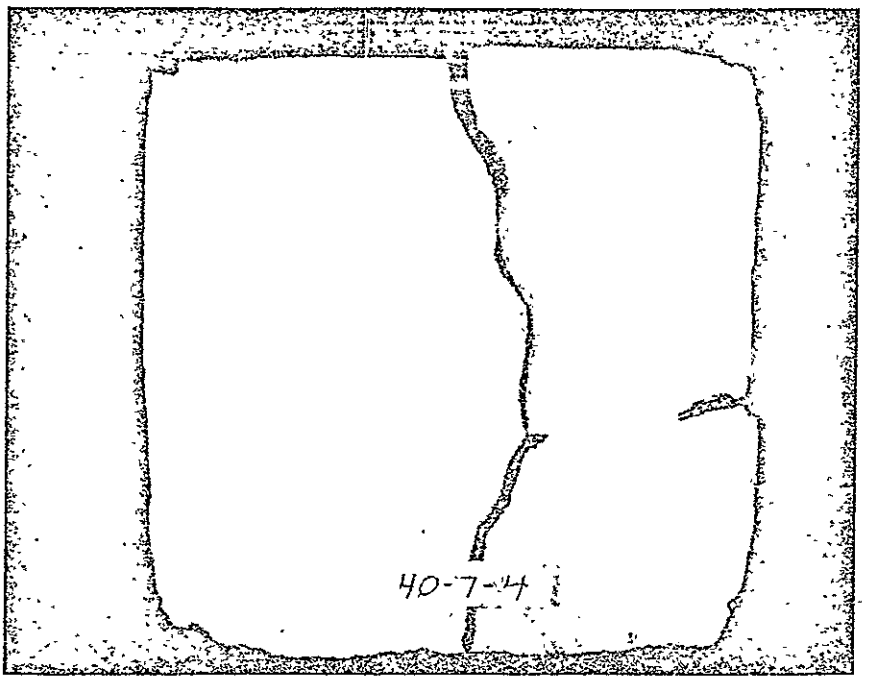


Figure 30. Photograph of Tile 40-7-4 After Firing.

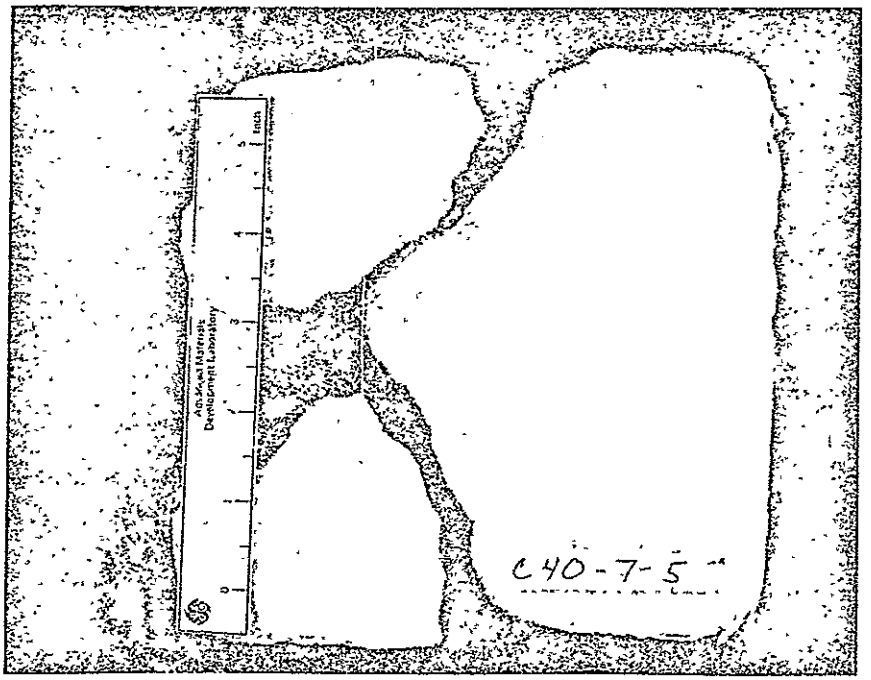


Figure 31. Photograph of Tile 40-7-5 (C) After Third Firing.

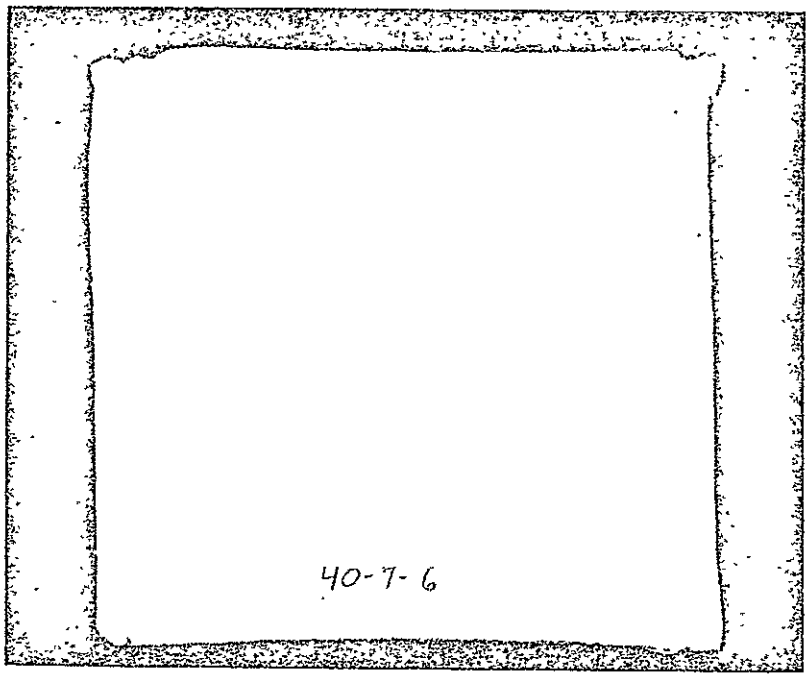


Figure 32. Photograph of Tile 40-7-6.

