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Research on Graphite Reinforced Glass Matrix Composites

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UNITED TECHNOLOGIES RESEARCH CENTER
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ANNUAL REPORT
Contract NAS1-14346

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SUMMARY

Graphite fiber reinforced glass matrix composites which offer excellent structural performance at temperatures up to 875 K, low density, excellent environmental stability, and low cost have been synthesized. Further, these composites can be made so that consistent properties are obtained together with 93% retention in flexural strength after exposure to air at 813 K for 100 hrs or complete strength retention after 100 hrs in air at 723 K. The oxidation resistance of a Hercules HMS graphite fiber reinforced C.G.W. 7740* +2% SiO_2 glass matrix composite is in contrast with the result found at the end of the first year's research for similar Hercules HMS graphite fiber glass matrices where only 72% of their original strength was retained after 4 hrs exposure to air at 833 K. The increased oxidation resistance of the Hercules HMS graphite fiber reinforced glass matrix composite is believed to be due both to the introduction of a new slurry and the fact that the composite is formed at a higher temperature, 1723 vs 1473 K. These changes also yielded a Hercules HMS graphite fiber reinforced glass matrix with higher flexural strength; its three-point bend strength is 1030 MPa (150 000 psi) and the four-point flexural strength is 964 MPa (140 000 psi), and a higher percent strain to failure (up to 0.52%) as well as a composite modulus of 200 GPa or 29 million psi. Results obtained with Hercules HTS, Thornel 300 and Thornel Pitch, and Celanese Type DG-102 graphite fibers reinforced C.G.W. 7740 and 7740 +2% SiO_2 glass matrix composites are also included but are not yet as impressive as are the results with the Hercules HMS graphite fiber reinforced C.G.W. 7740 +2% SiO_2 glass matrix composites.

The work of characterizing the Hercules HMS graphite fiber reinforced C.G.W. 7740 + 2% SiO_2 and of developing the process for making it has started. At the current stage of development, graphite fiber reinforced borosilicate glass matrix composites have exhibited a strength which increases with temperature up to 875 K (the softening point of the glass), excellent fracture toughness, no influence of 100 thermal cycles from 383 to 833 K in argon or 100 flexural fatigue cycles from low load to high load on the residual strength, and no strength degradation when painted with sea salt concentrates and thermally cycled in argon to 833 K. The Hercules HMS graphite fiber reinforced C.G.W. 7740 glass matrix composite made with one of the new slurries but without added silica has an average interlaminar shear strength of 39.8 MPa (5780 psi). Such graphite fiber reinforced glass matrix composites can be made as uniaxial, biaxial, or multiaxially reinforced

*C.G.W. is Corning Glass Works; C.G.W. 7740 is their code for a borosilicate glass or one of their Pyrex compositions

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composites. They can also be made from tapes containing sufficient glass that no additional glass between layers need be added, and these tapes can be transferred from take-up spool to die without loss of glass. Further, three thin composites can be hot pressed at one time just as easily as one thicker composite, and using the presently available equipment at the Research Center, composites can be formed as large as squares 10 cm x 10 cm. Again, tapes with 12 layers of slurry impregnated graphite fiber can be used as readily as the usual uni-layer tapes to form composites. When the coefficient of thermal expansion of uniaxial graphite fiber reinforced glass matrix composite is measured in the 90° direction, the value obtained for the coefficient of thermal expansion is only one-eighth that of a similar graphite fiber reinforced epoxy resin indicating the greater dimensional stability of the glass matrix composite. Despite these advances, much work remains to be done to more completely characterize the Hercules HMS graphite reinforced C.G.W. 7740 + 2% SiO_2 glass matrix composite and similar composites and in further simplification of the process for forming the composite.

INTRODUCTION AND BACKGROUND

Fiber reinforced composites are widely accepted as structural materials because of their desirable attributes of high strength, high modulus and low density. At the inception of this program the sales of high performance fiber reinforced composite materials exceeded a million pounds yearly. In general, most of these composites were organic polymer (epoxy resins, polyimides, polycarbonates, and similar materials) matrices reinforced with a great variety of fibers including Kevlar*, carbon, graphite, fused silica, glass, and boron. In general, almost all of these composites were limited to use temperatures not exceeding 575 K and many of these to temperatures not exceeding 425 K.

At the start of this contract, there were no reinforced glass matrix composites commercially available except the age-old wire reinforced glass used for improving the burglar resistance of homes and stores and the AVCO developed tungsten mesh reinforced fused silica intercontinental ballistic missile nose cones. Yet if one conceives of glass as just a high-temperature thermoplastic, the substitution of a glassy matrix for the low temperature polymers in composite materials seems a natural way to proceed. This concept, however, had attracted sparse attention in the past. Upon examining the technical literature, only 12 references by British and American scientists (Refs. 1-12) could be found. Since these references were discussed in detail in the first annual report on this subject (Ref. 13), it is sufficient to indicate that the fabrication approach has followed along the directions suggested by Sambell, et al (Ref. 4) and Levitt (Ref. 7) and has emphasized the use of a slurry in forming the graphite fiber reinforced glass matrix composite to the virtual exclusion of the other possible procedures. The materials and process are considered in more detail in the next sections.

*Aramid Fiber, trademark of DuPont

EXPERIMENTAL PROCEDURE

Materials

Glass

The types of glasses which were considered for use on this program are shown in Table I. Just as the graphite fibers show individual characteristics, the glasses also vary widely in their nature possessing different coefficients of linear expansion, different chemical compositions, varied environmental stability, and, of course, different temperature working ranges. Although all the glasses in the table have relatively low thermal expansion coefficients, only the titanium silicate glass has an expansion coefficient as low as that of the graphite fibers.

Just how different the working characteristics of these glasses are is shown in Fig. 1. It is apparent, therefore, that any resultant graphite fiber-glass matrix composites will have their own fabrication conditions. The glasses as they actually arrive at UTRC are shown in the scanning electron micrograph of Fig. 2. Although each glass is purchased solely on the basis that 90% must pass through a 360 mesh screen; actually all glasses contain numerous fine particles under one micron in size, and it is believed that these fine particles contribute greatly to the fabrication process to be described in the next section.

Graphite Fiber

The types of fibers readily available in this country for a research program on the generation of new types of graphite fiber reinforced glass matrix composites are shown in Table II. It will be noted that they vary widely in several important characteristics such as the number of fibers in each, the strength and modulus of the fiber, the precursor used to make the fiber, and the price. It is perhaps not so obvious that the use of each fiber presents a distinct surface chemistry problem, but if one considers the finish on the fiber surface and the chemical elements found on the fiber surface as shown in Table II the problem is evident. This is particularly true if one examines the distinctive shape of each carbon fiber as shown in Fig. 3. It is apparent, therefore, that any given glass matrix reinforced with a given graphite fiber will show its own characteristic behavior.

To broaden the investigation as much as practicable, UTRC purchased some of each carbon fiber shown in Table III.

Table I

Characteristic Properties of Glasses Used

Type of Glass	Nature of Glass	Strain Point $*10^{13.5}$	Anneal Point $*10^{12.0}$	Soften Point $*10^{6.5-7}$	Liquidus	Working Point $*10^{3}$	Density kg/m^3	Index of Refract.	Dielectric Constant	Coef. Linear Expansion cm/cm K $\times 10^{-7}$	Modulus GPa
C.G.W. 7740	Boro-silicate	833 K	833 K	1094 K	1290 K	1525 K	2230	1.474	4.6	32.5	63
C.G.W. 1723	Alumino-silicate	938	983	1181	1343	1441	2640	1.574	6.3	46	88
Ferro S	Magnesio-alumino-silicate	1033	1083	1243	1323		2490	1.547	5.2	29	85
C.G.W. 7913	High silica	1163	1293	1803	1973		2180	1.458	3.8	5.5	68
C.G.W. 7940	Pure silica	1229	1357	1853	1973		2200	1.459	3.8	3.5	72
C.G.W. 7971	Titanium silicate		1273	1773	1873		2210	1.484	4.0	-2	68

