FINAL REPORT

PROJECT A-793

IMPROVING THE MECHANICAL PROPERTIES OF SLIP-CAST FUSED SILICA BY FIBROUS REINFORCEMENT

By

W. J. CORBETT, A. T. SALES, and J. D. WALTON, JR.

CONTRACT NO. 16-2092

Prepared for

SANDIA CORPORATION
ALBUQUERQUE, NEW MEXICO

1 JULY 1964 to 30 JUNE 1965
Issued 6 August 1965

Engineering Experiment Station
GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia

GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station
Atlanta, Georgia

FINAL REPORT

PROJECT A-793

IMPROVING THE MECHANICAL PROPERTIES OF SLIP-CAST FUSED SILICA BY FIBROUS REINFORCEMENT

By

W. J. CORBETT, A. T. SALES and J. D. WALTON, JR.

CONTRACT NO. 16-2092

1 JULY 1964 to 30 JUNE 1965
Issued 6 August 1965

Prepared for
SANDIA CORPORATION
ALBUQUERQUE, NEW MEXICO

TABLE OF CONTENTS

		Page
	LIST OF FIGURES	iii
	LIST OF TABLES	iv
	SUMMARY	v
I.	INTRODUCTION	1
II.	FABRICATION OF COMPOSITES	3
	A. Materials	3
	B. Slip Preparation	4
	C. Casting	8
	D. Sintering	10
III.	TESTING OF COMPOSITES	11
	A. Techniques	11
	B. Data Reduction	12
	C. Alumino-Silicate Fiber Composites	15
	D. Synthetic Mullite Fiber Composites	15
	E. Zirconia Fiber Composites	19
	F. Silicon Carbide Whisker Composites	23
	G. Slip-Cast Fused Silica	23
IV.	DISCUSSION OF RESULTS	26
V.	CONCLUSIONS	34
VI.	RECOMMENDATIONS	35

This report contains 36 pages.

LIST OF FIGURES

Page

1. Distribution of Fiber Length-to-Diameter Ratios for Ball-Milled Alumino-Silicate Fibers 5

2. Distribution of Fiber Length-to-Diameter Ratios for Ball-Milled Zirconia Fibers 6

3. Distribution of Fiber Length-to-Diameter Ratios for Chopped Alumino-Silicate Fibers 9

4. Dynamic Elastic Modulus of a Synthetic Mullite Fiber Composite As a Function of Density and Cristobalite Content (2-1/2 volume per cent fiber). 17

5. Dynamic Elastic Modulus of a Synthetic Mullite Fiber Composite As a Function of Density and Cristobalite Content (5 volume per cent fiber). 18

6. Dynamic Elastic Modulus of a Zirconia Fiber Composite As a Function of Density and Cristobalite Content (2-1/2 volume per cent fiber) . . 21

7. Dynamic Elastic Modulus of a Zirconia Fiber Composite As a Function of Density and Cristobalite Content (5 volume per cent fiber) 22

8. Dynamic Elastic Modulus of Slip-Cast Fused Silica As a Function of Density and Cristobalite Content. 25

9. Dynamic Elastic Modulus of Slip-Cast Fused Silica As a Function of Per Cent of Theoretical Density 29

LIST OF TABLES

Page

I. PROPERTIES OF ALUMINO-SILICATE FIBER COMPOSITES 15

II. PROPERTIES OF SYNTHETIC MULLITE FIBER COMPOSITES. 19

III. PROPERTIES OF ZIRCONIA FIBER COMPOSITES 20

IV. PROPERTIES OF A ZIRCONIA FIBER COMPOSITE WITH A LARGE FIBER LENGTH-TO-DIAMETER RATIO. 23

V. PROPERTIES OF A SILICON CARBIDE WHISKER COMPOSITE 24

VI. PROPERTIES OF SLIP-CAST FUSED SILICA. 24

SUMMARY

The principal objective of this study was to determine if the mechanical properties of slip-cast fused silica could be improved by the incorporation of discontinuous, randomly-oriented, ceramic fibers.

The potential reinforcements investigated were an amorphous alumino-silicate fiber, a zirconia fiber, a synthetic mullite fiber and silicon carbide whiskers. Three techniques were developed for producing slips containing fiber and finely-divided silica. These were: (1) ball milling of fiber and fused silica slip, (2) blending of dried and reground fused silica slip with chopped fiber and water, and (3) direct incorporation of whiskers into fused silica slip. Casting slips with fiber concentrations as high as 50 volume per cent were obtained using the ball milling technique. The per cent solids content of the fiber slips was dependent on the volume per cent fiber and was in the 70 to 82 per cent range.

The slips were cast, using plaster molds, as flat plates, cylinders and a small radome shape. Good fiber dispersion was obtained with a random orientation of the fiber. The sintering parameter which most influenced the mechanical properties of these composites was the cristobalite content. This parameter was established for a firing temperature of 2200° F. Sintering time was varied to control the cristobalite formation for a particular volume per cent fiber in the slip.

The variation of elastic modulus with per cent cristobalite and per cent of theoretical density, modulus of rupture, tensile strength, and impact strength for fused silica were used as standards to determine any degree of fiber reinforcement. Although no reinforcement was detected, volumes of 2-1/2 per cent and 5 per cent synthetic mullite and 2-1/2 per cent zirconia fibers were not detrimental to the mechanical properties of fused silica when evaluated on the basis of per cent of theoretical density for fused silica. The elastic moduli of 5 per cent zirconia fiber and 7-1/2 per cent silicon carbide whiskers were respectively 50 and 25 per cent greater than fused silica at the same porosity.

When used to determine the strength of composites which are dependent on short fibers for reinforcement, the value of the modulus of rupture test was challenged since the geometric computations are based on the strength of the

outer surfaces. Since the surfaces of these composites did not contain appreciable amounts of fiber, this critique seemed confirmed by the test results. Similarly the significance of the Izod impact strength and tensile strength, using the diametral compression test, were critically analyzed. The value of Weibull statistics in the analysis of these data for brittle materials demonstrated the value of the tensile strength test.

It was demonstrated that the incorporation of discontinuous, randomly-oriented, ceramic fibers into slip-cast fused silica is possible, without sacrificing the fabrication advantages of the slip-casting process. The feasibility of obtaining significant improvements in the physical properties of slip-cast fused silica by the incorporation of discontinuous, randomly-oriented, ceramic fibers was not conclusively demonstrated, but a foundation for further study was established with every indication this is possible. An outline of an advanced research program of further investigation is presented.

I. INTRODUCTION

A number of investigations in recent years have established slip-cast fused silica as an excellent candidate material for aerospace thermal protection systems, EM window applications and high intensity nuclear radiation environments. The combined properties of low thermal conductivity, low coefficient of thermal expansion, low density, low and stable dielectric properties, and excellent thermal shock resistance are unknown in any other single material. However, for large structures or for applications requiring a material to withstand very high acceleration rates, the mechanical properties of slip-cast fused silica are often deficient.

The objective of this study was to determine if the mechanical properties of slip-cast fused silica could be improved by the incorporation of ceramic fibers. It is well known that improvements can be obtained in the tensile strength, impact strength, modulus of rupture and modulus of elasticity of metals and plastics through the incorporation of fibrous reinforcement. However, unlike such composite materials as glass fiber reinforced plastics and whisker or fiber reinforced metals, where the matrix is more ductile than the reinforcement, simply incorporating a high-strength fiber into a ceramic matrix, even with good fiber-to-matrix bonding, does not insure reinforcement. To take full advantage of a high-strength, high-modulus fiber in a fiber reinforced composite, a significant proportion of the load must be carried by the fibers. Accomplishing this in a composite where the elongation of the matrix at its ultimate strength is greater than the maximum elongation of the fiber at failure is no particular problem, provided there is good matrix-to-fiber bonding. However, in the case where a ceramic matrix is reinforced with high-strength, high-modulus fibers, the fiber may not be able to assume a significant portion of the load before the matrix has reached its maximum elongation. Therefore, to reinforce a ceramic matrix successfully, particularly with the aim of improving the tensile strength, prestressing of the fiber in the fabrication of the composite is required. Such prestressing is most readily accomplished, of course, by selecting a matrix-fiber system where the fiber has a greater coefficient of thermal expansion. Slip-cast fused silica, as a ceramic matrix, has a singular advantage from this standpoint because of its very low coefficient of thermal expansion.

With the aim of preserving the fabrication advantages of the slip-casting process and avoiding anisotropic mechanical properties, this study was concerned only with the use of discontinuous fibers, randomly oriented within the matrix.

II. FABRICATION OF COMPOSITES

A. Materials

The refractory, fibrous reinforcements investigated were on amorphous alumino-silicate fiber, a synthetic mullite fiber, a crystalline zirconia fiber and silicon carbide whiskers. The amorphous alumino-silicate fiber was of the type normally produced for insulation purposes and sold under various trade names, such as Kaowool, Fiberfax, etc. This material was used principally for developing fabrication techniques, since it was relatively inexpensive compared to the high-strength, high-modulus fibers and whiskers. The strength and elastic modulus of this material were unknown. The average fiber diameter was about 3 microns, but the range of diameters was quite wide. The synthetic mullite fiber was an experimental product of the Babcock and Wilcox Company, Refractories Division, Augusta, Georgia. This material, as produced, exhibited tensile strengths of up to several hundred thousand pounds per square inch. The fiber diameters were in the range 2 to 10 microns. The crystalline zirconia fiber was obtained from the H. I. Thompson Fiber Glass Company, Gardena, California. This was a stabilized zirconia fiber containing 10 to 15 per cent neodymia. The tensile strength of this fiber was reported by the manufacturer to range from 35,000 to 150,000 psi, and the elastic modulus from 30×10^6 to 50×10^6 psi. The fiber diameters of the zirconia were in the range of 2 to 8 microns. The silicon carbide whiskers were obtained from the Carborundum Company, Niagara Falls, New York. The dimensions of these single crystal fibers were 0.5 to 3.0 microns diameter, and 10 to 300 microns length. The strengths of these whiskers are of the order of 10^6 psi.

The finely-divided fused silica used as the matrix material was a product of Glasrock Products, Inc., Atlanta, Georgia. This material was obtained both as an aqueous slip containing approximately 82 weight per cent solids and as a dry material that had been wet-ground, dried and reground. The particle size of the fused silica ranged from less than one micron to 50 microns with a median of about 8 microns. The cristobalite content of this material was less than 0.5 per cent.