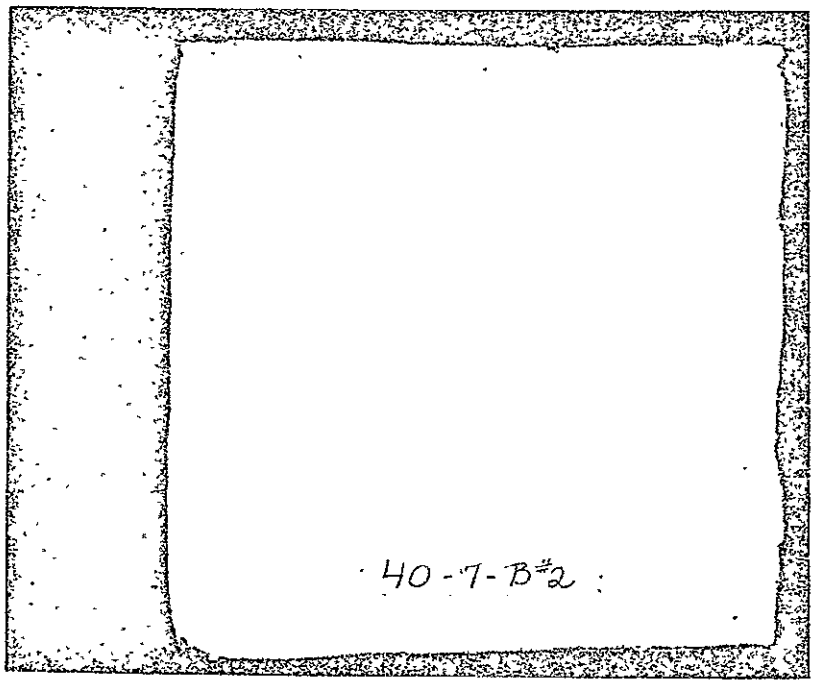


Figure 33. Photograph of Tile 40-7-B2 After Second Firing.

109

3.3.5.2 Significant Fabrication Development

The fabrication of the tiles using the 40μ m fiber were not successful. Several tiles were cast and dried which had a relatively good appearance but these were too friable to machine into useable test samples.

Because of the high density of these large diameter fibers, the small lengths of the fibers and their resulting small L/D ratios it does not appear feasible to produce composites with densities less than 60 lb/ft^3 which have sufficient strength and refractoriness to be considered Engineering Materials.

3.3.5.3 Use of 40 μm Fiber Composites

Very limited data were obtained from tiles made with 40μ m fibers. The limited mechanical strength and thermal conductivity data obtained are discussed in Section 4.

SECTION 4

PROPERTIES

4.1 INTRODUCTION

Table I (Page 4) lists the goals for property determinations in this program. The fabrication studies with the various fibrous composites, discussed in Section 3, were successful in producing material of good quality for the 10 μm diameter fiber considering the very limited amount of fiber (0.5 pounds) available for this effort. Sufficient composites using the 20 μm diameter fiber was processed to measure the material properties at a given density range (~48-52 lb/ft^3). However, within the material restraints both in quality (very short fibers), quantity (10# pounds of available material) and the time and funding restraints on the program property data at a second density range could not be achieved. Fabrication difficulties with the large (40 μm) diameter fiber resulted in composite material with insufficient strength to be used for properties determination except for some very limited data.

The following sections discuss and list the properties of the alumina fiber-composites.

4.2 PHASE STABILITY

Samples from tiles made with all three fiber types (10 μm, 20 μm and 40 μm) were submitted for x-ray diffraction studies to determine if the tile fabrication process alter the crystallinity of the fibers and to determine the phases present in the binder system. The composites were evaluated using identical techniques to those used to evaluate the virgin fibers as discussed in Section 3.2.3.

The results of this evaluation can be summarized simply by comparing Figure 34 which is the densitometric traces prepared from portions of the x-ray diffraction photographs of the composite samples with Figure 9 which is the densitometric traces for the fibers before processing into a tile. For all practical purposes these traces are very similar. The variations in intensities which may be observed are related to possible variations in; (a) capillary packing; (b) capillary diameter, and (c) in photographic processing.

4.3 THERMAL EXPANSION

Thermal expansion tests were run in the Theta dilatometer using a platinum standard. All measurements were made to 2300°F at a slow heating rate. Figure 35 shows the results of those measurements.

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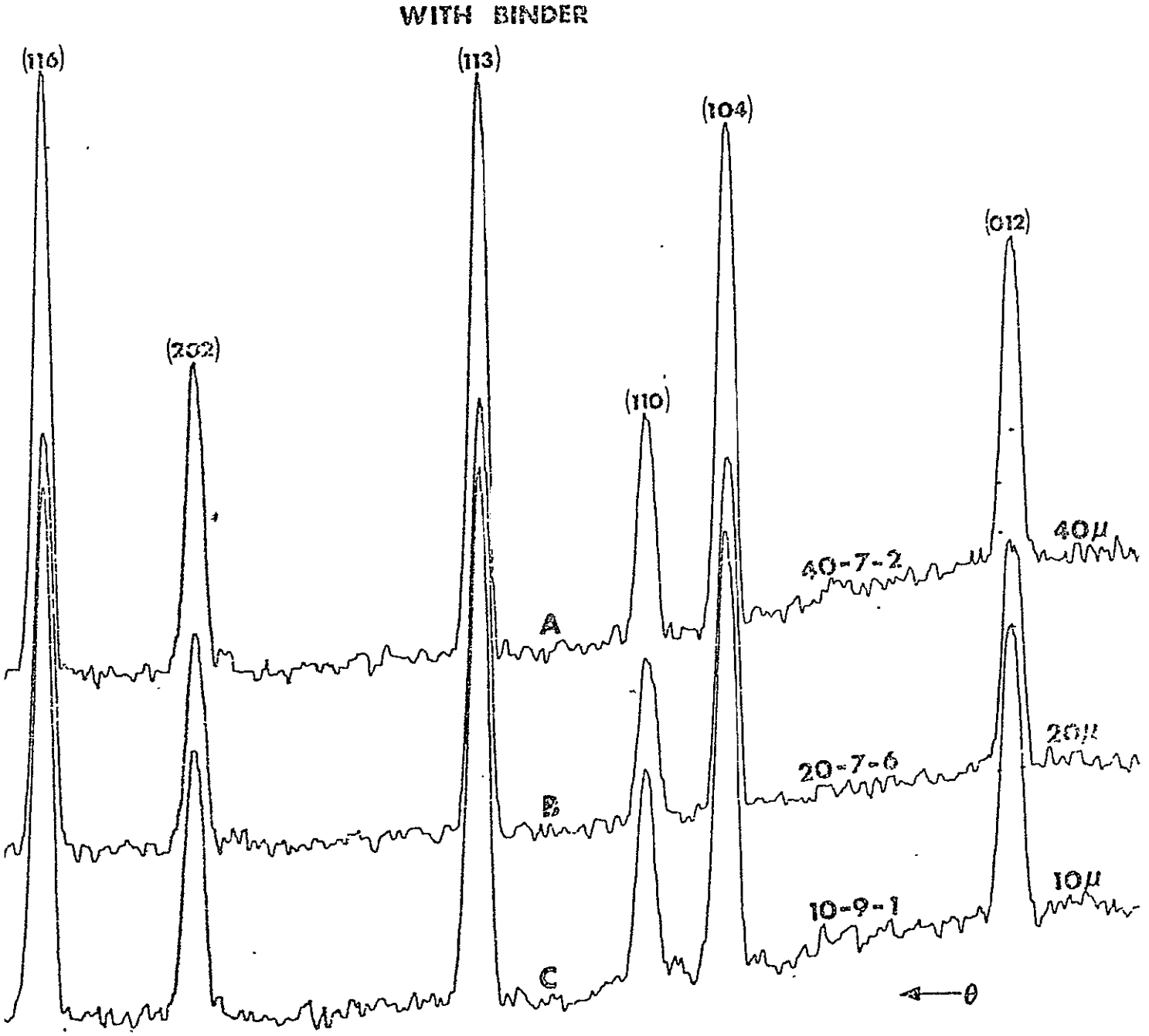