*viscosity, $N \cdot S/m^2$

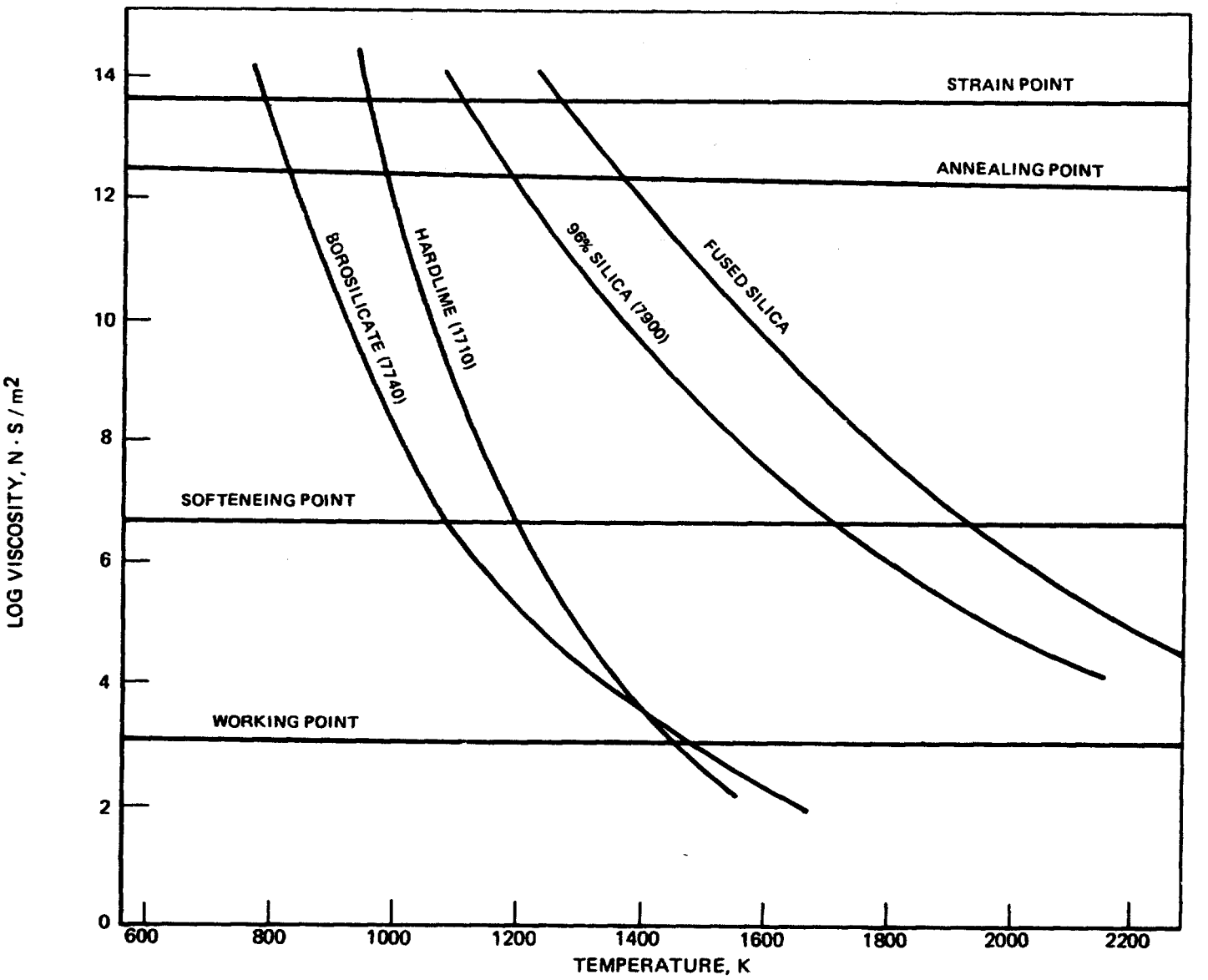

Figure 1. Viscosity – Temperature Curves

C.G.W. 1740 — 5μm

FERRO "S" — 50μm

C.G.W. 7913 — 10μm

C.G.W. 1723 — 5μm

Figure 2. Scanning Electron Micrographs of Glass Powders

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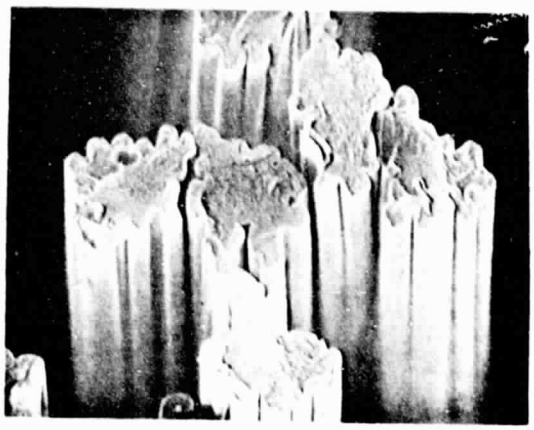
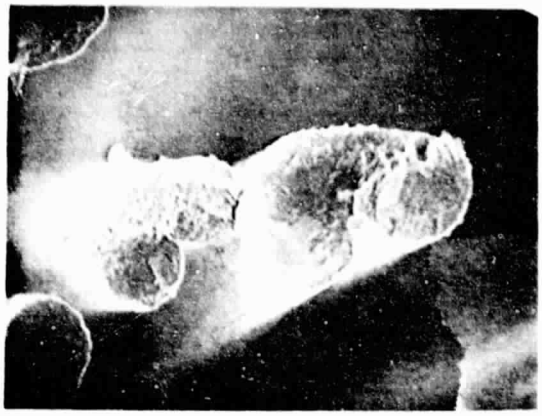
Table II

Carbon Fibers and Their Characteristic Properties

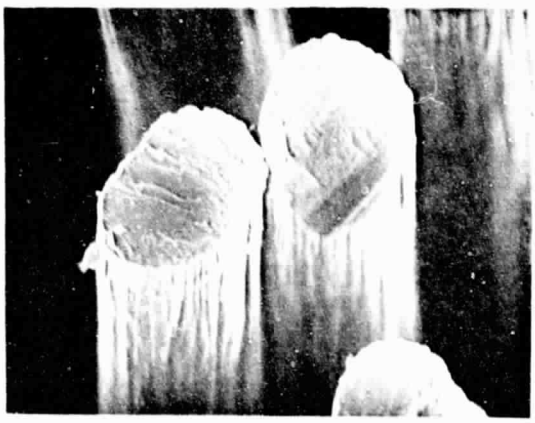
Type of Fiber	No. of Fibers in Tow	Finish Used	Precursor and Diameter of Fiber (microns)	Modulus GPa	Strength MPa	Density kg/m^3	Coeff. Linear Expansion cm/cm K (axial)	Cost per Pound $	Result of Spectroscopic Examination
Hercules HM/PVA	1 000	PVA 0.86	PAN	385	2427	1850		300	
Hercules HMS	10 000	Oxidized	PAN 7.3	351	2703	1808	-5.7×10^{-7}	90	High Na, high Si, Cr
Hercules HTS	10 000	Oxidized	PAN 7.6	256	2830	1658	-3.8×10^{-7}	75	High Na, very high K
Celanese DG-102	384	Oxidized	PAN 8	531	1724	1960		250	Very low Na highest Fe, Si, Ti, Zr
Thornel 300 Grade WYP30 1/0	3 000	UC 309	PAN 6.9	234	2482	1760		40	Very high Na, high Cu high Sn, Zn
Thornel 300 Grade WYP90 1/0	1 000	UC 309	PAN 8.4	228	2655	1750		32	Moderate Na high Mg, Sn, P
Thornel 75 Grade WYL160 1/2	720	PVA	Rayon 6.0	538	2620	1800		385	Intermediate Na very high P high Ca, Ta, Zn
Thornel 50 Grade WYG130 1/2	720	PVA	Rayon 6.6	393	2172	1660		320	



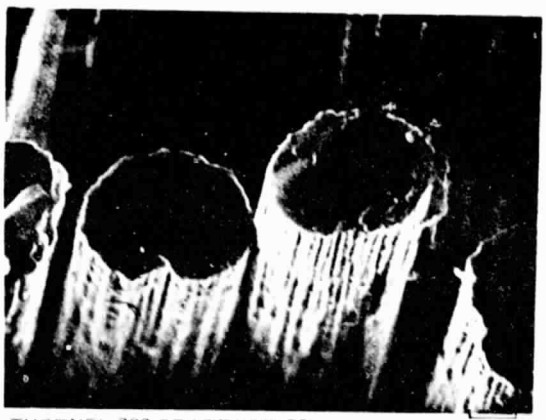
THORNEL 75 GRADE WYL 160 — 2μm



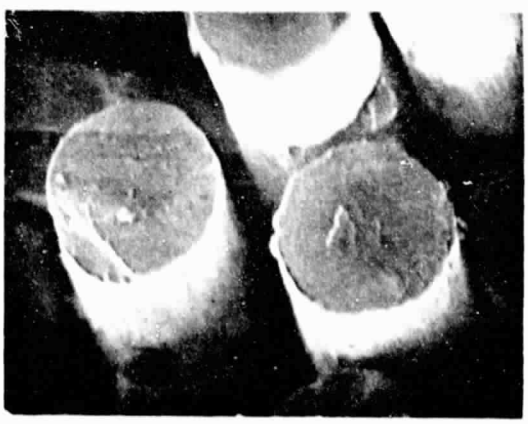
CELANESE DG 102 — 2μm



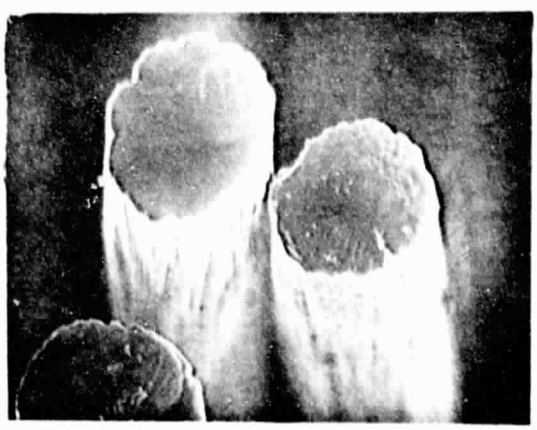
THORNEL 300 GRADE WYP 30 — 2μm



THORNEL 300 GRADE WYP 90 — 2μm



HERCULES HMS — 2μm



HERCULES HTS — 2μm

Figure 3. Typical Fibers as Seen in Scanning Electron Micrograph

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Table III

Carbon Fiber Obtained for this Study

	Number of Fibers in Tow	Tensile Strength MPa	Tensile Strength (ksi)	Young's Modulus GPa	Young's Modulus (10^6psi)	Cost ($/lb)
Hercules HTS	10 000	2979	432	234	34	75
Hercules HTS Special	1 000	2875	417	234	34	300
Hercules HM (μ) - PVA	1 000	2427	352	385	55.9	300
Hercules HMS - 10 K	10 000	2344	340	296-331	43-48	90
Hercules HMS - 3 K	3 000	2330	338	370	53.7	175
Thornel 50 WYG 130 1/2	1 540	2172	315	393	57	320
Thornel 75 WYL 160 1/2	1 540	2620	380	538	78	385
Thornel 300 WYP 30 1/2	3 000	2482	360	234	34	40
Thornel 300 WYP 90 1/0	1 000	2655	385	227	33	32
Thornel Pitch VS 0022-1	2 160	1145	166	469	68	55
Thornel Pitch VS 0022-2	2 160	945	137	345	50	55
Thornel Pitch VS 0022-3	2 160	993	144	414	60	55
Thornel Pitch VS 0032-1	720	1282	186	386	56	270
Thornel Pitch VS 0032-2	720	1083	157	400	58	270
Celanese DG-102	384	1724	250	531	77	250

Composite Fabrication

Slurry Technique

While several methods exist for coating the fiber as required in the construction of a fiber reinforced glass composite, much the simplest and lowest cost method, if it can be made to work, consists of pulling the graphite fiber tow through a slurry containing a suspension of the finely ground glass particles.