B. Slip Preparation

Three different techniques were developed for producing slips of the fiber and fused silica particles. The first of these consisted of ball-milling the fiber into a preprepared slip of fused silica. The fiber was added as the dry staple in the case of the synthetic mullite and the zirconia, since the staple was fairly short to begin with and the fibers were quite brittle. In the case of the amorphous alumino-silicate fiber, where the material was initially in batte form, the material received a prior chop in a Waring Blendor for one or two minutes. The fiber was chopped in water with the fiber concentration less than 10 weight per cent. The fiber was then dried and added to the slip. The milling technique was not used with the silicon carbide whiskers.

It was found in using the milling technique that the fiber charge had to be introduced incrementally. Otherwise, the entire mixture would become so stiff as to prevent any grinding action. The usual procedure for preparing slips with the milling technique was to charge a 10-inch diameter porcelain ball mill with approximately two liters of slip containing 82 weight per cent finely-divided fused silica, sufficient water to produce the desired final solids concentration, and three kilograms of high-density, 13/16-inch grinding cylinders. The fiber was then added in 50 or 100 gram increments until the desired quantity of fiber had been incorporated into the slip. An increment of fiber was not added until the previous charge had been dispersed. The milling times for preparing slips by this method varied from about one hour to 15 hours, depending on the fiber content of the slip.

The distribution of length to diameter ratios of the individual fibers after incorporation into the slip by milling are presented in Figures 1 and 2 for the amorphous alumino-silicate fibers and the zirconia fiber. These were typical results and were also representative of the fiber sizes obtained when slips were prepared with synthetic mullite fibers. It appeared, as a matter of fact, that a smooth slip, free from fiber lumps, could not be obtained until the fiber lengths had been reduced to several hundred microns or less. Attempts to produce slips with a total solids concentration of 70 to 82 weight per cent in a similar manner with a Waring Blendor were totally unsuccessful. The fibers, whose lengths were greater than those obtained by ball milling, would matte and lump, and a smooth, fluid slip could not be obtained.

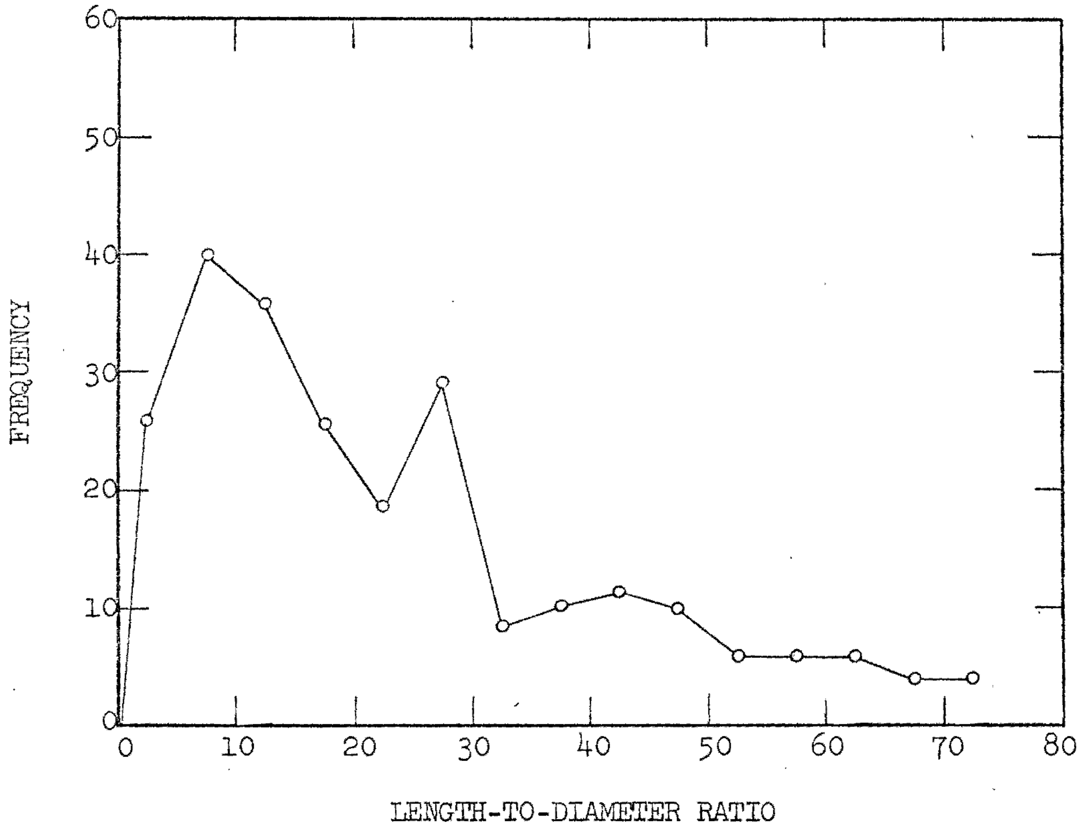

Figure 1. Distribution of Fiber Length-to-Diameter Ratios For Ball-Milled Alumino-Silicate Fibers.

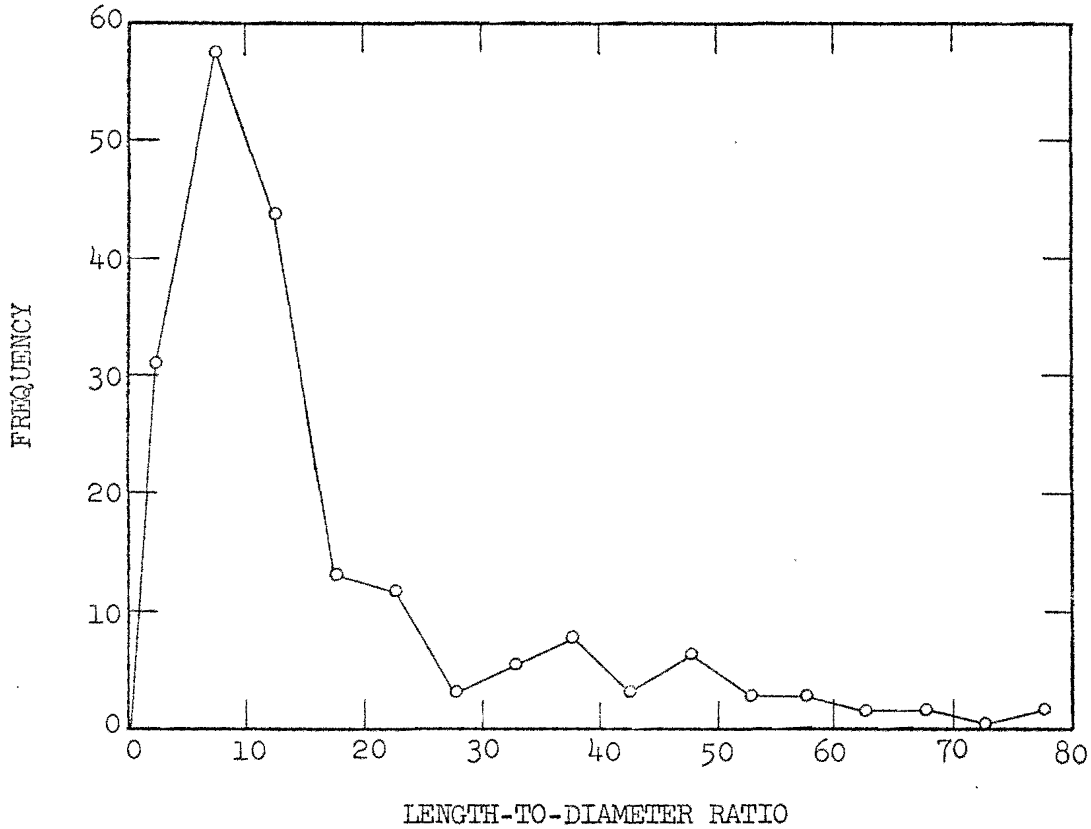

Figure 2. Distribution of Fiber Length-to-Diameter Ratios For Ball-Milled Zirconia Fibers.

As the fiber was added to the ball mill, in that technique for producing slips, the viscosity of the slip would rise sharply after the addition of more than about 5 volume per cent fiber*. This could be overcome by the addition of water in excess of that normally contained in the silica slip**. However, this could be overdone. A slip that was too thin would not cast properly. The solids would settle too fast and a true cast could not be achieved. It was found, in general, that satisfactory slips containing up to 5 volume per cent fiber could be prepared by adjusting the total solids concentration to about 80 to 82 weight per cent. Satisfactory slips containing 10 to 30 volume per cent fiber required adjustment to about 75 weight per cent solids. Slips with fiber concentrations as high as 50 volume per cent were obtained, but the total solids concentration had to be held to only about 70 weight per cent. It should be mentioned, that it was equally important that slip not be too viscous as for it not to be too thin. A very viscous slip would not cast either. Rather, it would gell after the mold had absorbed very little of the water, and a true cast could not be obtained. The best casting viscosity was found to be in the neighborhood of 150 centipoise, as measured by a Brookfield Viscometer using a number 3 spindel at 30 rpm.

The second technique developed for preparing slips from fiber and finely-divided fused silica involved the use of silica that had been wet-ground, dried, and reground. In this technique, the fiber was chopped in a large excess of water (e.g., 100 grams of fiber in 750 ml of water) with a Waring Blendor. The fiber could be reasonably well-dispersed in a very few minutes. The dried reground silica was then added, with further mixing, to obtain the desired fiber-fused silica ratio. The slurry was then allowed to stand for about 24 hours to settle the solids. The necessary quantity of water was then decanted from the slurry until the solids concentration was in the neighborhood

---

*The fiber concentrations in this work are stated as the volume percentage of the total solids content. This eliminates any confusion or conversion in going from a discussion of slips to a discussion of the composite body.

**Considerable effort was devoted to investigating the feasibility of reducing the slip viscosity while maintaining a solids concentration of 82 weight per cent by pH adjustments. However, the deleterious side effects of the cations added were too great, and adjustment of the solids concentration was determined to be the most satisfactory method of reducing the slip viscosity.

of 80 weight per cent. The slip was then resuspended by rolling, without grinding media, on a rolling mill. Some additional adjustment of the water content was often necessary to obtain the proper slip viscosity. In general, the relationship between fiber content, solids concentration and slip viscosity was similar to that found for the milling technique. Slips with fiber contents greater than 10 volume per cent were not prepared with this technique. The desirable aspect of this technique was that the dispersed fiber had greater length-to-diameter ratios than could be obtained in the milling technique. The data for alumino-silicate fibers, presented in Figure 3, are representative of the distribution of length-to-diameter ratios produced with this technique.