Figure 34. Densitometer traces prepared from portions of x-ray diffraction photographs. Nickel filtered copper x-radiation, diffraction range $\approx 25^{\circ} < 2\Theta < 58^{\circ}$. Alumina fibers in composites (fibers plus binder). A, sample 40-7-2 (containing 40 μm fibers). B, sample 20-7-6 (containing 20 μm fibers). C, sample 10-9-1 (containing 10 μm fibers).

112

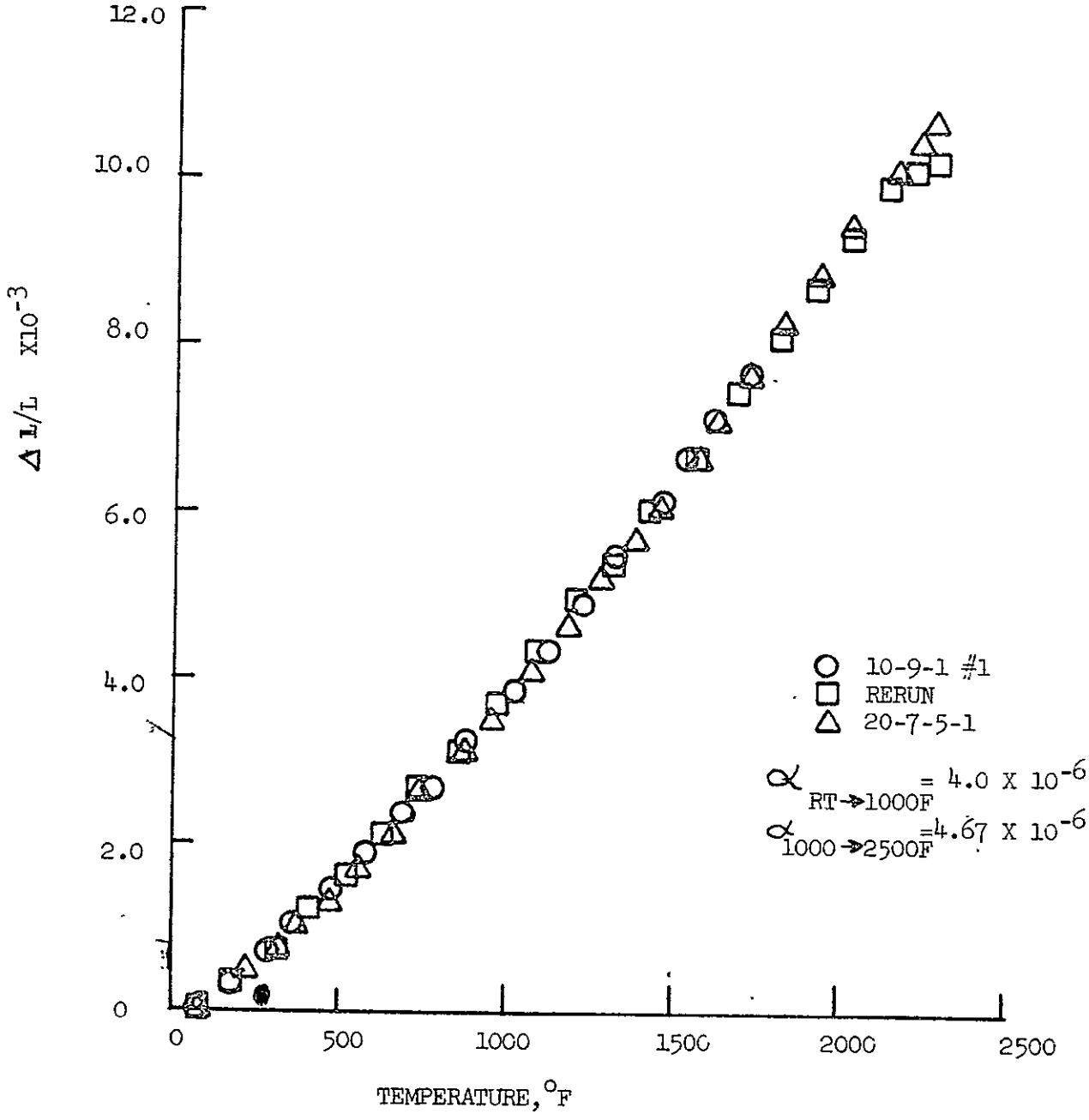


Figure 35. Thermal Expansion of Alumina Fiber Composites made from 10 μm diameter and 20 μm diameter fibers.

113

Samples from tile 10-9-1 (10 μm fibers) and 20-7-5 (20 μm fibers) were measured. The thermal expansion of both composites were for practical purpose the same, as is illustrated in the figure. The coefficient of thermal expansion was measured as 4.0×10^{-6} in/in/^{o}F from RT to 1000^{o}F and 4.67×10^{-6} in/in/^{o}F from 1000^{o}F to 2500^{o}F.