In the slurry process for coating the graphite fiber with glass, the graphite fiber is unwound from the spool and pulled through an agitated organic solution containing a suspension of fine glass particles. The process is shown schematically in Fig. 4. The slip may be composed of 40 grams of powdered glass and 3 grams of polyvinyl alcohol dissolved in 100 grams of water to which 2 grams of ethylene glycol is added as a plasticizer. Alternately, the slip may comprise 85 grams of glass in 225 ml of toluene to which 5 grams of polystyrene and 5 drops of tergitol have been added. Excess glass and solvent are removed by pressing a squeegee against the drum as it winds. The ground glass used is sized, so that 90% passes through a 325 mesh sieve. After the tape is dry (sometimes heating with a radiant heat source is required to remove excess solvent) it is cut and removed from the drum and then cut into strips or squares which are layed up to give unidirectional or cross-plied fiber alignment and then hot pressed.

The effect of the amount of glass in the slurry used to form the graphite fiber-glass tape is shown in Table IV where it is shown that doubling the glass added to the slurry results in a decrease of strength. Similar tests run with 45 grams of glass and with 135 grams of glass in the slurry confirm that the best choice seems to be 85 grams of glass i.. 200 grams of isopropyl alcohol, 10 grams of polyvinyl alcohol and 5 drops of a wetting agent such as tergitol H.D. 527.

Slurry Variation

The procedure just described was used in all of the earlier work, i.e. up to and including (cf Appendix A) sample LB 174. As mentioned, the isopropyl alcohol furnished the solvent or suspension vehicle and the polyvinyl alcohol formed the plasticizer part of the suspension and is Slurry A. This process worked well until a specific supply of polyvinyl alcohol was exhausted. Then, although polyvinyl alcohol, reagent grade, under the same formula number from Baker Chemicals was reordered, the new supply of polyvinyl alcohol would not either dissolve or stay in suspension in the isopropyl alcohol with a consequence that all the new graphite fiber-glass powder tapes made lacked green strength and lost copious

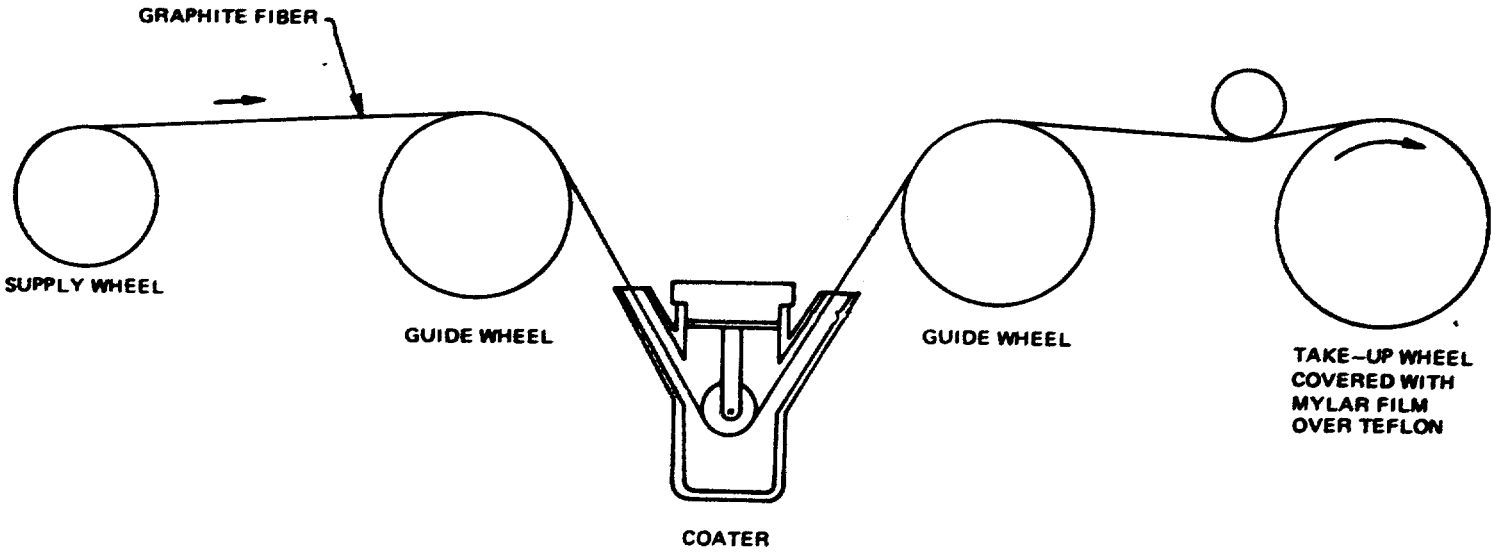

Figure 4 Slurry Method of Coating Graphite Fiber

Table IV

Effect of Amount of Glass in Slurry A on Achieved Flexural Strength of Graphite Fiber Reinforced Glass Composite

Specimen	Glass	Fiber	Temp. of Hot Press K	Pressure MPa	3-Point Flexural Strength MPa	3-Point Flexural Strength psi	Glass in Slurry gms	Glass Added Between Layers gms
LB 75-2	7740	Thornel 300	1323 argon	13.8	287	41 700	170	0.11
-3	↓	↓	↓	↓	277	40 200	↓	↓
-5					242	35 000		
-6					261	37 800		
-7					271	39 300		
-9					306	44 400		
Average					274	39 700		
LB 78-1	7740	Thornel 300	1323 argon	13.8	418	60 600	85	0.063
-2	↓	↓	↓	↓	326	47 300	↓	↓
-4					504	73 100		
-5					355	51 500		
-7					456	66 200		
-8					505	73 400		
Average					427.5	63 000		

amounts of glass powder on handling. Since then a number of organic solvents and plasticizers have been tried without finding anything as useful as the old polyvinyl alcohol-isopropyl alcohol combination. As a result of these efforts, however, a superior slurry consisting of isopropyl alcohol, polyethylene glycol and a small amount of polystyrene was discovered. This combination of ingredients yields a tape with considerable "green" strength which can be handled without shedding much of its glass powder. Further, the amount of glass picked up by the graphite fiber with these organic materials present in the slurry is so great that no glass powder need be added between the layers of material as they are charged in the die for hot pressing. Elimination of this step of adding carefully weighed amounts of glass powder between the tape layers both greatly speeds up the process of filling the die and eliminates a significant factor in the variability due to nonuniform distribution of the glass powder between layers. This newer slurry was used for samples GC 256 through GC 291 (cf Appendix A). The remarkable success achieved with this slurry, hereafter called slurry B, in achieving a uniform distribution of glass powder on the tape is shown in Table V where the weight of 12, 7.62 cm squares of tape cut from a larger tape are compared. It will be noted that these squares vary in weight by less than 1%. Slurry B specifically consisted of 85 grams of glass in 260 ml of isopropyl alcohol, 24 grams of polyethylene glycol and 2 grams of polystyrene with 5 drops of a wetting agent added.

Further investigation of slurry modification has resulted in a third slurry which is similar to that used previously except that it contains 6 grams of DuPont Company's Ludox* H.S. 30 in place of the 2 grams of polystyrene. The results obtained with this slurry to which only 6 grams of Ludox H.S. 30, containing approximately 2 grams of silica, have led to remarkable improvements in graphite fiber reinforced glass composites. This slurry hereafter called slurry C has been used in preparing all composites from GC 292 to GC 360 inclusive.

Hot Pressing Procedures

All of the specimens prepared in the second year of this contract were fabricated using a Centorr Hot Press shown in Fig. 5. The equipment can be used for the fabrication of specimens as large as 15 x 10 x 2.5 cm (7.6 cm thick before hot pressing). The press can provide a load of 530 kN, temperatures up to 3373 K, and a vacuum of 21 $\mu N/m^2$ (10^{-6} Torr) or alternately it can operate in argon. The press is double acting in contrast to the single acting presses used during the first year of this program.

*Registered trademark, E. I. DuPont de Nemours Corporation, Wilmington, Delaware

Table V

Comparative Weight of 7.62 cm Squares of Graphite Fiber-Powdered Glass Cut from One Large Tape, GT 234 (Slurry B)

Square	Weight grams	Difference from Average grams	% Variation from Average
1	4.727	+0.027	0.57
2	4.728	+0.028	0.60
3	4.683	-0.017	0.36
4	4.676	-0.024	0.51
5	4.737	+0.037	0.79
6	4.713	+0.013	0.28
7	4.706	+0.006	0.13
8	4.642	-0.058	1.23
9	4.771	+0.071	1.51
10	4.729	+0.029	0.62
11	4.644	-0.056	1.19
12	4.642	-0.058	1.23
Average	4.700		±0.75