The third, and simplest technique developed, lent itself only to the production of slips containing whiskers. In this technique, the pre-prepared silica slip and enough excess water to reduce the total solids concentration to approximately 80 weight per cent, were placed in a blender jar. The whiskers were then added incrementally with continuous mixing. A very satisfactory slip, containing 7-1/2 volume per cent silicon carbide whiskers, was prepared in this manner.

C. Casting

The composite bodies were cast using gypsum plaster molds. The composites were cast both as flat plates 1/2 x 3-1/2 x 7-1/2 inches, and as cylinders 3/4-inch in diameter and approximately 7 inches in length. These shapes were chosen with a view to the techniques to be used in measuring the physical properties of the composites, and their dimensions were chosen so that multiple specimens could be obtained from each composite. For example, from each flat plate, about twelve 1/2 x 1/2 x 3-1/2 inches, specimens for elastic modulus and modulus of rupture or impact testing could be obtained, or six modulus of rupture specimens could be obtained having dimensions of 1/2 x 1/2 inches by about 7-1/2 inches. The cylindrical bars were suitable for sectioning into approximately twelve 3/4-inch diameter cylinders 3/4 inches in length. The cylinders were used for obtaining a measure of the tensile strength.

The body shape appeared to have no influence on the fiber orientation within the cast composite. Microscopic investigations of composites, cast from slips with the proper viscosity, revealed the fiber to be well-dispersed with a completely random orientation. Segregation of the fiber was encountered

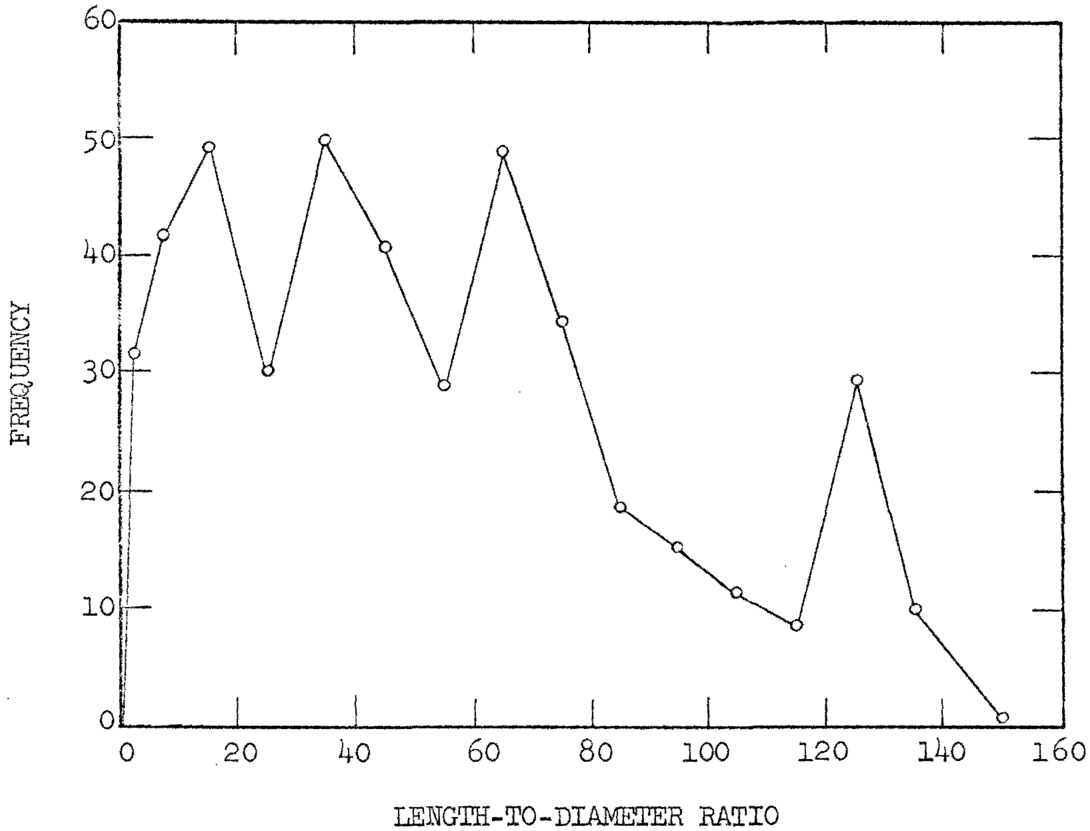

Figure 3. Distribution of Fiber Length-to-Diameter Ratios For Chopped Alumino-Silicate Fibers.

only when the slip was too thin. Then the fiber would be concentrated in the center of the cylindrical bars, and on one side of the plates. The plate mold used a glass plate on one of the large, flat sides and was filled from one end. It was at the surface next to the glass plate that the fiber would be concentrated when the slip was too thin. If the slip was too thick, it would gell in the mold rather than cast, and the resulting body would be extremely weak and porous.

One complex shape, a small radome 6 inches high and 5-1/2 inches at the base, was cast using a slip with a fiber content of 10 volume per cent. The wall thickness of the cast radome was purposely held to about 0.1-inch. The fiber dispersion in this body appeared to be extremely good and the body had very good green strength.

D. Sintering

The normal procedure for sintering slip-cast fused silica is to fire in an electric furnace in the range 2100° to 2300° F for an appropriate time. In most sintering operations, of course, the firing time is dictated by the maximum density that can be reasonably obtained since, usually, the greater the density the better the physical properties of the sintered body. Unfortunately, however, fused silica transforms to cristobalite at an appreciable rate in this temperature range, and the firing time is controlled by the amount of devitrification that occurs, rather than by the amount of densification that is obtained.

Cristobalite undergoes a sharp decrease in specific volume in the neighborhood of 400° F. This leads to the formation of internal stresses on cooling from the sintering temperature unless elaborate precautions are taken to anneal these stresses. Even then the resistance of the sintered body to subsequent, sudden, extreme changes in temperature is drastically reduced if an appreciable amount of cristobalite is present.

Therefore, an optimum sintering time is established by determining the point at which the deleterious effects of the cristobalite overcome the improvement in physical properties due to densification. Unfortunately, the exact rate of devitrification is dependent on such factors as the furnace atmosphere, moisture content, cross section of the casting, etc., and this point must be determined experimentally. Such was also found to be the case with the fiber-fused silica composites.

III. TESTING OF COMPOSITES

A. Techniques

The specific physical properties for which improvement was sought by incorporation of refractory, fibrous reinforcements were modulus of elasticity, modulus of rupture, tensile strength and impact strength. Measurement of the elastic modulus of the specimens prepared in this study were made using a sonic resonance technique. In this nondestructive technique, the specimen was vibrated, in flexure, with sound waves. The fundamental resonance frequency was established, and from this the dynamic elastic modulus was computed 1/.

Originally, the modulus of rupture measurements were made with the same size specimens used for the elastic modulus and impact strength measurements. The samples were loaded on a 2-inch span in quarter-point loading. However, the results from these measurements were not consistent with previously obtained data for slip-cast fused silica using greater span-to-depth ratios 2/. Also, the location of the failure in the 4:1 span-to-depth specimens did not appear to be randomly distributed. Rather, there appeared to be a bias toward failure under one of the upper loading points. Therefore, a span-to-depth ratio of 12:1 was adopted with the specimens being loaded over a 6-inch span in third-point loading. All values for the modulus of rupture reported in this work were made under these conditions unless otherwise noted.

As is generally recognized, measurements of the tensile strength of brittle materials are accomplished only with the greatest difficulty. This is particularly true if the classical tensile test, using dogbone, or similar reduced cross section specimens, is employed. A critical survey of various techniques for determining the tensile strength of brittle materials revealed a very promising technique, known as the diametral-compression test 3/. This

---

1/S. Spinner and W. E. Tefft, "A Method for Determining Mechanical Resonance Frequencies and for Calculating Elastic Moduli From These Frequencies," A.S.T.M. Proc. 61, 1221-1238 (1961).

2/J. D. Fleming, "Fused Silica Manual," Final Report, U. S. Atomic Energy Commission Contract No. AT-(40-1)-2483, Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Georgia, September 1, 1964.

3/A. Rudnick, A. R. Hunter, and F. C. Holden, "An Analysis of the Diametral-Compression Test," Materials Research & Standards, 283-289 (April 1963).

test is also sometimes referred to as the Brazilian test or indirect tension test. In its simplest form, a right circular cylindrical specimen is compressed diametrically between two flat platens. The maximum tensile stresses are developed normal to the loading direction across the loaded diameter and are proportional to the applied load. Under proper conditions, these tensile stresses cause the cylinder to fracture along the diametral plane joining the lines of contact of the specimen and the platens. The tensile strength can then be computed from the load at fracture.

The diametral-compression test does produce values which are dependent on the specimen size, as do many other "tensile test" techniques for brittle materials; and, therefore, it cannot be stated that the results represent the "true tensile strength." However, it is an experimentally simple technique for obtaining the characteristic strength of a specimen of brittle material, having a particular size and in a state of tensile stress. Therefore, it was extremely well-suited to this research program because any improvement in this characteristic strength was evaluated by reference to the value obtained for unreinforced slip-cast fused silica.

The impact strengths were determined with a Testing Machines, Inc., Model TM 52004, impact tester using the Izod test. An unnotched specimen, 1/2 x 1/2-inch in cross section, was employed. The specimen protruded 1-1/4 inches above the upper edge of the Izod vise. The tests were conducted in the 0-2 ft-lb range of the tester, where the scale is calibrated in 0.01 ft-lb increments.

The porosity, or per cent of theoretical density, of the composites was determined by weighing and measuring the dimensions of precision sawn specimens. The cristobalite content of the composites was determined by quantitative x-ray diffraction referred to an arbitrary standard used by this organization. In comparing the area under the cristobalite diffraction peak for a powdered sample of a composite to the area for the cristobalite standard, a correction was made for the volume of the composite sample that was occupied by the fibrous reinforcement.