4.4 FLEXURE TESTS

Small flexure bars were machined from REI alumina and tested in four-point flexural loading at room temperature. A two-inch support span with a one-inch load span was used. Deflection was measured with an Linear Variable Differential Transducer (LVDT).

Table X lists the flexure strength for samples machined from 4 different tiles made with 20 μm diameter fibers. Table XI lists the flexure strength for some samples from tile 40-7-1 (40 μm diameter fibers).

Refiring tile 20-7-5 to 2800^{o}F increased the strength of this tile. The range of flexure strength after refiring this tile was quite wide (108 to 370 psi). The average strength was 277 psi. The wide range indicates non-homogeneity within the panel. Tile 20-7-5 had much higher strength than the average strength of tile 20-7-6 ($\sim$ 95 psi) and tile 20-7-6 ($\sim$ 97 psi) both of which were fired to 2700^{o}F. The higher firing temperature increased the density of the tile from about 45-48 lb/ft^{3} to 50-53 lb/ft^{3}.

4.5 BUTT TENSILE TESTS

Small (1x1x1/4") specimens made from both 20 μm and 40 μm diameter alumina fibers were bonded to aluminum blocks, then pulled in a tensile loading mode at room temperature. Deformation was measured with an extensometer. Results are listed in Table XII.

Only limited data were obtained using this technique. Three (3) samples from panel 40-7-3 (40 μm diameter fibers) and four (4) samples from panel 20-7-3 were tested. This test measures through-the-thickness strength of the composite.

4.6 TENSILE TESTS

Small dogbone type specimens were machined from REI alumina and tested at room temperature. An extensometer was used to measure deformation.

Figure 36 is a drawing showing the configuration of in-plane tensile specimen used in this study. Figure 37 is a photograph of a tensile specimen from tile 20-9-3 before test.

The results of the in-plane tensile tests on alumina fiber composites with the 20 μm diameter fibers are listed in Table XIII.

TABLE X

FLEXURE TEST OF ALUMINA FIBER COMPOSITES MADE FROM 20 μm FIBERS

Tile No.	Sample Number	Density (lb/ft^3)	M.O.R. (psi)	Deflection (inches)	Modulus of Elasticity
20-7-5	5	52.2	180	.005	158,000
	6	49.8	158	.010	114,000
	7	53.5	379	.008	463,000
	8	49.8	108	.008	99,800
	9	53.2	309	.010	296,000
			$\bar{X}$ 227	.008	227,000
			S.D. 113	.002	153,000
20-7-6	10	48.7	64.2	.008	62,900
	11	47.1	113.0	.010	85,800
	12	48.7	131.0	.006	178,000
	13	39.5	80.6	.012	55,700
	14	46.1	92.4	.009	75,900
	15	45.1	87.0	.010	64,000
			$\bar{X}$ 94.7	.010	87,000
			S.D. 23.9	.002	45,800
20-7-6	3	46.4	95.8	.009	87,000
	4	45.9	108.0	.013	62,400
	5	45.2	107.0	.010	79,500
	6	45.3	77.2	.010	59,700
			$\bar{X}$ 97.0	.010	72,150
			S.D. 14.3	.002	14,000
20-9-3	3	48.1	85.0	.020	37,800
	4	48.8	82.1	.019	31,000
	5	50.1	147.0	.022	54,500
	6	44.7	69.8	.019	30,200
	7	47.7	44.2	.010	39,300
	8	48.6	73.9	.016	38,500
	10	46.7	98.9	.020	40,000
			$\bar{X}$ 83.8	.018	39,600

115

TABLE XI

FLEXURE TESTS OF ALUMINA FIBER COMPOSITES MADE FROM 40 μm FIBERS

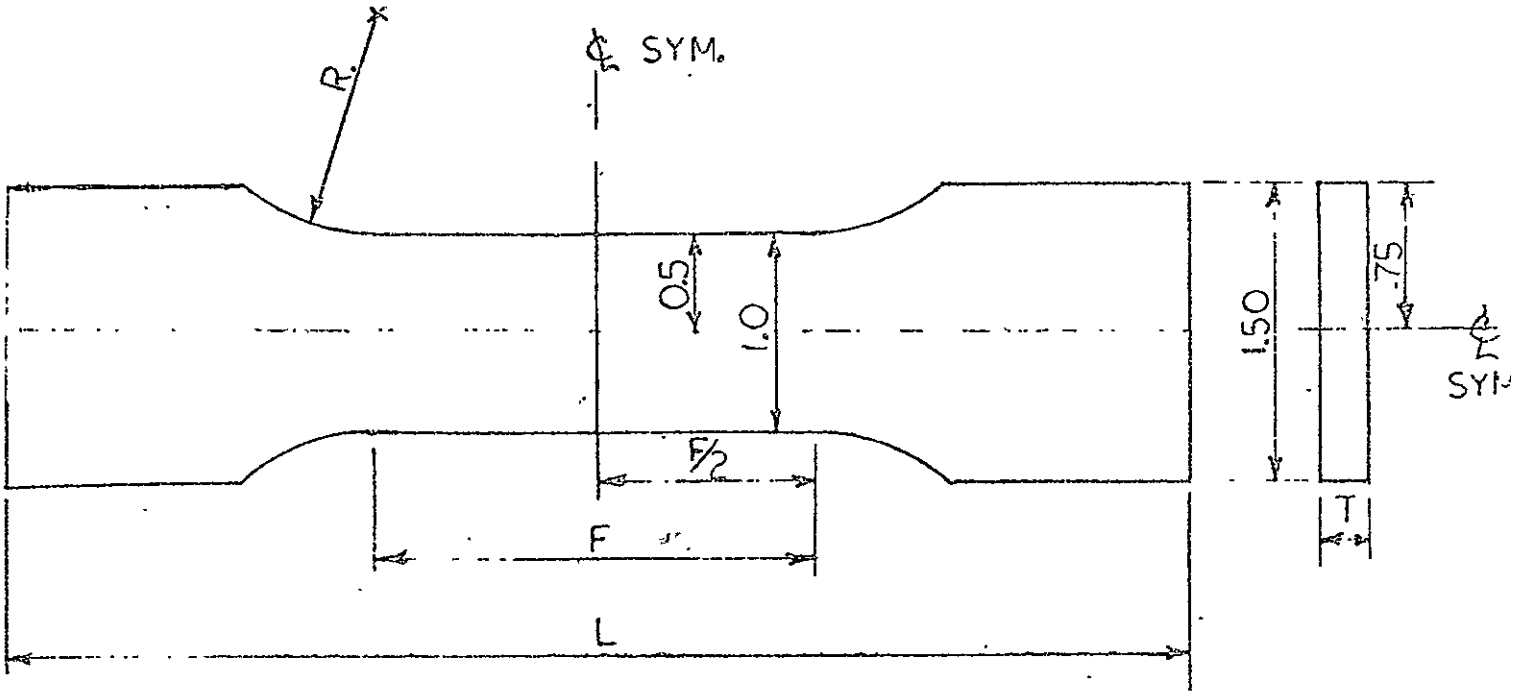
Tile No.	Sample Number	Density (lb/ft^3)	M.O.R. (psi)	Deflection (inches)	Modulus of Elasticity
40-7-1	1	52.2	186	.014	93,500
	2	52.0	23	.013	134,000
	3	51.7	81	.009	14,000
	6	51.2	251	.010	182,000
			$\bar{X}$ 135	.012	106,000
			S.D. 102	.002	71,100