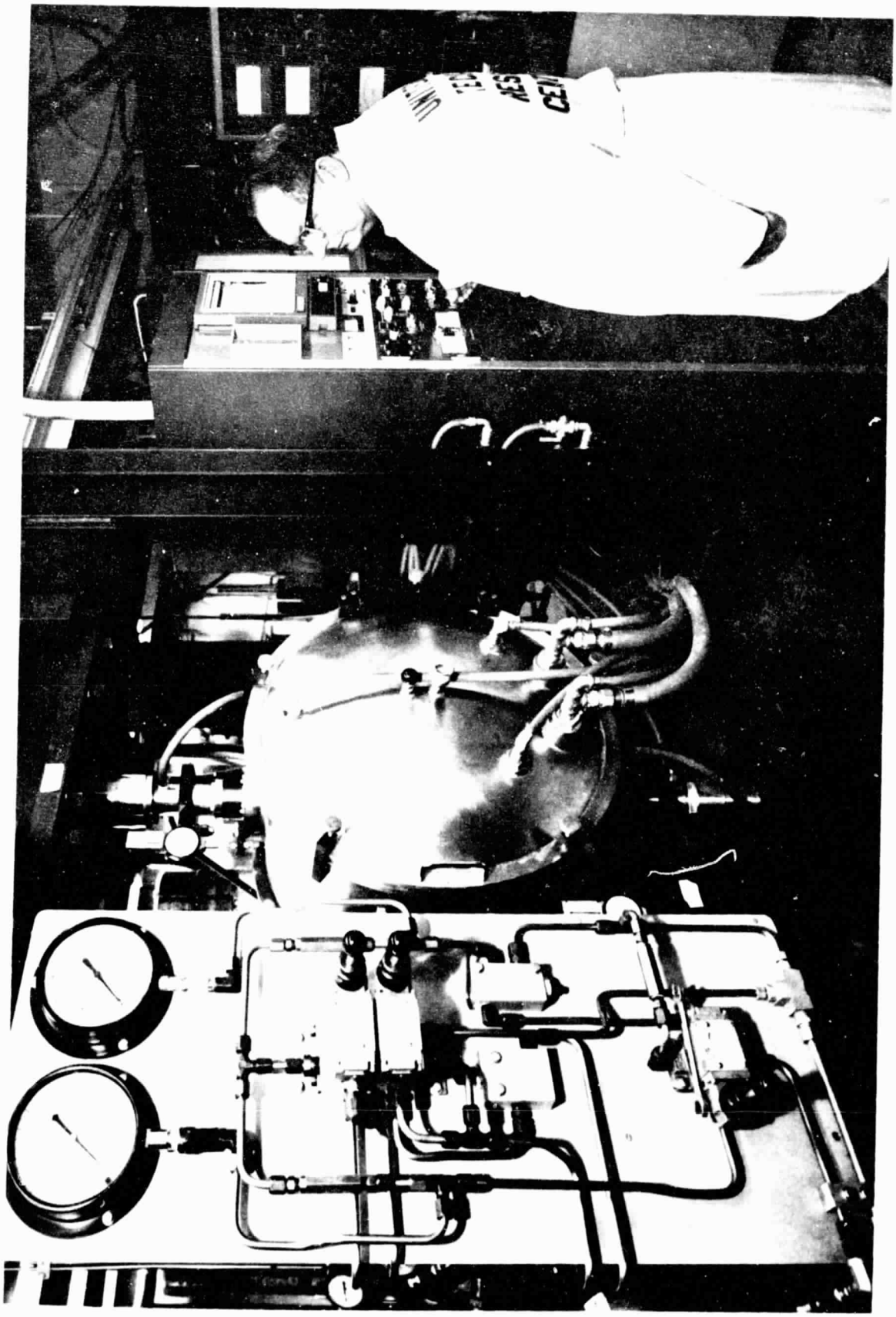

Figure 5. Centorr Hot Press at UTRC

In actual operation the HMS graphite fiber C.G.W. 7740 glass matrix composites made from slurry B tapes were usually hot pressed at temperatures of 1473 K, 13.8 MPa, 1 hr dwell time, argon atmosphere, and the pressure was not released until the sample had cooled to 773 K. Composites reinforced with Hercules HTS or Celanese DG-102 were prepared similarly. On the other hand, the HMS graphite fiber reinforced C.G.W. 7740 + 2% SiO_2 glass matrix composites, slurry C, were most generally prepared by hot pressing at 1723 K, 6.9 MPa, argon atmosphere, 1 hr dwell time and no release of pressure until the sample was cooled to 773 K. The Hercules HTS, Thornel Pitch, and Celanese DG-102 graphite fiber reinforced C.G.W. 7740 + 2% SiO_2 (slurry C tapes) were prepared in the same manner. As may be seen from Fig. 6, where the relative motion of the die plunger after application of full hot pressing pressure is shown, since most of the plunger motion takes place earlier than the usual 60 min dwell time, it may be possible to appreciably speed up the hot pressing operation. It is not known, however, whether the last relatively small motion of the plunger removes the last traces of porosity or whether it is caused by the extrusion of glass out of the die cavity. These questions would need to be studied before any drastic change in dwell time could be justified. All composites shown on this figure were formulated with slurry A and hot pressed at 1473 K, GC 221 and 223 at 13.8 MPa and GC 221 at 6.9 MPa.

Composite Characterization

Sample Preparation

The majority of the experimental composites prepared in the second year were of two sizes, either 7.6 cm x 7.6 cm x 0.25 cm or 6.67 cm x 2.22 cm x 1 cm. These composite plates were then cut into individual samples using diamond grit cutting and grinding wheels. In every case, except where specifically noted in this report, the surfaces of all specimens were ground flat and parallel thus exposing graphite fibers on all sides.

Flexural Testing and the Effect of Span-to-Depth Ratio

Flexural tests have been used for determining the strength properties of these composites. This technique has been chosen because of simple shapes (bars) required and because it avoids all the difficulties associated with gripping the specimen.

The fracture of a composite specimen during three-point flexural strength testing can be controlled by the applied flexural stresses or the applied shear stresses. The relative levels of these stresses, and the relative levels of inherent composite tensile and shear strength determine material performance. This complex type of behavior can be expressed using an interaction diagram

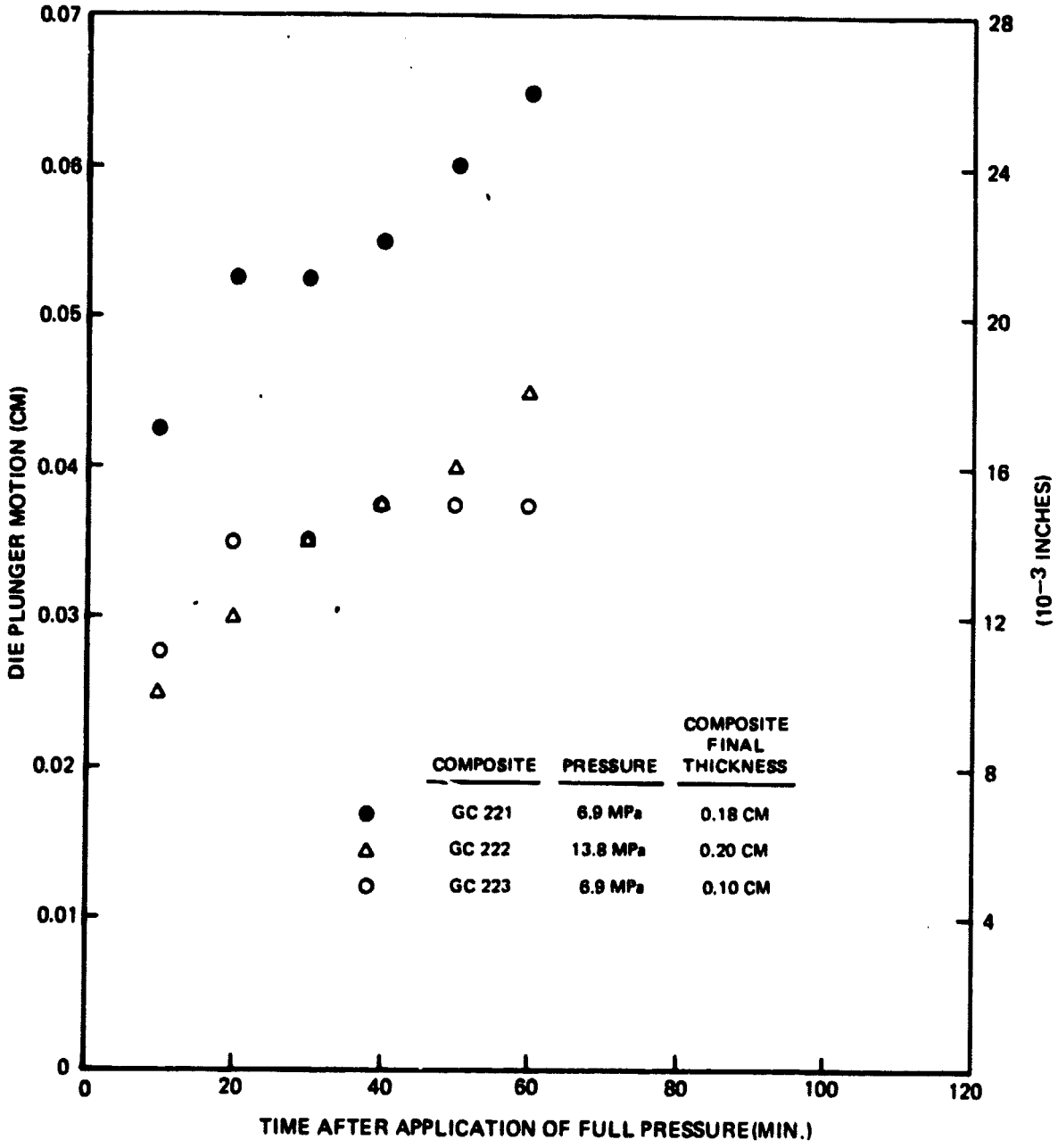

Figure 6. Relative Motion of Die Plunger After Application of Full Pressure During Hot Pressing, Slurry B

approach. By this method both the flexural strength and shear strength of each composite specimen are calculated and plotted as a function of test specimen span-to-depth ratio (L/h). At low values of L/h specimen failure should be controlled by shear deformation, while at high values of L/h the flexural strength of the specimen should control. This type of representation has been successfully used in the past for a wide range of composites (Refs. 14,15).

A uniaxially reinforced specimen containing 50 vol % HMS fiber in 7740 glass was fabricated and tested over an L/h range of 10 to 40. All specimen surfaces were machined prior to testing and the resultant data are presented in Figs. 7 and 8. The shear interaction diagram, Fig. 7, was obtained by calculating the maximum shear stress applied to each specimen based on the maximum applied load at fracture. Also included in the figure are two calculated curves that would represent the maximum applied shear stress of specimens that failed in flexure with actual material flexural strengths (σ_o) of 689 MPa and 550 MPa.