B. Data Reduction

Since, as is usually the case for brittle materials, measurements of such properties as modulus of rupture, tensile strength and impact strength on a number of similar specimens produced a statistical distribution of values for the property under test, every effort was made to assign an indication of the statistical significance to the mean obtained from these values. For the modulus of rupture and tensile strength data Weibull statistics 4/ were used. To establish a good fit of empirical data to any failure distribution (including the Weibull) requires hundreds of data points. However, this does not imply that statistical tools developed for numerically large tests do not have applicability to smaller tests. Where as few as 10 specimens are involved, it is possible to develop an estimate of the true failure distribution with a graphical technique. In the case of the Weibull distribution, ranking tables have been developed for small tests (numerically less than 50) for estimating the most likely distribution curve as a function of the number of specimens tested and for generating a 90 per cent confidence interval about this estimate 5/. This technique of "median ranks" was used to obtain estimates of the Weibull distribution curves of the data for modulus of rupture, and tensile strength, obtained from the composites tested in this study. The number of specimens tested was usually between 10 and 50. When the property under test (e.g., dynamic elastic modulus) was not described by the Weibull function (i.e., weakest link hypothesis), an arithmetic mean was computed. In the presentation of data, when the mean was obtained from an estimate of the Weibull distribution, the value of the slope of the Weibull curve, m, is given to provide an indication of the degree of variation in the data*. When the mean value of a particular property was obtained arithmetically, a conventional confidence interval is presented at the 95 per cent level.

4/W. Weibull, "A Statistical Distribution Function of Wide Applicability," J. Appl. Mech. 73, 293-297 (1951).

5/L. G. Johnson, The Statistical Treatment of Fatigue Experiments, New York: Elsevier Publishing Company, 1964.

*A rather low value of m, 1 to 3 or 4, indicates a large variation in the data from which the mean was obtained. Larger values, 10 or greater, indicate a very small variation in the data from which the mean was obtained.

A supplementary benefit was derived from the use of the estimates of Weibull curves in the data reduction. A straight line fit of the median rank points on Weibull paper is a good indication that the failure distribution can be represented by a Weibull function. Occasionally, however, the data can be best fitted only by two or more straight line segments. This generally implies that two or more failure modes are active, and often multi-segmented distribution curves can be correlated with particular characteristics of the specimen failures so that the cause of the different modes of failure can be identified. Such was the case in this investigation. In the analysis of the data on tensile strength from the diametral-compression test, it was noted that the data could usually be fitted only by the use of two straight lines. The low strength specimens failed in a single mode, which, according to the Weibull slope, was an exponential, or random, distribution. Above a certain strength level, however, the specimens all failed in a distinctly separate mode, which, according to the Weibull slope, was a normal distribution. Subsequent investigation of the test specimens revealed a definite correlation between physical condition and the two apparently separate failure modes. The low-strength specimens, which exhibited a random distribution of tensile strengths, all had one large void, or a series of very small voids along their axes. This was traced back to a characteristic in the casting of the cylindrical samples from which the specimens were cast. In the casting of the 3/4-inch diameter, 7-inch long, cylinders, even with a slip containing only finely-divided fused silica, these voids were formed at various points along the bar. When the bar was subsequently cut into a number of specimens, some would contain these flaws and others would not. The larger voids were apparently caused by a bridging effect of the solids at the center when the casting was almost complete. The smaller voids were caused either by a similar bridging of only a few large particles, or by the progressive rejection of entrained air from the slip as it cast, with the eventual entrapment of this air as fine bubbles at the axis of the casting. Various techniques such as pressure casting, vibratory casting and prior de-airing of the slip failed to correct this condition. Fortunately, however, the application of Weibull statistics with visual inspection of the fractured specimens enabled these nonrepresentative specimens to be identified and rejected.

C. Alumino-Silicate Fiber Composites

As mentioned earlier, alumino-silicate fiber was used in the early phases of this investigation principally for its economy. Large quantities of fiber were being consumed in studies of slip-making techniques and composite casting. In spite of the fact that nothing was known about the fiber strength or elastic modulus, and there were no particular reasons to think that they were outstanding, some of the composites made with these fibers were fired and tested. This was done as much to gain familiarity with the firing and testing of the composite structures as to determine the potential of the alumino-silicate fiber as a reinforcement. The slips for these composites were prepared by milling and, therefore, contained fibers with length-to-diameter ratios in the neighborhood of 10:1. The properties of these composites are presented in Table I.

TABLE I

PROPERTIES OF ALUMINO-SILICATE FIBER COMPOSITES

Fiber Concentration (v/o)	10	30
Composite Density (% of theoretical)	80	80
Cristobalite Content (v/o)	31	32
Elastic Modulus (psi x 10^6)	2.48 $\pm$ 0.04	2.39 $\pm$ 0.08
Impact Strength (ft-lb/inch)	0.42 $\pm$ 0.06	0.40 $\pm$ 0.07
Tensile Strength (psi)	1650 (m = 7.8)	1550 (m = 10.4)
Modulus of Rupture [a] (psi)	2450 (m = 8.7)	1150 (m = 1.1) [b]

[a] Determined with a 4:1 span-to-depth ratio on a span of 2 inches.

[b] Specimens exhibited some fiber segregation.

D. Synthetic Mullite Fiber Composites

Composites were prepared with the synthetic mullite fiber, initially, with fiber contents of 10 and 20 volume per cent. However, the sintered castings exhibited much buckling and cracking. It was known that this fiber underwent a significant shrinkage in the neighborhood of 2200° F. Therefore, it was reasoned that this shrinkage, coupled with the prestress due to the difference in coefficient of thermal expansion between the fiber and the matrix, was inducing too great a compressive load on the matrix and causing failure. In an effort to overcome this, samples of the fiber were densified by heating to 2200° F for about 15 minutes. Slips were prepared using the preshrunk fiber, and composites cast containing 10 and 20 volume per cent fiber. The sintered bodies again buckled and cracked.

Following the results with the preshrunk fiber, it was tentatively concluded that fiber concentrations of 10 volume per cent or greater placed too much compressive load on the matrix due to the prestress from the difference in coefficient of thermal expansion. A very simple analysis of the load induced on the matrix by thermal prestressing appeared to confirm this conclusion. However, some doubt existed at this point also, as to whether or not the cristobalite contents of the previously prepared composites were optimum (it will be remembered that the effect of the cristobalite content on physical properties was discussed under FABRICATION OF COMPOSITES). The cristobalite contents had been 20 volume per cent or greater. Therefore, composites containing 2-1/2 and 5 volume per cent of the preshrunk fiber were prepared, by milling, and the firing conditions were carefully investigated. This was accomplished by, initially, bisque-firing the flat-plate samples. The plates were then sawn into the usual 1/2 x 1/2 x 3-1/2-inch specimens, about 12 specimens being obtained from a single casting, as usual. The cristobalite content, per cent of theoretical density and dynamic elastic modulus of these specimens were then determined. The value of all these properties was quite low, as was to be expected.

Each of the specimens prepared in the above manner was then fired, separately, at 2200° F for varying lengths of time. The cristobalite content, per cent of theoretical density and elastic modulus were again determined for each of these specimens. Each specimen, of course, had developed a different cristobalite content and density due to the different firing times, and the influence of these on the properties of the specimen was reflected in the dynamic elastic modulus. These data, for both the 2-1/2 and 5 volume per cent composites, are presented in Figures 4 and 5.

The data presented in Figures 4 and 5 indicated quite clearly that an optimum cristobalite concentration did exist, and that it was in the range of

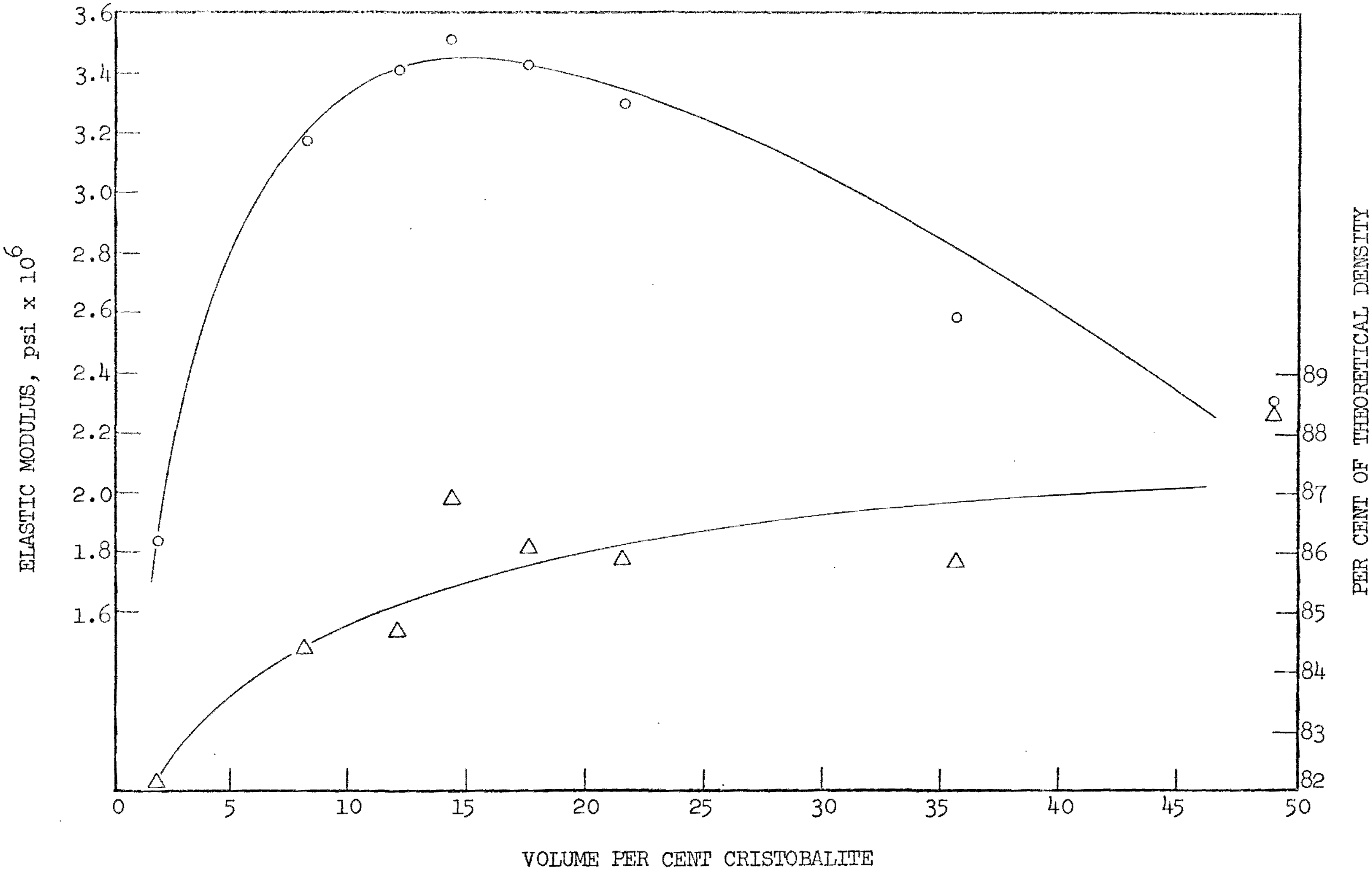

Figure 4. Dynamic Elastic Modulus of a Synthetic Mullite Fiber Composite As a Function of Density and Cristobalite Content (2-1/2 volume per cent fiber).