TABLE XII

BUTT-TENSILE STRENGTH OF ALUMINA COMPOSITES MADE FROM 40 μm FIBERS (40-7-1) AND 20 μm FIBER (20-7-3) (THROUGH-THE-THICKNESS STRENGTH)

Tile No.	Sample Number	Density (lb/ft^3)	M.O.R. (psi)	Deflection (inches)	Modulus of Elasticity
40-7-1	7	52.0	18.5	.06	25,500
	8	53.7	29.2	.16	47,100
	9	51.8	25.0	.24	10,400
			$\bar{X}$ 24.2	.15	27,700
20-7-3	8	40.6	14.2	.21	7,840
	9	40.6	14.2	---	7,950
	10	40.6	13.2	.21	12,000
	11	40.3	10.8	.28	4,750
			$\bar{X}$ 13.1	.23	8,140

116



DIMENSIONS				
SPECIMEN	L	F	T	R
A	6.0	2.25	$0.25^{+.000}_{-.050}$	1.0
B	6.0	2.25	$0.50^{+.000}_{-.050}$	1.0
C	8.0	4.25	$0.25^{+.000}_{-.050}$	1.0
D	8.0	4.25	$0.50^{+.000}_{-.050}$	1.0
E	4.0	1.50	$0.25^{+.000}_{-.050}$	0.25
F	4.0	1.50	$0.50^{+.000}_{-.050}$	0.25

NOTE: DO NOT UNDERCUT 1.0" DIMENSION AT POINT OF TANGENCY TO RADIUS.

117

Figure 36. Tensile Specimen for Low Density Insulation.

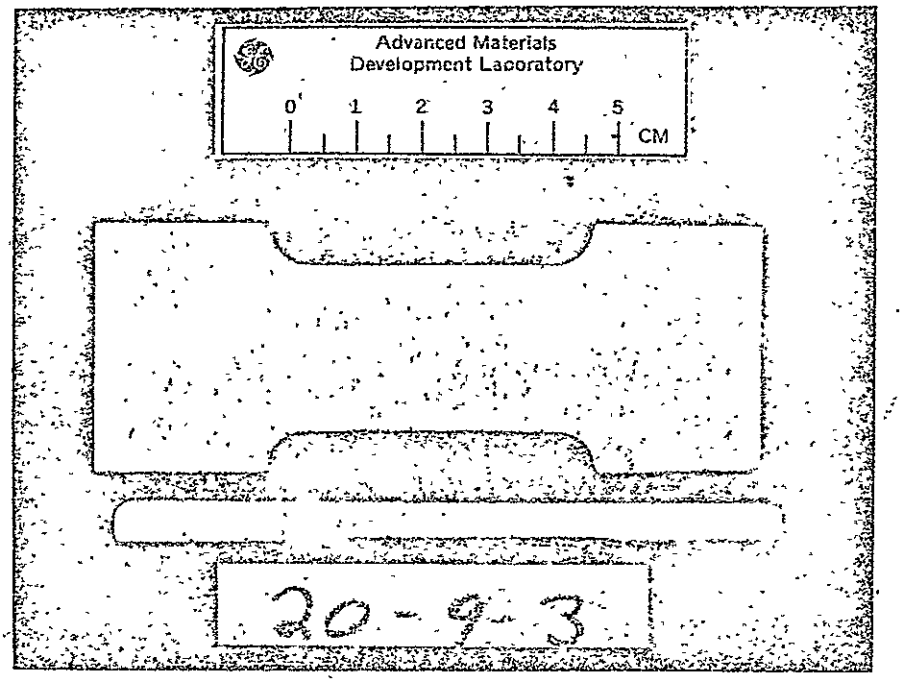


Figure 37. Photograph of In-Plane Tensile Specimen. (Specimen from Tile 20-9-3)

118

TABLE XIII

IN-PLANE TENSILE STRENGTH OF ALUMINA FIBER COMPOSITES PROCESSED USING 20 μm FIBERS

Tile No.	Sample Number	Density (lb/ft^3)	Ultimate Strength (psi)	Failure Strain (%)	Modulus of Elasticity (psi)
20-7-5	10	51.2	63.9	----	---
	11	54.2	51.0	.057	20.7×10^4
	12	53.7	87.8	----	---
			$\bar{X}$ 67.6		
20-7-6	1	41.3	16.1	0.10	5.6×10^4
	3	44.5	56.9	0.03	20.9×10^4
	4	48.3	45.6	0.02	27.7×10^4
	6	48.6	21.1	----	28.1×10^4
	7	44.4	33.7	0.03	12.1×10^4
			$\bar{X}$ 34.7	0.05	18.9×10^4
20-7-7	9	49.0	31.5	0.02	18.1×10^4
20-9-3	12	46.9	48.8	.05	13.8×10^4
	13	49.4	62.9	.04	51.2×10^4
	14	48.2	24.1	----	---
	15	47.9	74.1	.04	80.2×10^4
			$\bar{X}$ 52.5	.04	48.4×10^4

119

These results are similar to the results obtained in the flexure tests. Refiring the tile to 2800°F improved the strength of the material but also increased the density. The strength increased about 65% but the density was only increased about 13%.