The same specimen data used in Fig. 7 are replotted in Fig. 8; however, in this case flexural strengths were calculated and plotted as (L/h). Again, calculated lines are included for specimens failing by flexure at 689 MPa and 550 MPa. In addition, the line for a specimen failing by shear at a level of 16.2 MPa was plotted. This shear strength is equal to the average value of shear stress calculated for L/h = 10 from Fig. 7.

Although the data do exhibit the trends expected, it is also clear that the scatter in data is very significant. Additional testing during the later phases of this program will provide additional data; however, the practice in this program of testing specimens for flexural strengths at (L/h) values above 30 in general is amply justified.

Oxidation Studies

The investigation of the resistance to oxidation of various graphite fiber reinforced glass matrix composites was carried out by heating samples prepared for flexural testing to the test temperature in air. The temperature was controlled within $\pm$ 5 K at temperatures of 723, 813 and 833 K for times of 4 hrs, 24 hrs, and 100 hrs. At the end of these exposures the flexural strength of the sample was measured at room temperature.

Thermal Expansion

The thermal expansion of the composite specimen was measured using a Dilatronic III High Resolution dilatometer purchased from Theta Industries Inc. of Port Washington, New York. In this instrument the change in length of the specimen is measured in reference to an NBS fused silica standard (SRM #739).

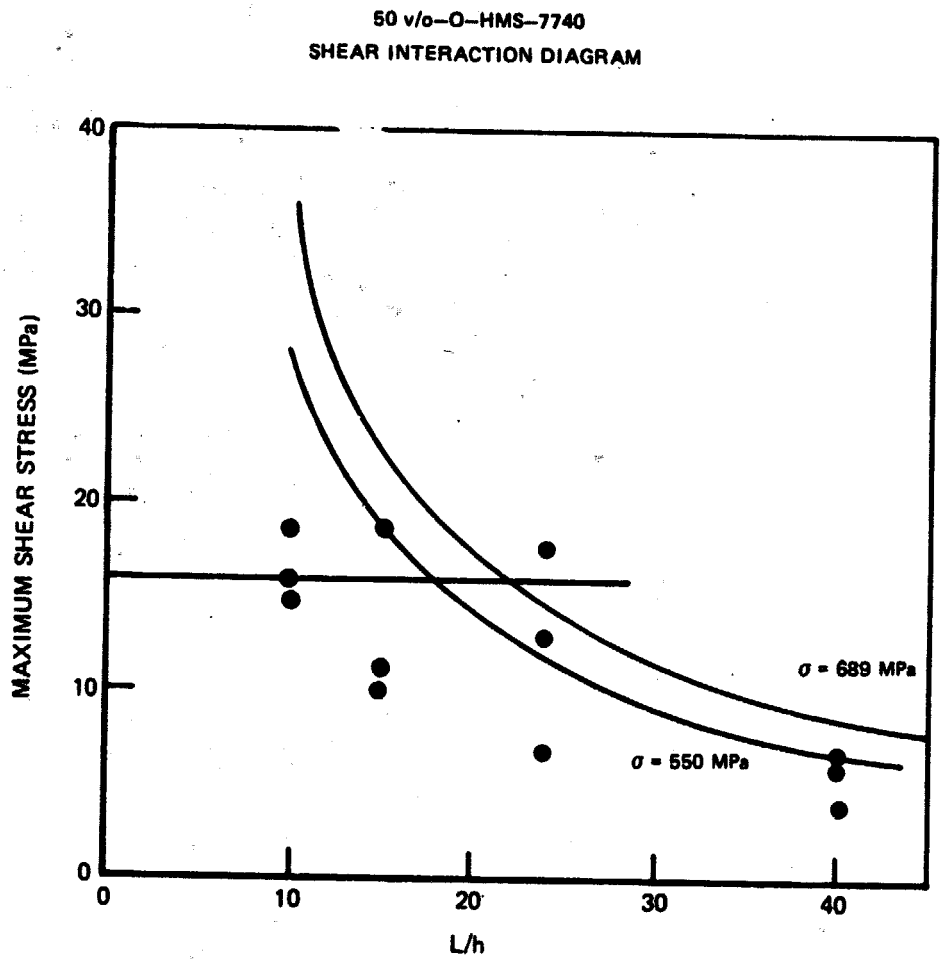

Figure 7. Calculated Values of Maximum Applied Shear Stress at Failure for Three Point Bend Testing as a Function of Specimen Span (L) to Depth (h) Ratio

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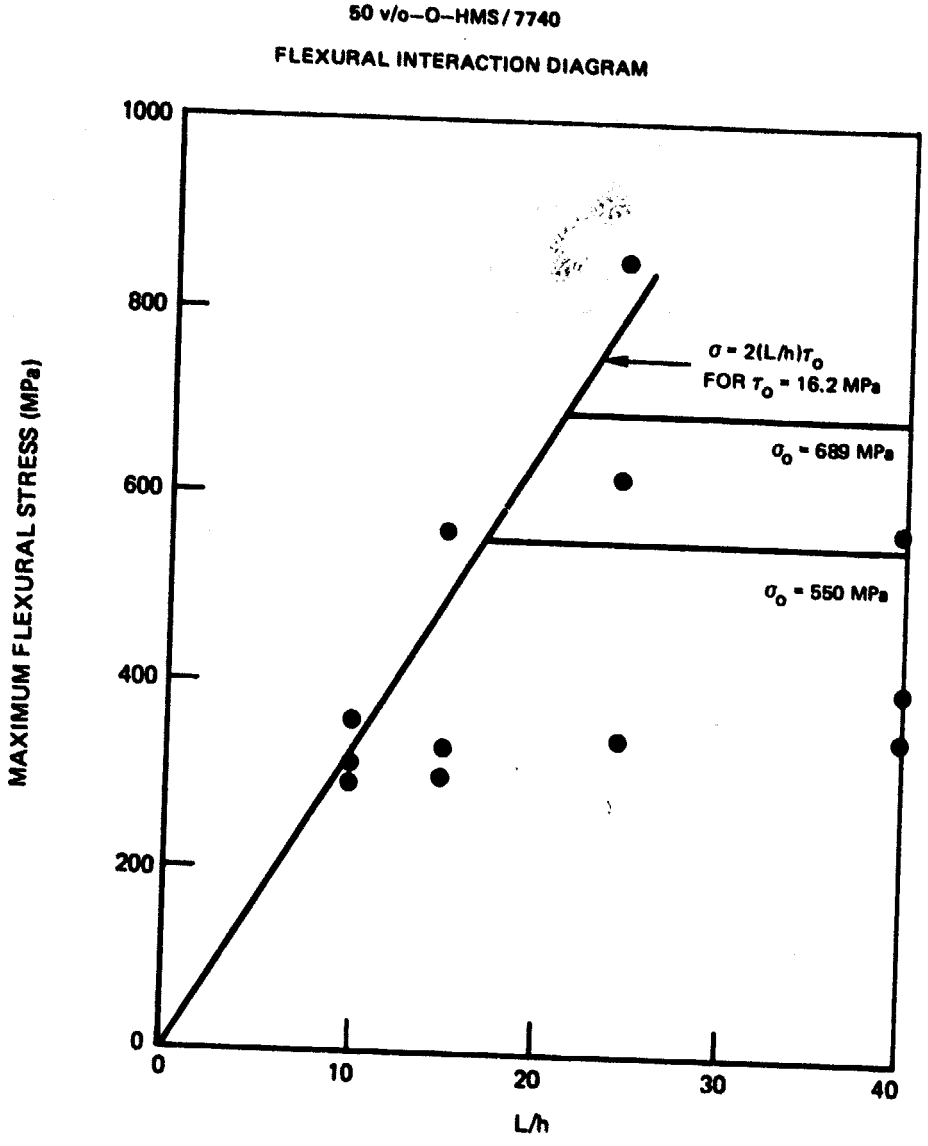


Figure 8. Calculated Values of Maximum Applied Flexural Stress at Failure for Three Point Bend Testing as a Function of Specimen Span (L) to Depth (h) Ratio

77-11-221-2

The absolute expansion is determined by correcting the measured curve for the expansion of the standard and for the expansion of the specimen holder if the sample and standard are not the same length. The change in length is referred to the initial length of the specimen at 293 K.

Exposure to Sea Salt

To simulate exposure to spray with sea water and sea air damage it was necessary to improvise since UTRC does not at this time possess a standard salt spray controlled humidity cabinet. This was done by painting standard flexural test specimens with a solution containing six times the normal concentration of sea salt, drying, repainting to give a total of eight coats of sea salt. The coated flexural specimen was then sealed in a silica tube in an argon atmosphere and thermally cycled from 383 to 833 K for 100 cycles at the rate of 1 cycle every eight minutes.

Cycling Under Flexural Load

Cycling under a flexural load which drops to 1/20th of the assessed strength of the sample and rises to 8/10ths of this load was carried out under a four-point bend mode.

Instrumented Impact

A Charpy test is an impact failure conducted in three-point bending. This test is a measure of the toughness of a material at moderate impact velocities (up to 3.6 meters/sec). While the value of the energy required for fracture is dependent on the size of the specimen, and therefore is not an intrinsic material value, the tests are useful for comparative purposes. The instrumented Charpy test in particular has been a valuable asset for the comparison of material toughness and for illustration of the fracture modes under dynamic conditions. The impact machine is instrumented with strain gages so a record can be made of the force as a function of time.

Thermal Cycling

Premachined flexural test specimens were cycled between 383 and 833 K while encapsulated in glass tubes containing argon. The use of an inert atmosphere permitted the exclusion of any effects due to specimen oxidation.

RESULTS AND DISCUSSION

In the appendices are tabulated specific data that are not needed for an understanding of the results obtained in this study. In Appendix A, a summary listing of the graphite fiber reinforced glass matrix composites is given. In Appendix B, data which are mainly represented in the report by figures are tabulated. A paper based on this sponsored research entitled "Glass Matrix Composites I - Graphite Reinforced Glass" and authored by K. M. Prewo and J. F. Bacon was presented at the Second International Conference on Composite Materials (Ref. 14).