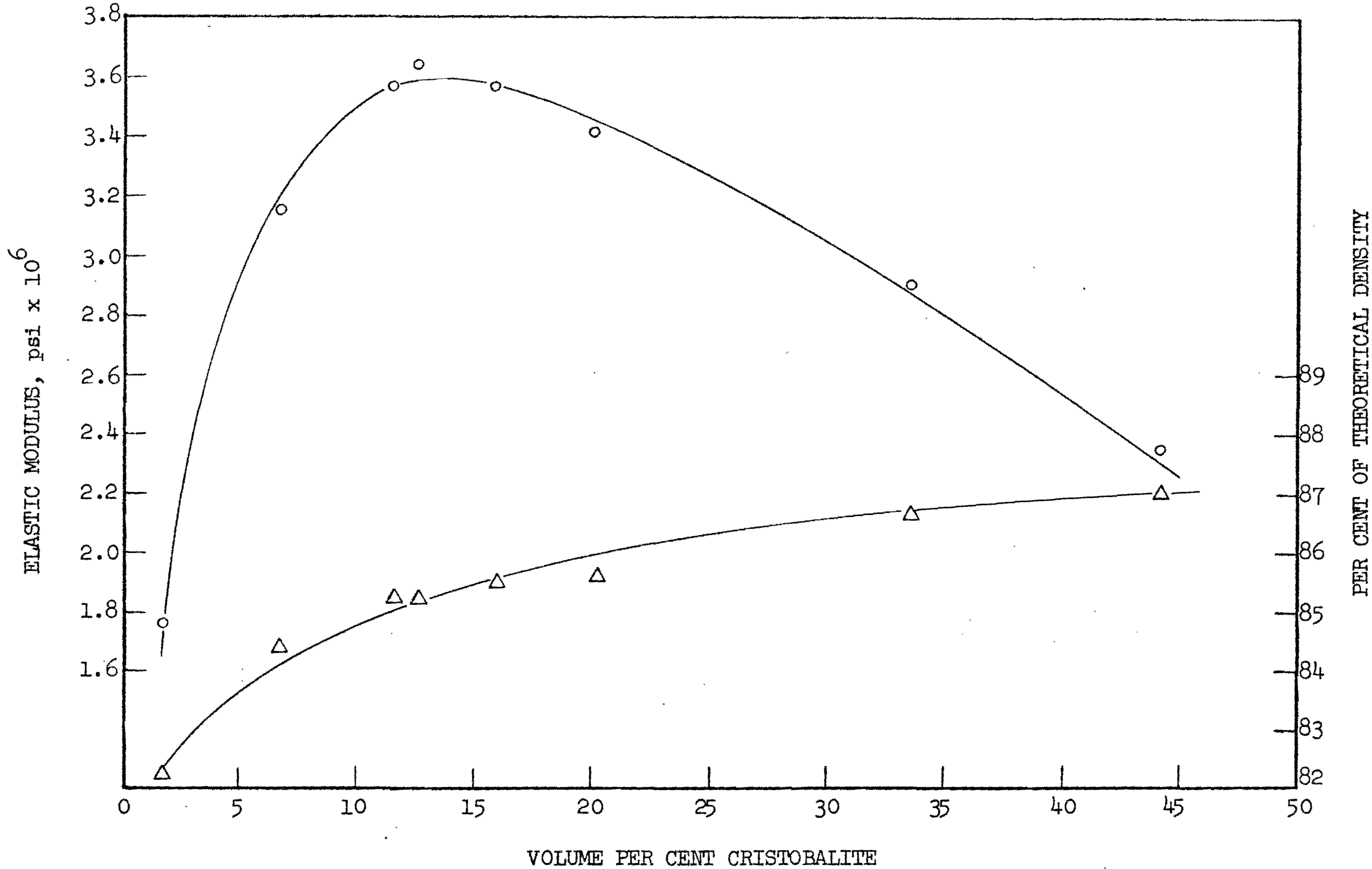

Figure 5. Dynamic Elastic Modulus of a Synthetic Mullite Fiber Composite As a Function of Density and Cristobalite Content (5 volume per cent fiber).

12 to 16 per cent. Therefore, additional composite samples, containing 2-1/2 and 5 volume per cent of synthetic mullite fiber, were fired at 2200° F for the length of time necessary to develop approximately this amount of cristobalite*. The physical property data obtained for these samples are contained in Table II.

TABLE II

PROPERTIES OF SYNTHETIC MULLITE FIBER COMPOSITES

Fiber Concentration (v/o)	2-1/2	5
Composite Density (% of theoretical)	85	85
Cristobalite Content (v/o)	14	14
Elastic Modulus[a] (psi x 10^6)	3.50	3.60
Impact Strength[a] (ft-lb/inch)	0.32	0.33
Tensile Strength (psi)	1800 (m = 12.7)	1600 (m = 16.4)
Modulus of Rupture (psi)	3450 (m = 9.0)	3700 (m = 12.5)

[a] Insufficient number of data points to establish confidence intervals.

E. Zirconia Fiber Composites

The investigation of composites produced with high-strength zirconia fiber was being conducted simultaneously with the investigation of the composites containing synthetic mullite fiber, and followed very similar lines. These composites also exhibited buckling and cracking in the initially-studied

*It had been deduced from the previous study of cristobalite development that this time was approximately one hour for the particular sample dimensions, nature of the furnace, furnace atmosphere, etc. However, it cannot be emphasized too strongly that the time required to develop a particular amount of cristobalite is extremely dependent on these variables, and that this particular time interval is valid only for the conditions used in this study. The time necessary to develop a particular cristobalite content for a different set of conditions, unfortunately, must be determined empirically under those conditions. There were even indications, from this research, that the total time interval is dependent upon whether or not the firing is interrupted. This difference could not be reasonably accounted for by the time lag involved in bringing the sample back to temperature after the interruption.

concentrations of 10 and 20 volume per cent. Likewise, this fiber, which also underwent considerable shrinkage in the neighborhood of 2200° F, was preshrunk and additional composites prepared containing 10 and 20 volume per cent fiber. These composites buckled and cracked, and it appeared as though the prestress on the matrix was too great, as was thought for the synthetic mullite fiber.

Simultaneously with the synthetic mullite fiber composites, an investigation of the effect of cristobalite content on the properties of the zirconia fiber composites was conducted. Composites containing 2-1/2 and 5 volume per cent preshrunk zirconia fiber were cast using slips that had been prepared by milling. These composites were bisque-fired and sawn into 1/2 x 1/2 x 3-1/2-inch specimens. The cristobalite content, per cent of theoretical density, and dynamic elastic modulus were determined, and the specimens refired for various lengths of time. The cristobalite content, per cent of theoretical density, and dynamic elastic modulus were then redetermined for each specimen. These data are presented in Figures 6 and 7, and an optimum range of cristobalite content is clearly indicated.

Following the determination of the optimum cristobalite content for the zirconia fiber composites, additional 2-1/2 and 5 volume per cent composites were prepared by milling, using the preshrunk zirconia fiber. These composites were fired to bring them into this optimum range and the physical properties were determined. These data are contained in Table III.

TABLE III

PROPERTIES OF ZIRCONIA FIBER COMPOSITES

Fiber Concentration (v/o)	2-1/2	5
Composite Density (% of theoretical)	86	83
Cristobalite Content (v/o)	13	12
Elastic Modulus (psi x 10^6)	3.67[a]	4.67 ± 0.01
Impact Strength (ft-lb/inch)	0.36[a]	0.31 ± 0.03
Tensile Strength (psi)	1550 (m = 6.5)	3150 (m = 4.2)
Modulus of Rupture (psi)	3200 (m = 25.7)	3600 (m = 18.8)

[a]Insufficient number of data points to establish a confidence interval.