4.7 THERMAL CONDUCTIVITY

Thermal conductivity measurements were performed on four samples of alumina fiber composites. Three measurements were made by the guarded hot plate technique (ASTM-C177) and one, (the 40 micron fiber material), for which only a small quanity of material was available, was made by an axial heat flow comparator method. The measurements were made in 1 atmosphere air and a partial vacuum of 10 mm Hg, with air backfill.

The results are listed in Table XIV and shown in the graph of Figure 38 compared to GE/RESD's Mod. 1A REI Silica and Mullite. As a group, the alumina composites have about 3 to 5 times higher thermal conductivity than the Mod. 1A GE silica and mullite REI's at a typical temperature such as 500°F. Their temperature dependence is, however, basically different, generally declining with temperature over the range of measurement, 150-1600°F. This behavior has been previously predicted (Ref. 5), and is based on a combination of the intrinsically higher thermal conductivity of the alumina fibers (the "solid" thermal conductivity) and the higher density and fiber volume fraction of the alumina fiber materials. Note however that at high temperatures, the conductivities of the three classes converge, due to the greater radiation, transport component in the lower density mullite and silica REI's.

Within the sample group of four alumina REI's themselves, there is an obvious inverse relation of the conductivity and density. The two 20 micron fiber diameter samples with densities of 50 and 46.5 pcf have the highest conductivity in the group.

A single curve has been drawn through the data for these samples, but the 50 pcf sample apparently has about 20% higher conductivity in air at 400°F than the 46.5 pcf sample. The reduction in ambient pressure to 10mm Hg for this sample also reduces the conductivity by 1/3 across the full temperature range.

The REI fabricated from ten micron diameter fibers has the lowest conductivity of the four above 1000°F. Due to scarcity of this material, the two guarded hot plate test specimens for this measurement had to be fabricated as two 4" diameter discs, surrounded by 8" O.D., 4.1" I.D. annular rings cut from the two 8" O.D., 46.5 pcf, 20 micron fiber specimens first tested. The second set of 20 micron samples were also tested in this manner. (See notes on Table XIV). The conductivity of the 40 micron fiber material was measured by a comparator technique because only one sample 2-1/2" square was available. This instrument has a maximum temperature capability of 600°F, as compared to 1800°F maximum for our guarded hot plate. The curves for the 40 micron fiber REI in

120

TABLE XIV

THERMAL CONDUCTIVITY OF ALUMINA FIBER COMPOSITES

Plotting Symbol	Temperature (°F)	Thermal Conductivity (10^{-5} BTU/ft.sec°F)	Ambient Pressure
○	Panel 20-9-1, 46.5 lb/ft^3		
	398	4.63	1 atm
	805	4.28	1 atm
	1202	4.36	1 atm
	410	3.42	10 mm
	809	3.05	10 mm
	1203	3.00	10 mm
	1613	2.28	10 mm
	1614	2.25	10 mm
□	Panel 20-9-2 and 20-9-3, 50 lb/ft^3		
	397	5.5	1 atm
	1005	4.69	1 atm
	401	4.16	10 mm
	1018	2.87	10 mm
◇	Panel 10-9-1, 27.7 lb/ft^3		
	402	3.24	1 atm
	401	3.21	1 atm
	1002	3.0	1 atm
	405	2.86	10 mm
	405	2.86	10 mm
	1007	2.41	10 mm
	1600	2.35	10 mm
	1601	2.37	10 mm
	1601	2.36	10 mm
	1603	2.32	10 mm
△	Panel 40-7-6, 49 lb/ft^3		
	148	3.39	1 atm
	397	3.64	1 atm
	597	3.74	1 atm
	143	2.63	10 mm
	148	2.60	10 mm
	396	2.54	10 mm
	397	2.60	10 mm
	602	2.53	10 mm
	589	2.54	10 mm