Digest of First Year's Research

Since an annual report has been issued (Ref. 13) detailing the first year's research on graphite fiber reinforced glass matrix composites, this section of the report contains only those results which serve to characterize results of these composites which were not repeated in the second year's research.

Strength, Distribution of Strength, High Temperature Strength

Strengths as high as 977 MPa or 142 ksi (Appendix B - Table 1) had been achieved by the end of the first year with HMS graphite fiber reinforced 7740 glass matrix composites made with slurry A using the old press at 1273 K and 13.8 MPa. More usually, composites made with HMS graphite fiber and 7740 glass matrix under the same conditions would have an average strength of 689 MPa or 99.98 ksi (Appendix B, Table 1). Such composites showed a very narrow strength distribution as shown in the probability paper plot of Fig. 9 and tabulated in Appendix B, Table 1. These HMS graphite fiber reinforced 7740 glass matrix composites can be used to temperatures of 873 K. The slurry A data of Fig. 10 and Table 2, Appendix B, demonstrate that a typical HMS fiber-7740 glass composite has an average strength of 825 MPa (120 ksi) at room temperature and increases in strength to 1213 MPa (175 ksi) at 873 K when studied by means of three point bend tests, and only at 973 K does the specimen deform excessively. A similar increase in strength with temperature is shown for slurry A composites of Celanese DG-102 graphite fiber reinforced C.G.W. 7740 glass matrix composites (Table 3, Appendix B). These Celanese DG-102 graphite fiber 7740 composites start out lower in strength, however, and never approach the level of the HMS graphite fiber reinforced composites.

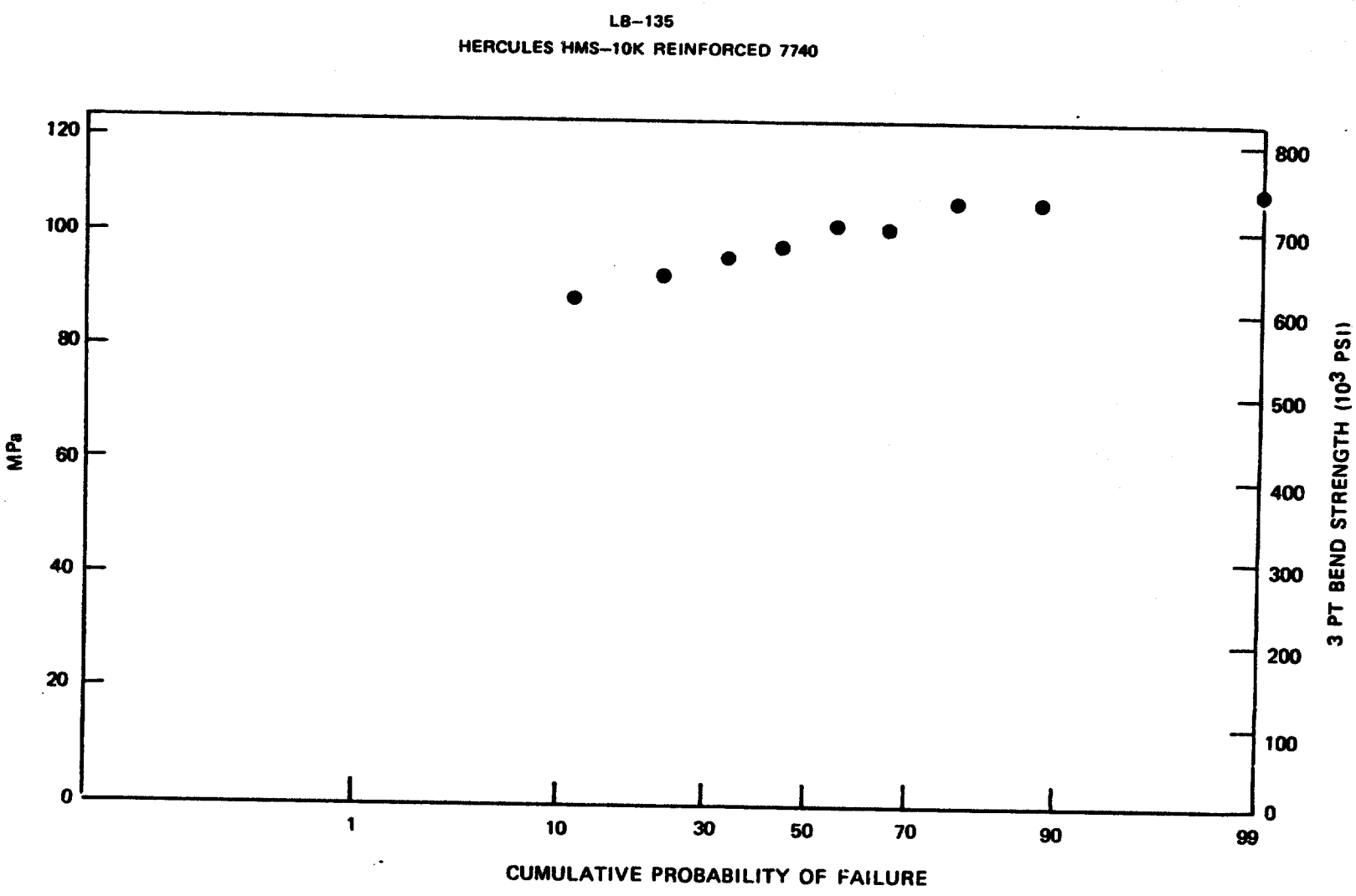


Figure 9. Three Point Bend Strength of Specimen Tested at 295 K , Slurry A

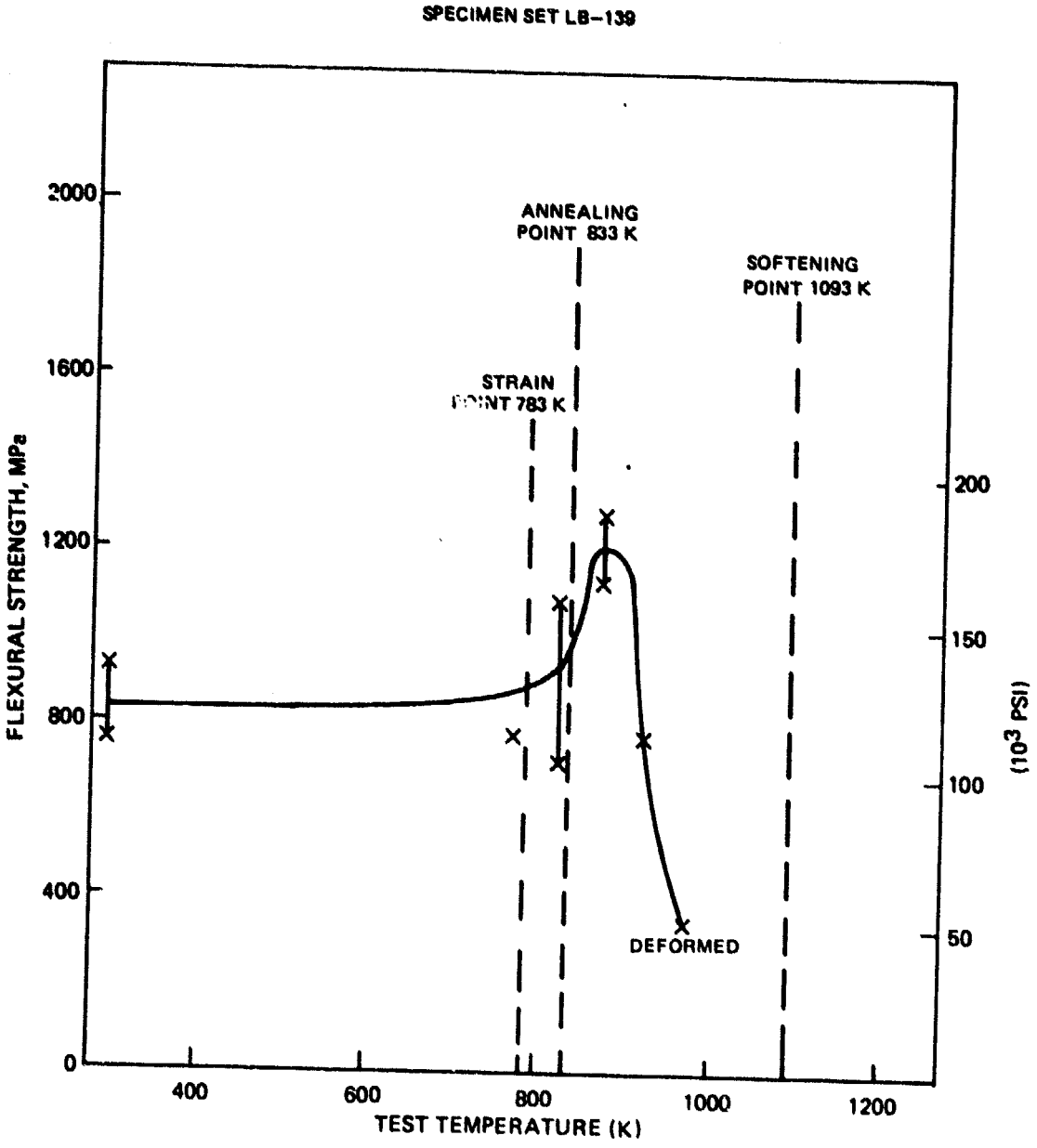


Figure 10. Flexural Strength of Hercules HMS – 10 K Fiber Reinforced 7740 Glass as a Function of Test Temperature, Slurry A

76-10-147-1

The manner in which these HMS graphite fiber reinforced C.G.W. 7740 glass matrix composites fail is shown by the four-point flexural test data of Fig. 11. Again these composites were made with slurry A, old press, temperature 1273 K and pressure of 13.8 MPa. Both totally linear and combined linear-nonlinear deflections are shown; however, in all cases specimens did not fracture completely but instead cracks were diverted in the interior of the specimen so that failed specimens remained visibly intact after test.