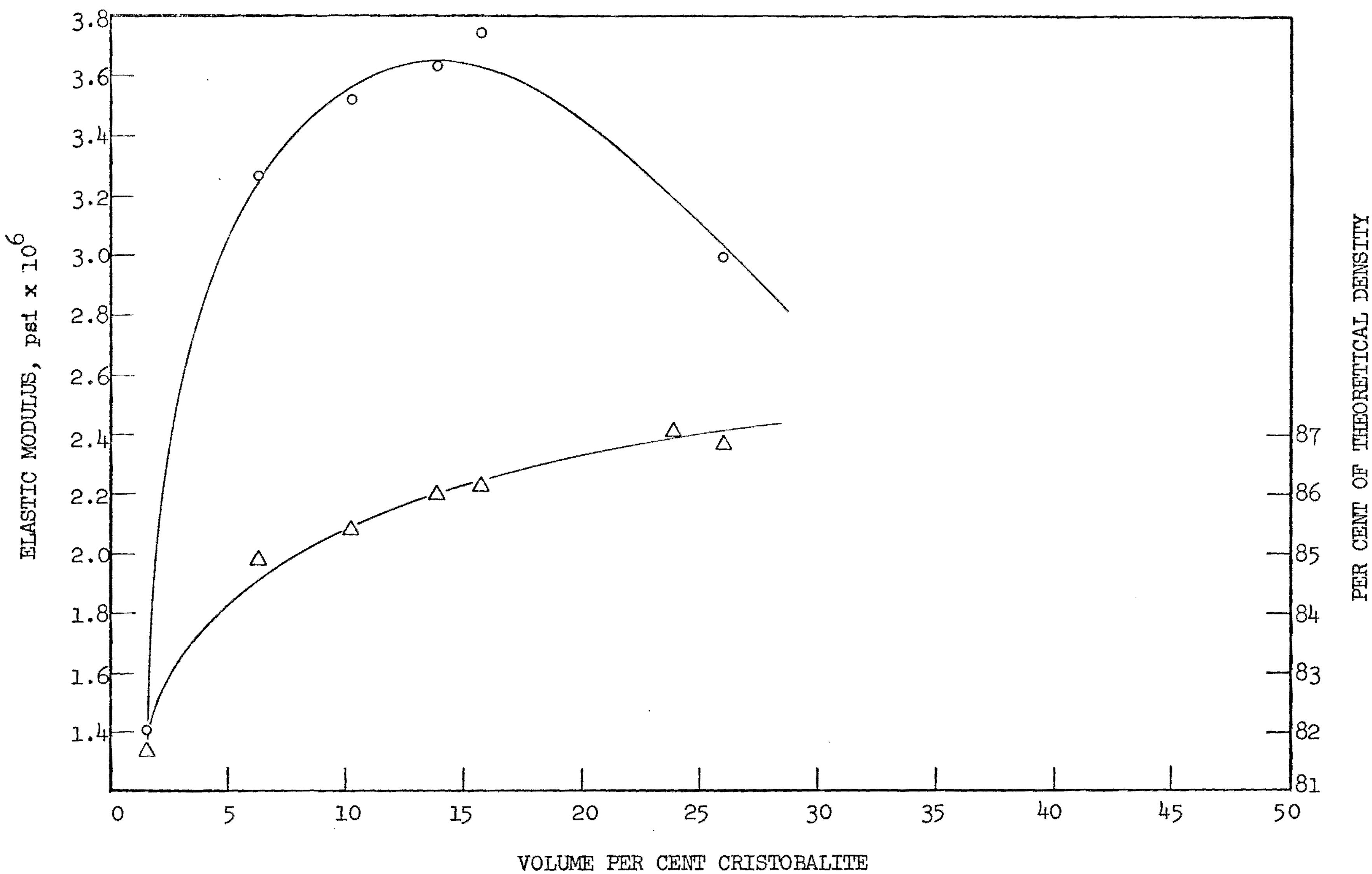

Figure 6. Dynamic Elastic Modulus of a Zirconia Fiber Composite As a Function of Density and Cristobalite Content (2-1/2 volume per cent fiber).

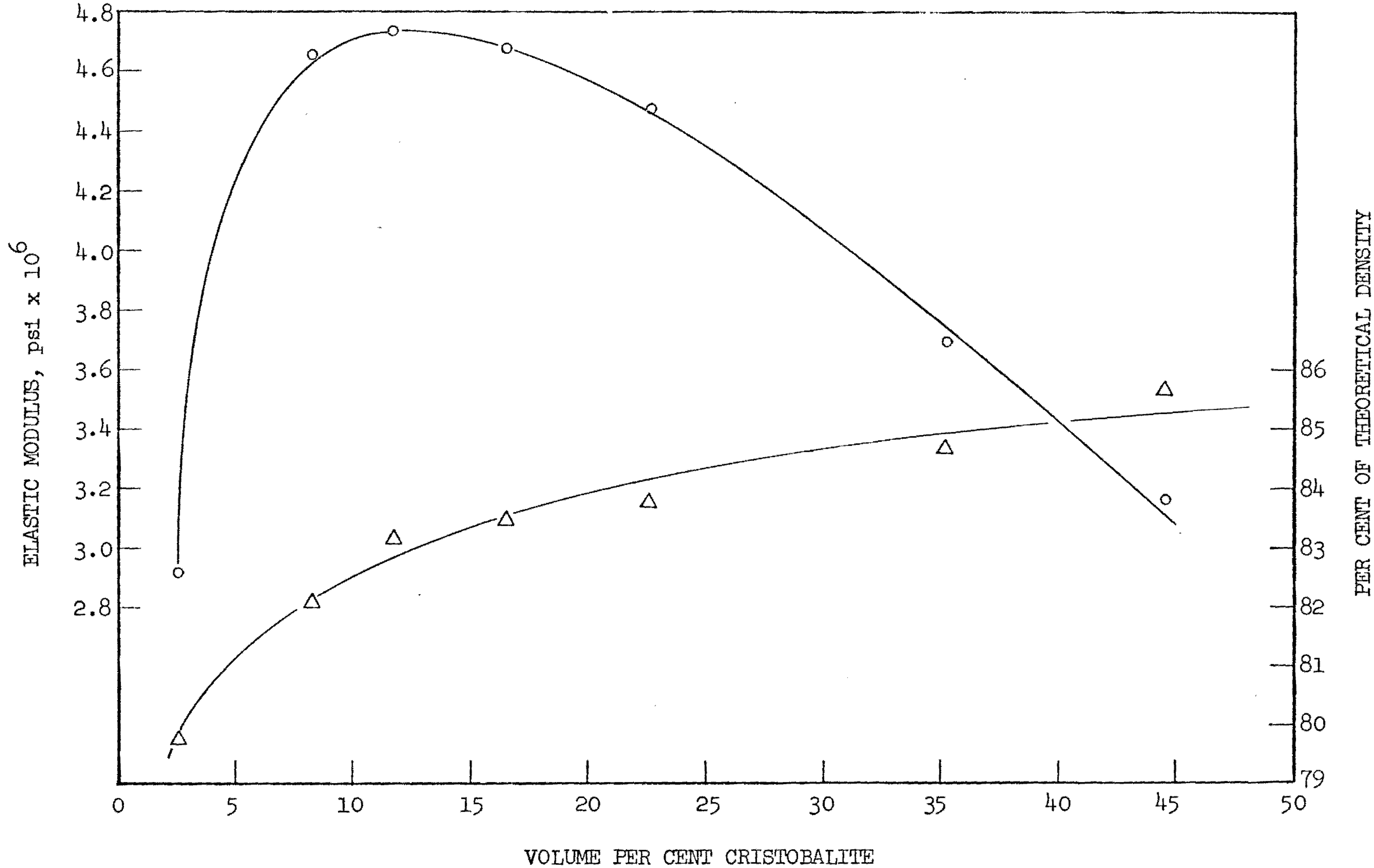

Figure 7. Dynamic Elastic Modulus of a Zirconia Fiber Composite As a Function of Density and Cristobalite Content (5 volume per cent fiber).

In an effort to obtain an indication of the effect of the length-to-diameter ratio of the reinforcing fiber on the properties of fiber-reinforced, slip-cast fused silica, a slip was then prepared with preshrunk zirconia fiber and dried regound silica slip as described in FABRICATION OF COMPOSITES. The fiber content of this composite was 10 volume per cent, and the mean length-to-diameter ratio of the fiber was approximately 50:1. This composite was fired using the previously-obtained data for optimum cristobalite content as a guide. The physical property data obtained for this composite are contained in Table IV.

TABLE IV

PROPERTIES OF A ZIRCONIA FIBER COMPOSITE WITH A LARGE FIBER LENGTH-TO-DIAMETER RATIO

Fiber Concentration (v/o)	10
Composite Density (% of theoretical)	81
Cristobalite Content (v/o)	10
Elastic Modulus (psi x 10^6)	1.64 ± 0.01
Impact Strength (ft-lb/inch)	0.29 ± 0.02
Modulus of Rupture (psi)	2050 (m = 6.8)

F. Silicon Carbide Whisker Composites

A limited quantity of single crystal silicon carbide whiskers was obtained for an investigation into the potential of this ultra-high-strength material for reinforcing slip-cast fused silica. A slip was prepared with the technique outlined for whisker material in FABRICATION OF COMPOSITES. Unfortunately, there was only enough of this material to produce one 1/2 x 3-1/2 x 7-1/2-inch, flat-plate sample with a fiber content of 7-1/2 volume per cent. The sample was fired at 2200° F to a cristobalite content of 11 volume per cent, and the physical properties were determined. These data are contained in Table V.

G. Slip-Cast Fused Silica

In order to determine if reinforcement was being obtained by the incorporation of fibers, it was necessary to determine typical values for the physical

TABLE V

PROPERTIES OF A SILICON CARBIDE WHISKER COMPOSITE

Fiber Concentration (v/o)	7-1/2
Composite Density (% of theoretical)	81
Cristobalite Content (v/o)	11
Elastic Modulus (psi) x 10^6)	3.48 ± 0.03
Impact Strength (ft-lb/inch)	0.30 + 0.01
Tensile Strength (psi)	___[a]
Modulus of Rupture (psi)	3450 (m = 13.1)

[a] Sufficient material was not available to prepare tensile test specimens.

properties of unreinforced slip-cast fused silica, particularly with the testing techniques used in this program. Therefore, this was a continuing phase of this research program. Figure 8 contains the results of a study to determine the optimum cristobalite content, similar to that performed for the synthetic mullite fiber composites and the zirconia fiber composites, and Table VI contains what are considered to be the maximum, or best, physical properties obtainable with the material used in this study. Theoretical densities of 90 per cent are not always obtained without excessive cristobalite contents, but under the best conditions this is possible. Therefore, the property values presented in Table VI were the criteria against which the effects of fibrous reinforcement were judged.

TABLE VI

PROPERTIES OF SLIP-CAST FUSED SILICA

Density (% of theoretical)	90
Cristobalite Content (v/o)	11
Elastic Modulus (psi x 10^6)	4.85 ± 0.10
Impact Strength (ft-lb/inch)	0.35 ± 0.05
Tensile Strength (psi)	3100 (m = 11.3)
Modulus of Rupture (psi)	3500 (m = 10.7)