121

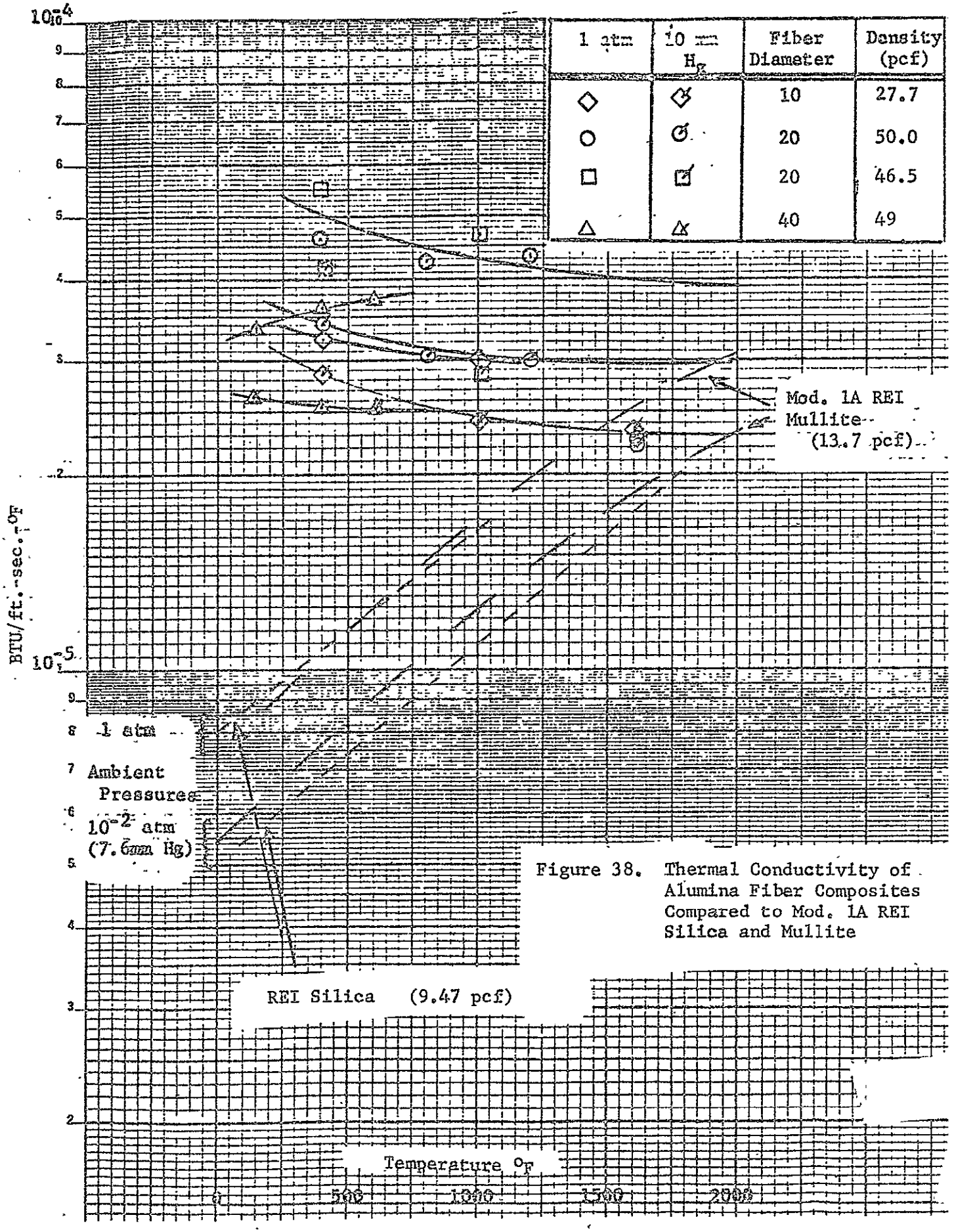


Figure 38. Thermal Conductivity of Alumina Fiber Composites Compared to Mod. 1A REI Silica and Mullite

Figure 38 straddle the 10 micron fiber case over the 100-600°F range.

It should be noted that extreme difficulty was experienced in performing the guarded hot plate measurements, especially at temperatures of 800°F and above. The alumel leg of the chromel-alumel thermocouples used to measure temperature gradients was repeatedly corroded to failure and open circuit. The high temperature 1613°F, 1614°F, 10^{-2} atmosphere points on the 20 micron, 46.5 pcf sample were disregarded for this reason in drawing the nominal 20 micron thermal conductivity curve in Figure 38.

The results of the thermal conductivity evaluation can be summarized as follows:

1. The alumina fiber composites all have a higher thermal conductivity at temperatures below 1500-2000°F than the Mod. 1A REI silica and mullite materials previously characterized at GE/RESD under the Space Shuttle Program.

   Above this temperature range, they appear to become competitive and even favorable on an insulation basis, but not on an insulation per unit weight basis. However, in any foreseeable application, alumina REI would not be used where silica REI and, above 2000-2200°F, mullite REI had first been examined for use. Above their maximum use temperature range of 2000-2500°F, the alumina would then have an insulation advantage in addition to its basic thermo-structural capability to survive these temperatures.

2. Within the group of four alumina fiber composites whose thermal conductivity was measured there is a strong dependence on fiber diameter, with the conductivity inversely proportional to fiber diameter, and for the same fiber diameter, also inversely proportional to density. The ten micron fiber diameter material showed the lowest thermal conductivity across the temperature range; but the 40 micron material, at the same nominal density as the two 20 micron samples, had an anomalously low conductivity at the lowest temperatures, 150-600°F.

123

SECTION 5

DISCUSSION OF RESULTS AND CONCLUSIONS

The fibers supplied by Alcoa Laboratories for this contract were quite uniform in properties. Unfortunately the fiber lengths in comparison to the fiber diameters were very small. These very low fiber length to fiber diameter ratios (L/D) created an extremely difficult fabrication problem. To achieve a low density requires that fiber volume concentration be relatively low. For example to produce a tile at 30 lb/ft^3 with an alumina fiber would require a tile that is essentially 88% void volume. At this high void volume it is very difficult to obtain good strengths unless each solid constituent (fiber) is firmly attached to other solid constituents (fibers). With very short fibers it is questionable that this condition can be achieved.

From a purely technical standpoint the majority of the 20 μm and 40 μm material studied on this contract do not meet the definition of a fiber as suggested by ASTM Committee D-30. The suggested definition is: (Ref. 3).

> Fiber* Any material in an elongated form such that it has a minimum length to a maximum average transverse dimension of 10:1, a maximum cross-sectional area of $7.9 \times 10^{-5} in^2$ (corresponds to a circular cross-section of 0.010 inch in diameter), and a transvere dimension of 0.010 inch.

In Section 3.2 the average length to diameter ratio for the 20 μm diameter fiber was determined to be 4.8 and for the 40 μm diameter fiber was 9.7. In all the previous work at RESD it was necessary to chop fibers to reduce the fibers to useable lengths so that rigidized tiles could be fabricated with uniform properties.

Tanzilli (Ref. 3) states "One of the most critical parameters in the panel fabrication process is the average fiber length that is produced during the fabrication process". The fiber lengths of the mullite fibers he investigated had the distribution as shown in Figure 39. Notice the fibers had been chopped before this distribution was determined. Compare the fiber length distribution of these mullite fibers, which had fiber diameters of 5-6 μm, with the distributions of the alumina fibers presented in Figures 10, 11 and 12 of this report.

* Suggested by ASTM Committee D-30 at Philadelphia, Pennsylvania, on October 5, 1966.