Comparison of Graphite Fiber Reinforced Glass Matrices with Other Composites

Three-point bend data for the Hercules HMS graphite fiber reinforced C.G.W. 7740 glass matrix composites have been compared with graphite fiber reinforced thermoplastics, graphite fiber reinforced aluminum, and BORSIC* fiber reinforced titanium alloy.

The data used to compare graphite reinforced thermoplastics with HMS graphite fiber reinforced C.G.W. 7740 glass matrix composites (slurry A) are shown in Fig. 12 and were obtained from a NASA-sponsored program at UTRC**. The fiber is the same Hercules HMS fiber used in this program and if one compares Figs. 12 and 10 it can be seen that the resin matrix composite maximum flexural strength at room temperature is approximately equal to the strength of the HMS-7740 composite at 873 K although greater at room temperature. The comparison also shows that the rate of strength decrease in the vicinity of the resin glass transition temperature is rapid and similar to that for the glass matrix composite above 923 K.

To compare the flexural strength of graphite reinforced glass matrix composites (slurry A) with that of graphite fiber reinforced aluminum, the recently published data of W. Harrigan of Aerospace Corporation shown in Fig. 13 was used. Again in comparing these data which are for wire and plates with the data of Fig. 10 for the HMS graphite fiber reinforced C.G.W. 7740 glass, it can be seen that the glass matrix composite is equal or superior to the aluminum matrix composite over the entire test temperature. As Fig. 13 also shows on a specific property basis, the glass matrix composite offers an additional advantage. The specific strength comparison of the graphite fiber reinforced aluminum with the HMS graphite fiber C.G.W. 7740 matrix specimen is shown in Fig. 14. The maximum use temperature of the glass matrix composite is significantly higher than that of the graphite aluminum.

*Trademark, United Technologies Corporation

**R. C. Novak, Graphite Fiber Reinforced Thermoplastic Resins, NAS3-20077, CR-135196, 1976.

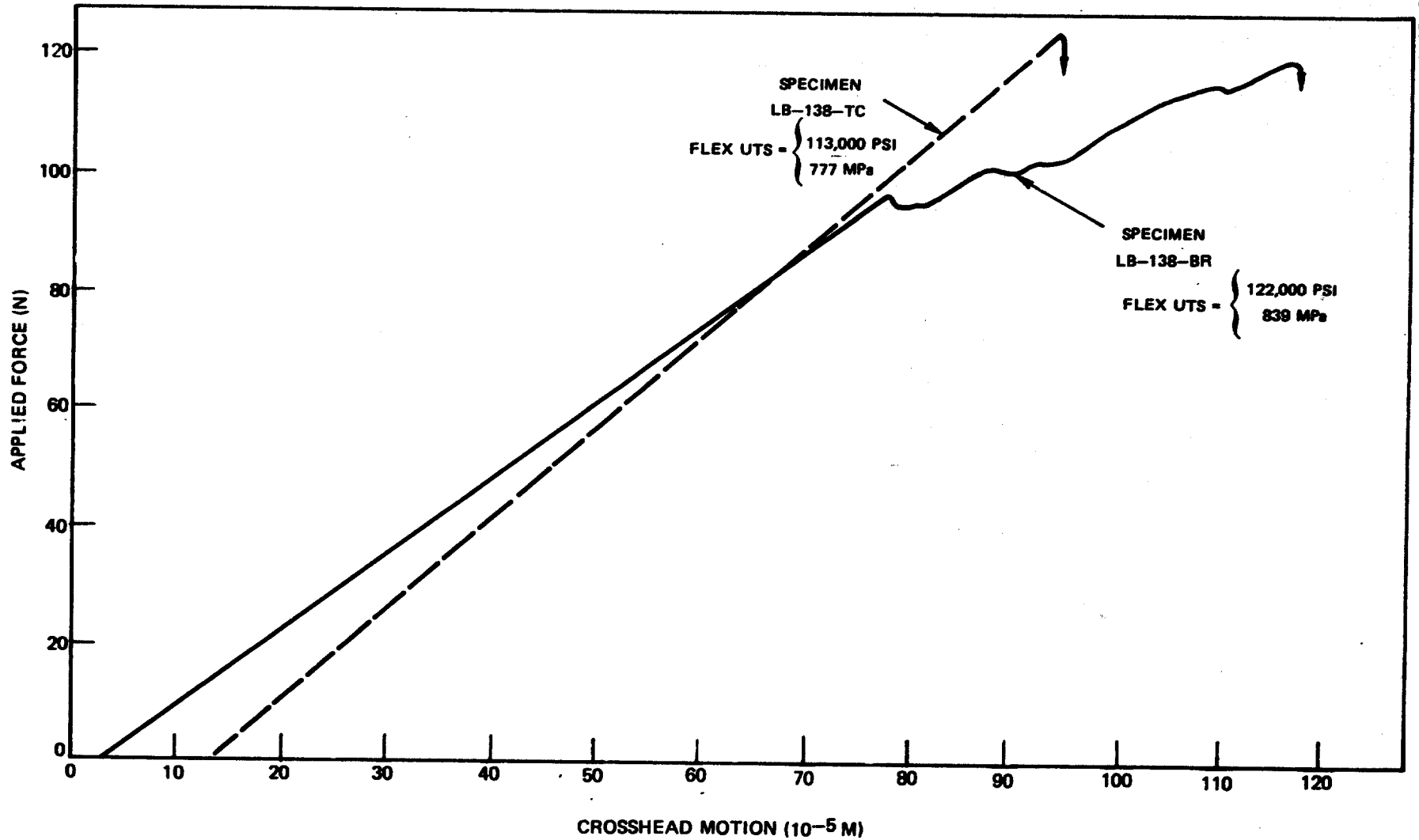
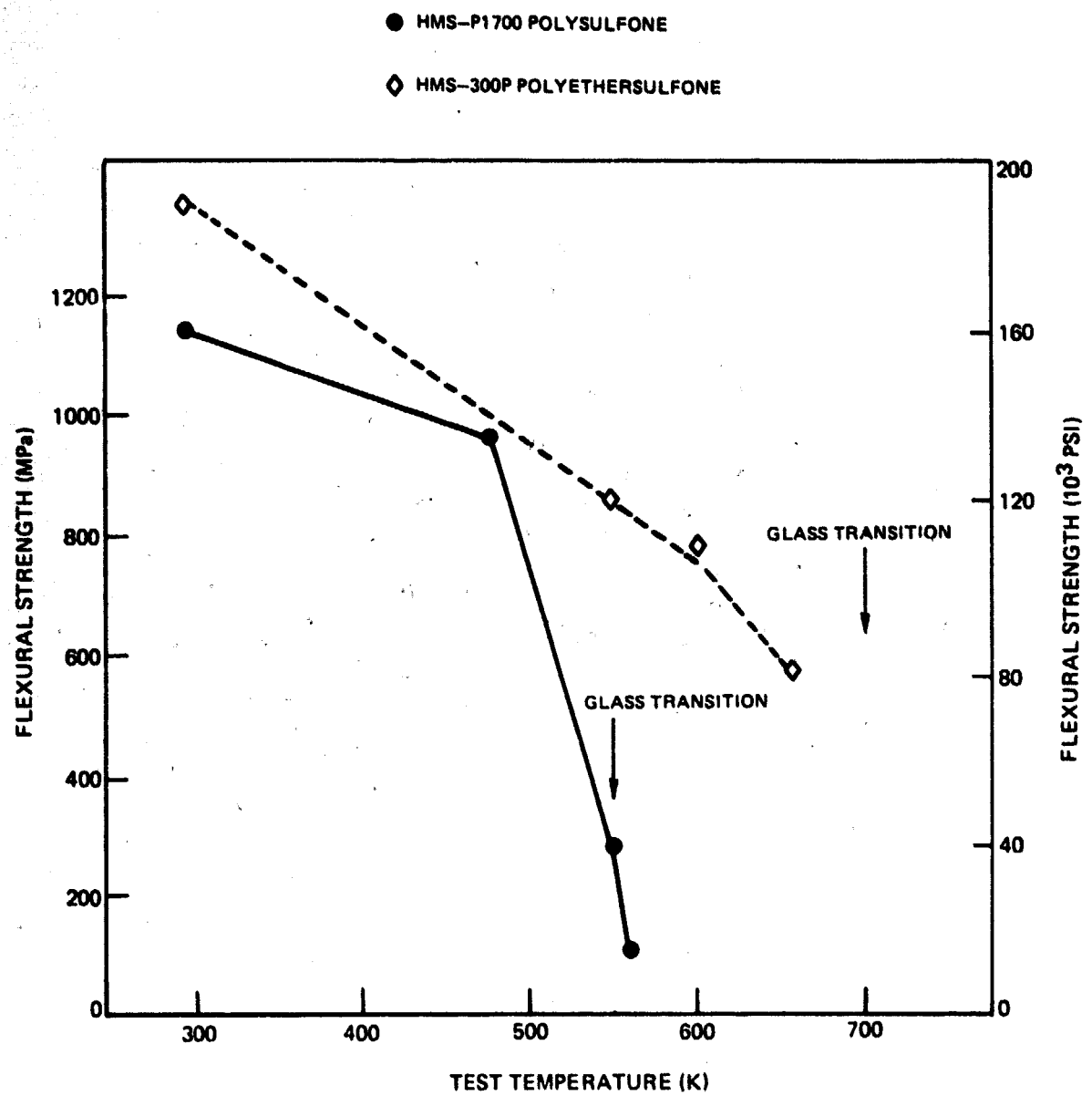


Figure 11. Load – Deflection Traces for the 4 – Pt. Bend Tests on Hercules HMS – 10 K Reinforced 7740, Slurry A



* UTRC CONTRACT NAS3–20077, 1976

Figure 12. Flexural Strength of Hercules HMS – 10 K Fiber Reinforced Thermoplastics as a Function of Test Temperature *