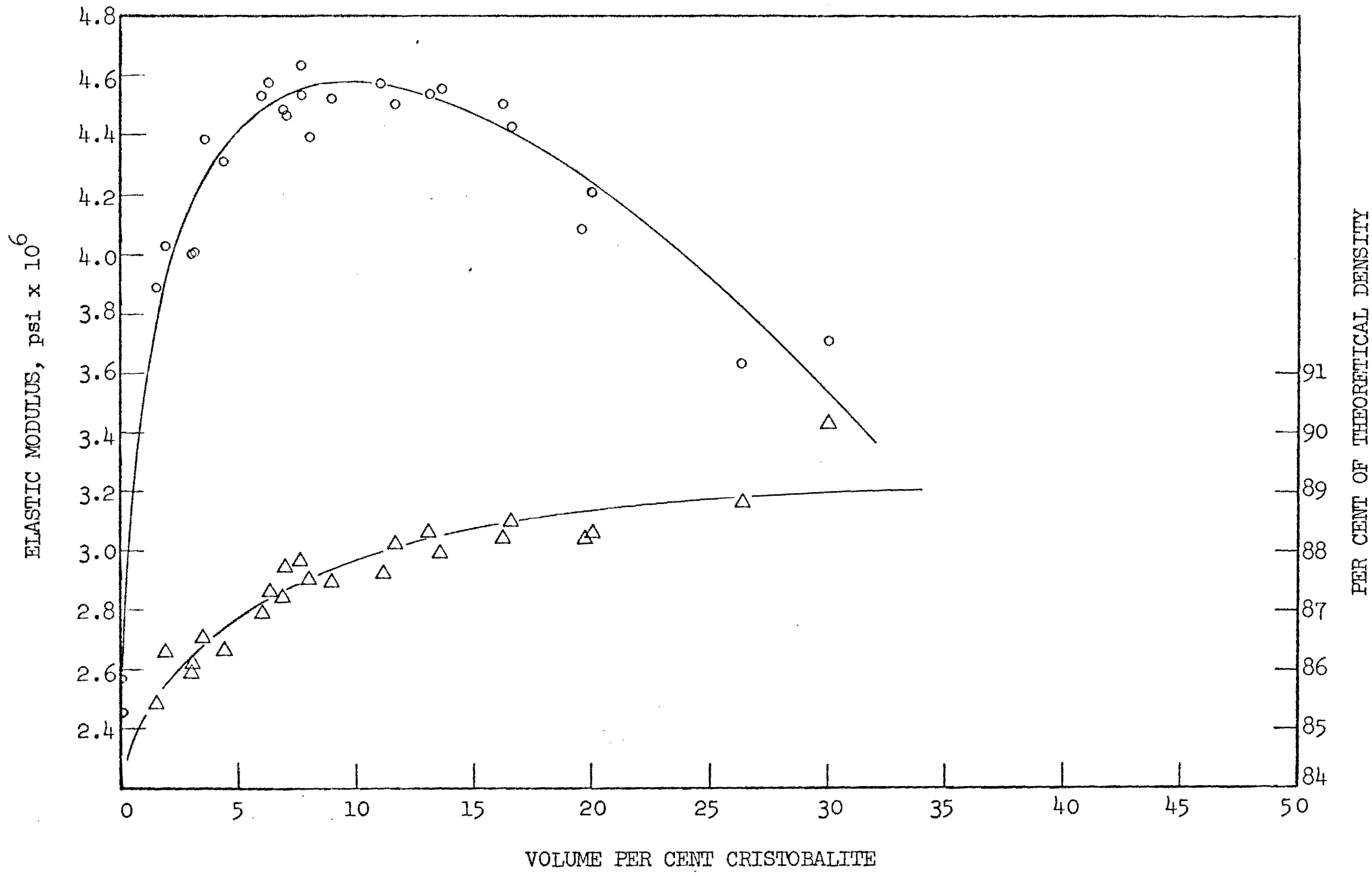

Figure 8. Dynamic Elastic Modulus of Slip-Cast Fused Silica As a Function of Density and Cristobalite Content.

IV. DISCUSSION OF RESULTS

All of the processing variables in the production of slips from fibers and finely-divided fused silica were not exhaustively investigated. However, the techniques developed in this work have been defined well enough that they are within the capabilities of anyone skilled in the art of slip casting.

The condition of the composites that must be obtained in the sintering process have been discovered, at least for the systems investigated in this work, and there is every indication that this condition is generally applicable. That is, the cristobalite content of the sintered body should be about 12 to 14 volume per cent of the total volume of the fused silica matrix*. The curves presented in Figures 4 through 7 show quite clearly that, as this cristobalite concentration is exceeded, the dynamic elastic moduli of the composites fall off, even though the density of the sintered body continues to rise. This can be attributed only to the development of micro-cracks from the internal stresses caused by the volume inversion of the cristobalite as it cools. The presence of these micro-cracks would certainly reduce the other physical properties. Therefore, it was only necessary to use the dynamic elastic modulus to locate the range where the optimum physical properties would be expected.

As is usually done, these samples were removed from the furnace at 2200° F and allowed to air-cool. Admittedly, the occurrence of this micro-cracking could possibly have been overcome by step-wise cooling of the composites in the furnace. However, this was considered to be unrealistic. If these composite materials were ever considered for use in severe thermal environments, as they reasonably must be, the micro-cracks would develop as soon as thermal shock conditions were encountered.

Figure 8, of course, demonstrates the similar behavior of slip-cast fused silica without any fibrous reinforcement. It has been recognized for some time

---

*These exact values are, of course, dependent upon the nature of the "cristobalite standard" that is used. An absolute cristobalite standard has not been developed, and any organization that develops its own (this is usually done by the prolonged heating of fused silica in the devitrification range) may obtain different values for the optimum range of cristobalite concentration. The important point is that, by using the technique developed in this work, this range can be established based on any arbitrary "cristobalite standard." There are indications that the standard used by this organization is no more than 80 volume per cent cristobalite, rather than the desired 100 volume per cent.

that an optimum range of cristobalite content existed for the slip-cast fused silica. However, to the knowledge of these investigators, this is the first time that this range has been accurately determined. It must be mentioned, though, that these data should be applied only to the particular material such as used in this work. If a material with a radically different particle size is used (which should result in a body with an appreciably different porosity), or if the material is fabricated into a body with considerably more porosity than in this work (e.g., fused silica foam), the optimum range of cristobalite content may differ from that found here. The results of the dynamic elastic modulus versus cristobalite content investigations graphically demonstrate that any determinations of the properties of slip-cast fused silica are of little value unless the cristobalite content of the specimens is stated.

It is obvious from the results of the optimum cristobalite content studies that the results obtained for the composites produced with the alumino-silicate fibers, and presented in Table I, are of little value. The cristobalite contents of these composites are undoubtedly too high and the resulting micro-cracking would have controlled the physical properties. The physical properties of the remainder of the systems studied (Tables II through VI) should be representative since the cristobalite contents were held to the optimum range.

One of the principal difficulties encountered, in attempting to determine if the properties of the fiber reinforced composites were superior to the best obtainable with unreinforced slip-cast fused silica, was the variation in porosity between the systems. This was an unavoidable situation. The slips containing fibers just would not cast to the same per cent of theoretical density that was obtainable with slip-cast fused silica alone; this was apparently due to the geometric interference of the fiber.

It is known that the influence of porosity on the properties of ceramic bodies is quite significant, and slip-cast fused silica is no exception (e.g., Gannon, Harris and Vasilos 6/). Therefore, many properties of the composites which are recognized as being porosity dependent cannot be compared directly to those of the relatively dense slip-cast fused silica as given in Table VI. Some

6/R. E. Gannon, G. M. Harris and Thomas Vasilos, "Effect of Porosity on Mechanical, Thermal, and Dielectric Properties of Fused Silica," Ceramic Bulletin 44, 460-462 (1965).

translation to account for the effect of porosity must be accomplished. In the case of elastic modulus, at least, this can be done by comparing data for slip-cast fused silica to that for the composite at the porosity level of the composite. Data for the elastic modulus of slip-cast fused silica as a function of porosity were used and are reproduced in Figure 9.

A comparison of the elastic moduli for the synthetic mullite composites (Table II) with the data of Figure 9 at the per cent theoretical density of the composites shows that the elastic moduli obtained for the composites is almost exactly the same as for the slip-cast fused silica. Therefore, there is no indication of the synthetic mullite fiber composites being superior in elastic modulus to slip-cast fused silica with the same porosity. Likewise, for the 2-1/2 volume per cent zirconia fiber composite (Table III), the elastic modulus of slip-cast fused silica is about 10 per cent greater at the same per cent of theoretical density and no improvement can be claimed for the incorporation of 2-1/2 volume per cent of zirconia fiber. However, the indications are very different for the composite containing 5 volume per cent zirconia fiber (Table III). In this case, the elastic modulus of the composite is about 50 per cent greater than slip-cast fused silica at the same per cent of theoretical density. As a matter of fact, the elastic modulus of this composite, at 83 per cent of theoretical density, is almost equal to the best obtainable with slip-cast fused silica alone (Table VI). Similarly, the elastic modulus of the silicon carbide whisker composite (Table V) is about 25 per cent greater than the elastic modulus of slip-cast fused silica at the same level of porosity. Therefore, there are, at least, indications that the incorporation of zirconia fiber or silicon carbide whiskers into slip-cast fused silica can improve the elastic modulus.

A comparison of the impact strengths for all the composites, with the impact strength given for slip-cast fused silica in Table VI, shows no evidence of improvement in this property. Due to the extremely short (several hundred microns) lengths of the fibers in most of these composites, this may not be too surprising.

A further complication in evaluating the fiber reinforced composites arises when the modulus of rupture data are examined. There is no significant indication of an improvement in this property by the incorporation of fibers. However, even more unusual, there is no significant variation in the modulus

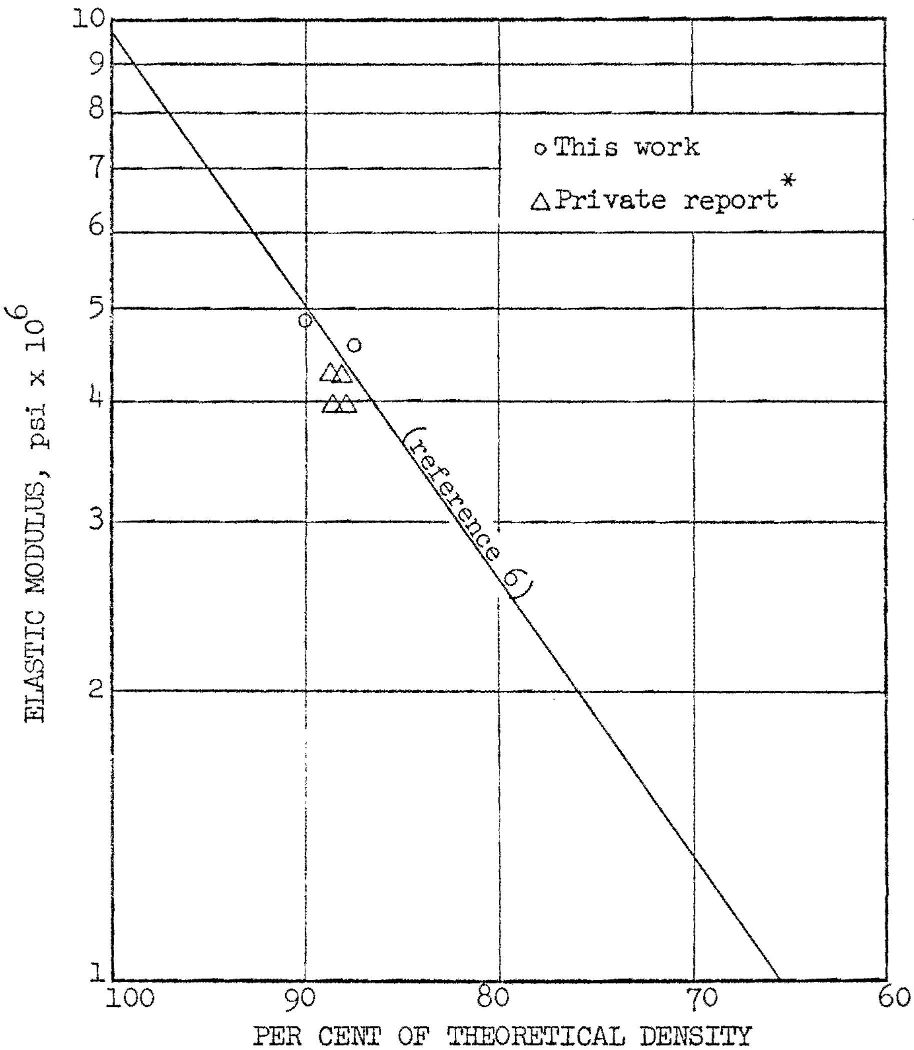

Figure 9. Dynamic Elastic Modulus of Slip-Cast Fused Silica As a Function of Per Cent of Theoretical Density.