124

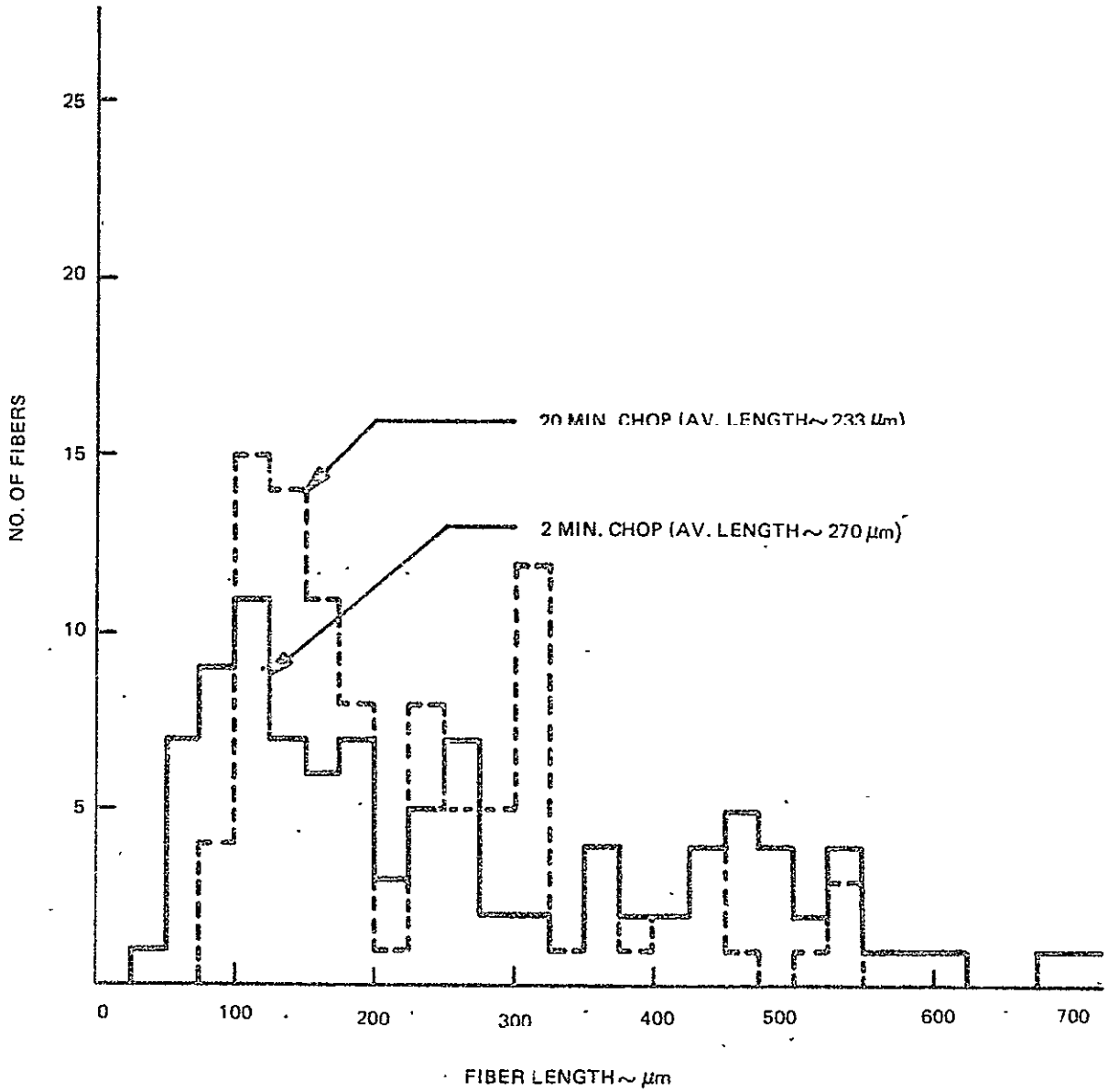


Figure 39. Comparison of fiber length distribution as a function of slurry chopping time

Note: From Reference 3.

125

The effect of fiber diameter on rigidized tiles has previously been reported by Gebhardt, Gorsuch and Brown (Ref. 4). These authors reported that the fiber diameter has a significant effect on rigidized panel strength. Panels made with mullite fibers with an average fiber diameter of 3.2 μm had strengths of 40% to 60% greater than rigidized tiles made using the same binder system but using mullite fibers with a diameter of 7.5 μm.

A comparion of mechanical properties of the 20 μm alumina fiber rigidized tiles with General Electric's Mod. 1B REI-Mullite is presented in Table XIV.

The data presented in Table XIV shows that the alumina fiber tiles fabricated in this investigation had strengths of 50% of the strength obtained previously on GE's REI Mod. 1B-Mullite rigidized fibrous insulation. Mod. 1B-Mullite is GE's most advanced and highest strength mullite fiber lightweight insulation. But it must be observed; however, that the density of the alumina panel is 4 times greater than the Mod. 1B REI-Mullite.

The thermal conductivity as presented in Section 4.7 indicates that alumina fiber composites may have distinct advantages for high temperature uses ($>2300^{o}F$). For use at lower temperatures the conductivity and the weight will be higher than other ceramic fiber insulations such as silica, mullite or alumina-silicate fibrous materials.

CONCLUSIONS AND RECOMMENDATIONS

(1) Alumina fibers with diameters $>40\ \mu$m did not appear to offer any engineering advantages. To obtain a fair evaluation, however, fibers with L/D ratio $>20/1$ would have to be evaluated.

(2) Alumina fibers with an average fiber diameter of 20 μm can be fabricated with reasonable strengths at densities of about 50 lb/ft^3.

(3) Mechanical properties of rigidized tiles using 20 μm diameter fibers could probably be increased significantly and thermal conductivity could be lower if fiber lengths could be increased by a factor of 3 or 4. Indications are that with a longer fiber lengths lower densities panels could be fabricated. Lower density panels would of course have lower thermal conductivity.

(4) Engineering materials can be fabricated from alumina fibers with 8 to 10 μm diameter fibers. It appears reasonably strong panels at densities of 15-20 lb/ft^3 are achievable. Applications requiring high temperature insulations could consider this material.

126

TABLE XIV

COMPARISON OF MECHANICAL PROPERTIES OF ALUMINA FIBER (20 μm) RIGIDIZED TILES WITH GE'S MOD. 1B REI-MULLITE TILES

	MOD 1B (REF. 4) REI-MULLITE (4.7 μm FIBER)	ALUMINA FIBER COMPOSITE (20 μm FIBER)
IN-PLANE		
Strength (psi)	120	67*
Strain (%)	0.25	0.06*
THRU-THE-THICKNESS		
Strength (psi)	25	13
Strain (%)	0.5*	0.23
DENSITY (lb/ft^3)	12	48

* Firing temperature 2800 °F

127

SUMMARY

Additional work is not recommended using 40 μm diameter fibers for lightweight insulation. Additional work is not recommended on the 20 μm alumina fiber unless fiber lengths can be significantly increased. Alumina fibers with diameters of < 10 μm can be used as Engineering Materials and would warrant further investigation if a sufficient quantity of material could be produced to permit a meaningful process optimization prior to attempting to measure material properties.

128

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(3) "Development of External Ceramic Insulation for Space Shuttle Orbiter", Part 2 Optimization, R.A. Tanzilli, Report NASA. CR-112257, March 1973.

(4) "Processing of Rigidized REI-Mullite Insulative Composites", presented to the NASA Symposium on Reuseable Surface Insulation for the Space Shuttle, J.J. Gebhardt, P.D. Gorsuch and M.A. Braun, November 1-3, 1972.

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