*Private report from Mr. C. F. Smith, Pfaudler Company (Division of Pfaudler Permutit, Inc.)

of rupture, except for the composite containing zirconia fiber with a high length-to-diameter ratio. This is so in spite of the fact that the composite densities vary down to 81 per cent of theoretical and the elastic moduli differ significantly. A careful consideration of this in the final analysis of this program has led to the conclusion that the modulus of rupture test was not significant in this work.

The above conclusion was reached in the following manner. In the modulus of rupture test, the outer layer of material (the "outer fiber") determines the load at which the specimen will fail. This is due to the intrinsic fracture behavior of a brittle material. Once the outer fiber has failed, the specimen breaks catastrophically. The modulus of rupture specimens tested in this research were always loaded with a cast face on the tension side. That is, the tension face was always the face that had been next to the mold during the casting of the composite. Due to the nature of the slip casting process, the material immediately next to the mold (the "skin") will usually be composed of the finest silica particles. Therefore, the skin on each casting can be expected to be very similar even if the body of the casting is more porous than usual due to the presence of fibers, or other void producing influences. As a result, except in the case of the one zirconia fiber composite containing unusually long fibers, the modulus of rupture of the castings was controlled more by the nature of this skin than any other factor. In the case of the zirconia fiber composite mentioned, the elastic modulus, or stiffness, of the specimens were unusually low which undoubtedly led to the lower modulus of rupture for this material.

If the fibers had been continuous and unidirectionally oriented, as the steel in prestressed concrete, the cast face might have been in a complete state of compression. In which case, the modulus of rupture would have been controlled by this condition rather than the density of the skin. However, with the discontinuous, randomly-oriented fibers, a complete, uniform state of compression was most unlikely. Also, if the reinforcing fibers had been ductile, as are metal fibers, they might have acted as crack arresters and influenced the modulus of rupture values. Being brittle themselves, though, they could not arrest the high velocity crack front once it had been initiated.

The conclusion regarding the invalidity of the modulus of rupture test was confirmed by the results of a few experimental tests and a microscopic examination of specimens containing fibers. A few specimens containing a satisfactory dispersion of fibers were broken in rupture, with the surface that had been against glass (see Casting under FABRICATION OF COMPOSITES) as the tension face. These specimens broke at a lower load than specimens of the same composite when the cast face was in tension. The surface which had been against the glass was not a cast surface since the casting direction is always toward the porous plaster. Also, fiber could be seen frequently on this surface, while it could not on the cast surface. The fiber was not observed to be present at the cast surface even if it was uniformly dispersed throughout the specimen.

It is now recognized, therefore, that the modulus of rupture test, to have any significance for composites similar to those in this work, should be conducted on a sawn surface. This would eliminate the anomalous results of the casting skin that is always present. However, at best, the modulus of rupture test probably has little real value for such composites except as a reflection of any increased stiffness that might result from an improvement in the elastic modulus by the fiber. The initiation of failure can still be expected to be controlled by the physical condition of the surface. And, unless the surface is in uniform compression, which is most unlikely with discontinuous fibers, any flaw will develop into a crack front when the specimen has flexed enough to produce the tensile stress necessary for propagation. It is extremely doubtful that the discontinuous, internal zones of compression produced by the prestressed fibers would arrest the crack front, and the brittle fibers certainly could not since they would already be in a state of tension. It appears therefore that the route to improvement in the modulus of rupture, or impact strength, lies with improving the elastic modulus through the incorporation of high-modulus fiber; unless, of course, a complete switch to ductile fibers is made in an effort to arrest the crack front.

The most valid test for any improvement in ability to withstand tensile stress obviously was the diametral-compression test. The entire center of the specimen is placed in an almost uniform state of tension, and the test is affected little, if at all, by the specimen surface condition. The validity of this test for determining any improvement in tensile load-bearing capability by the incorporation of fiber is supported by the data contained in Tables II and III. The tensile strength values for the synthetic mullite fiber, and zirconia fiber, composites correlate very well with the values for their elastic moduli. That is, the 2-1/2 and 5 volume per cent synthetic mullite fiber composites and the 2-1/2 volume per cent zirconia composite all had about the same elastic modulus and similar tensile strengths. The 5 volume per cent zirconia fiber composite, on the other hand, had a much higher elastic modulus and, as would be expected for the higher modulus material, a much higher tensile strength. Also, the tensile strength of this composite is almost identical to that obtained for the unreinforced slip-cast fused silica (Table VI). If the tensile test is valid, this would be expected since the elastic moduli of the two are very nearly the same.

The really encouraging fact in the similar tensile strengths obtained for the 5 volume per cent zirconia fiber composite and the unreinforced slip-cast fused silica is that the porosities of these two materials are significantly different. This difference in porosity would certainly be expected to be reflected in a lower tensile strength for the zirconia fiber composite, if the fiber were not contributing to the tensile strength. This, therefore, is considered to be a strong indication that an improvement in tensile strength can be obtained, with the zirconia fiber at least. Unfortunately, a sufficient quantity of silicon carbide whiskers was not available to produce both flat-plate samples and cylindrical bars. Therefore, tensile test specimens were not available for this composite.

The single attempt to investigate the effects of increasing the length-to-diameter ratio of the reinforcing fiber (Table IV) produced some really anomalous results. The per cent of theoretical density was very low, in keeping with the idea of geometrical interference of the fiber on the cast density: the longer the fiber, the greater would be the degree of interference. However, the reduction in the modulus of elasticity is even greater than would be expected, by comparison to the data for slip-cast fused silica presented in Figure 9. Rather, the measured modulus of elasticity is almost exactly what would be expected if the 10 volume per cent of fiber were acting as an additional 10 volume per cent porosity (see Figure 9). As a matter of fact, this is probably the explanation for the behavior of this composite. The additional 9 volume per cent of porosity of this sample (as compared to the best slip-cast fused silica) is probably localized in the neighborhood of the fiber and, as a result, the degree of contact between the fiber and the matrix is quite low. This would cause the fiber to appear as a void in the measurement of dynamic elastic modulus. As has already been pointed out, the lower modulus of rupture value obtained for this composite is most probably a reflection of the reduced stiffness. Time did not permit the determination of the tensile strength of this composite.

V. CONCLUSIONS

From the results obtained in this research program, the following major conclusions have been reached:

1. Composites of discontinuous ceramic fibers and finely-divided fused silica can be prepared by slip-casting.
2. The allowable amount of devitrification of the fused silica matrix during the sintering of these composites has been determined.
3. The maximum physical properties obtainable with the unreinforced slip-cast fused silica matrix material were established (Table VI).
4. The feasibility of obtaining significant improvements in the physical properties of slip-cast fused silica by the incorporation of discontinuous, randomly-oriented, ceramic fibers has not been conclusively demonstrated, but there were good indications that this is possible.
5. The biggest single problem that must be overcome, in order to demonstrate if reinforcement is possible, is densification of the composites.

VI. RECOMMENDATIONS

Although the results obtained do not demonstrate conclusively the reinforcement of slip-cast fused silica by discontinuous, randomly-oriented fibers, this program does provide the means to produce composites of previously unattainable percentages of fiber which can be fabricated to almost any configuration by the technique of slip-casting. To take advantage of the experience and knowledge acquired during the performance of this work it is advisable that the question of fiber reinforcement in fused silica be resolved with an advanced program.

The first effort in such a program would be toward obtaining greater composite densification. Until the composite theoretical densities are brought nearer to that obtainable with unreinforced slip-cast fused silica, unequivocal comparisons in properties cannot be made, nor can the reasons for any successes or failures in obtaining reinforcement be determined. The best approaches to obtaining increased densification appear to be slip-casting under pressure, or the use of fused silica with a much finer particle size. Slip-casting of fused silica under pressure has been previously accomplished 2/, and slips containing fused silica in smaller particle sizes are available commercially. Either of these approaches offer the distinct possibility of mitigating the apparent geometric interference of the fiber in the casting process, and should lead to greater cast densities. It is in the casting step that the improvement must be obtained, for the sintering time and temperature are dependent on devitrification.

The most promising reinforcements, of the ones examined in this research, appear to be zirconia fiber and silicon carbide whiskers although the others deserve more study. These should certainly be included in an advanced program. Oxidation resistant carbon fiber certainly merits investigation. At least two other fibrous materials are known to be under development by commercial organizations at the present time, and are very near market announcements. The properties of these fibers will make them immediately recognizable for inclusion in a future program.

It is possible to produce slips with a fiber concentration up to 50 per cent where previous investigations were complicated by excessive devitrification of the matrix. These ranges require further study to resolve the effect of fiber concentration on the reinforcement of fused silica.

The use of chemical precursors to produce improved bonding between the matrix and the fiber should be investigated. For example, zirconyl chloride might be added to a zirconia fiber-fused silica slip during preparation. When the cast composite is dried, the zirconyl chloride should be present on the surfaces of the particles and fibers. Upon firing, the zirconyl chloride will decompose to form zirconium oxide and quite possibly improve the bonding between the zirconia fiber and the matrix. There have also been indications from previous work that such precursors may also reduce the devitrification rate during firing. Therefore, an added benefit might be obtained in that greater densification could be obtained before the critical cristobalite content was reached.

An extended program is necessary to finalize the basic information obtained in this study. This would prevent a possible interpretation of these preliminary results as negative. Such premature conclusions could hinder future investigations of fiber reinforced brittle materials.