76–11–107–5

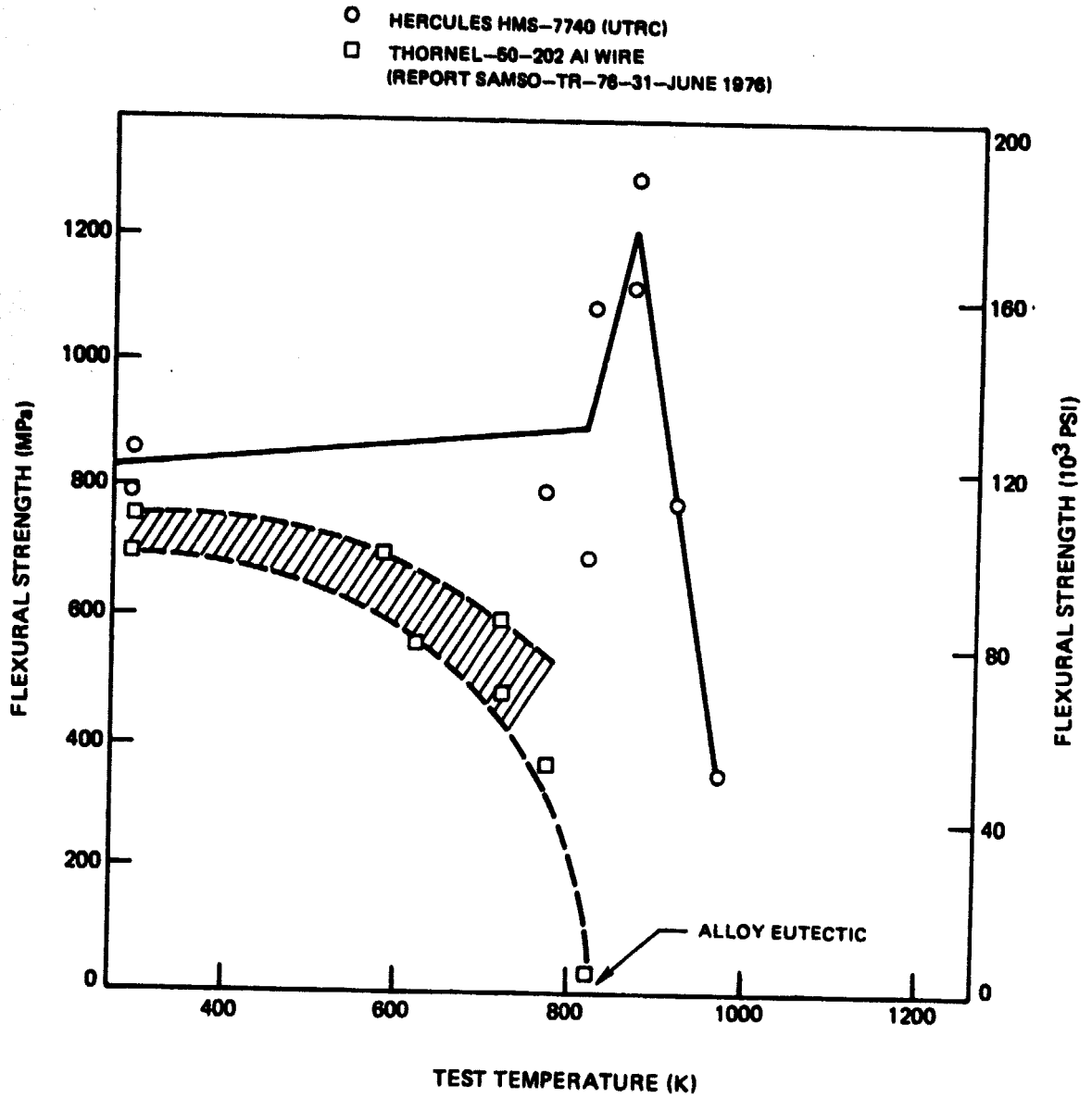


Figure 13. Flexural Strength Comparison

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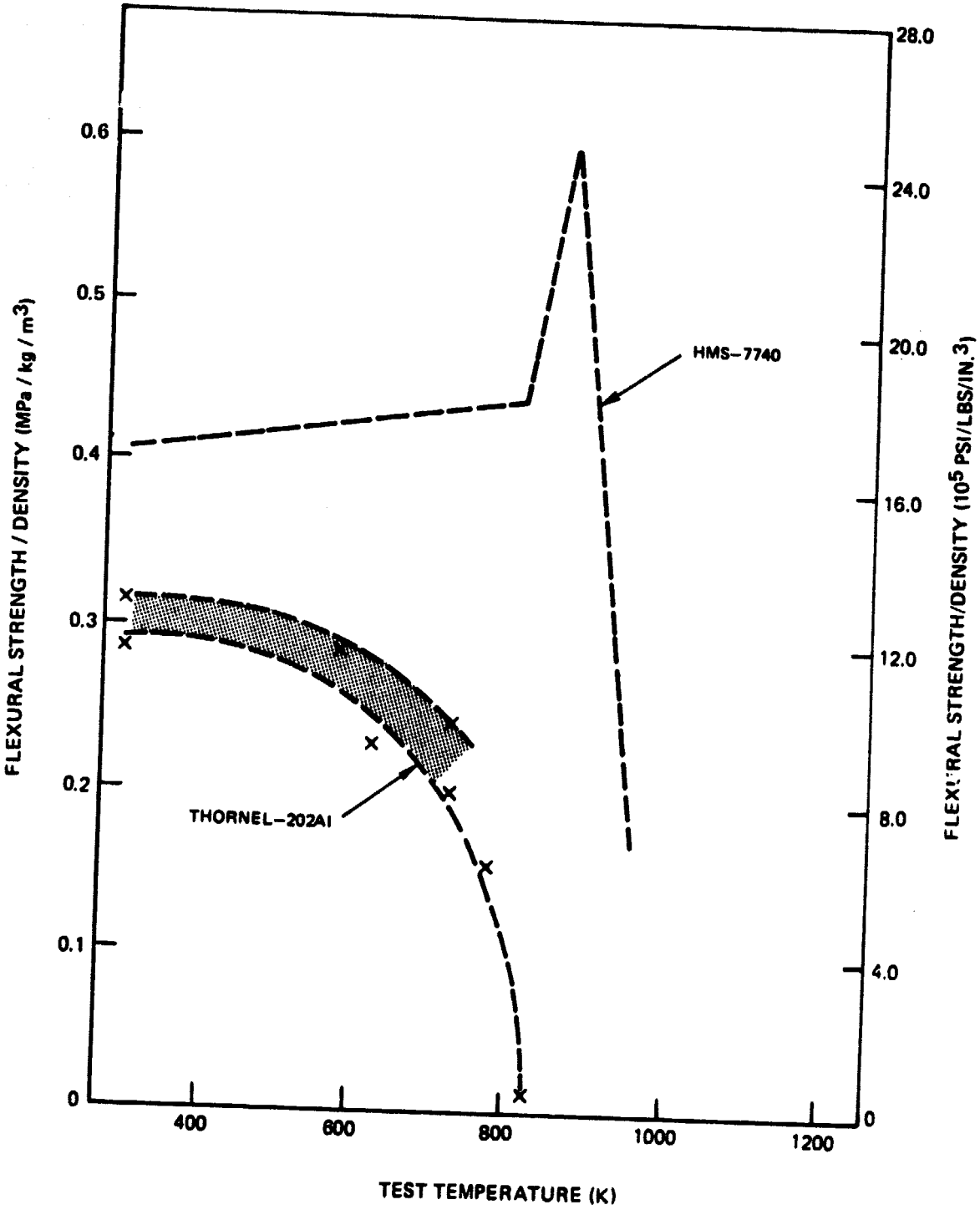

Figure 14. Specific Flexural Strength Comparison

76-11-107-7

The only metal matrix composite with a possible use temperature in the range of room temperature to 773 K (excluding the much higher density, reinforced super alloys) is Borsic fiber reinforced Ti-6Al-4V. It is important, therefore, to compare the HMS graphite fiber reinforced C.G.W. 7740 matrix, slurry A, with this titanium alloy system at temperatures above 573 K. The data are shown in Fig. 15. Unfortunately, the flexural data over the temperature range of interest are not available for the titanium alloy so that Borsic-Ti tensile data are used. To provide a more realistic comparison the Borsic-Ti tensile strengths were multiplied by a factor of 1.4, a factor experimentally determined at UTRC for the ratio of flexural strength to tensile strength at room temperature for the Borsic-Ti composite. In addition, the data were divided by composite density to obtain the specific flexural strength comparison shown in Fig. 16. At temperatures above 423 K the glass matrix composite is clearly superior to the titanium matrix composite.

The elastic modulus for HMS graphite fiber reinforced 7740 glass slurry A is compared with values of E_{11} characteristic of other composite systems in Table VI. The higher value for the glass matrix composite stands out.

Comparison of 3 Point and 4 Point Flexural Data for Graphite Fiber Glass Matrix Systems

The nature of the flexural strength test, i.e. whether it is a three-point or a four-point flexural strength test might be expected to affect the validity of a flexural-strength test for screening composite progress, but as Table VII shows, there is a definite relationship between the two tests.

Fracture Toughness Characteristics of HMS Fiber Reinforced 7740 Glass Matrix

Notched three-point bend systems were fabricated and tested in an attempt to characterize the fracture toughness of the HMS-7740 system. The specimen geometry is given in Fig. 17 and specimen dimensions with resultant data in Table VIII. As may be seen from the data of Table VIII, the fracture toughness does decrease with increasing temperature in a manner opposite to the variation in strength with temperature. It will be noted, however, that even the values obtained at the higher temperatures are favorable when compared to other composites and more conventional engineering alloys, Table IX.

Cyclic Testing of HMS Fiber Reinforced 7740 Glass Matrices

As in all the tests described to date, cyclic testing was carried out using uniaxial specimens of HMS fiber reinforced 7740 glass matrix composites. The thermal cycle interval was 8 min and 20 sec as shown in Fig. 18 and as may be seen from Fig. 19 and Table 4 of Appendix B the flexural strength of the HMS

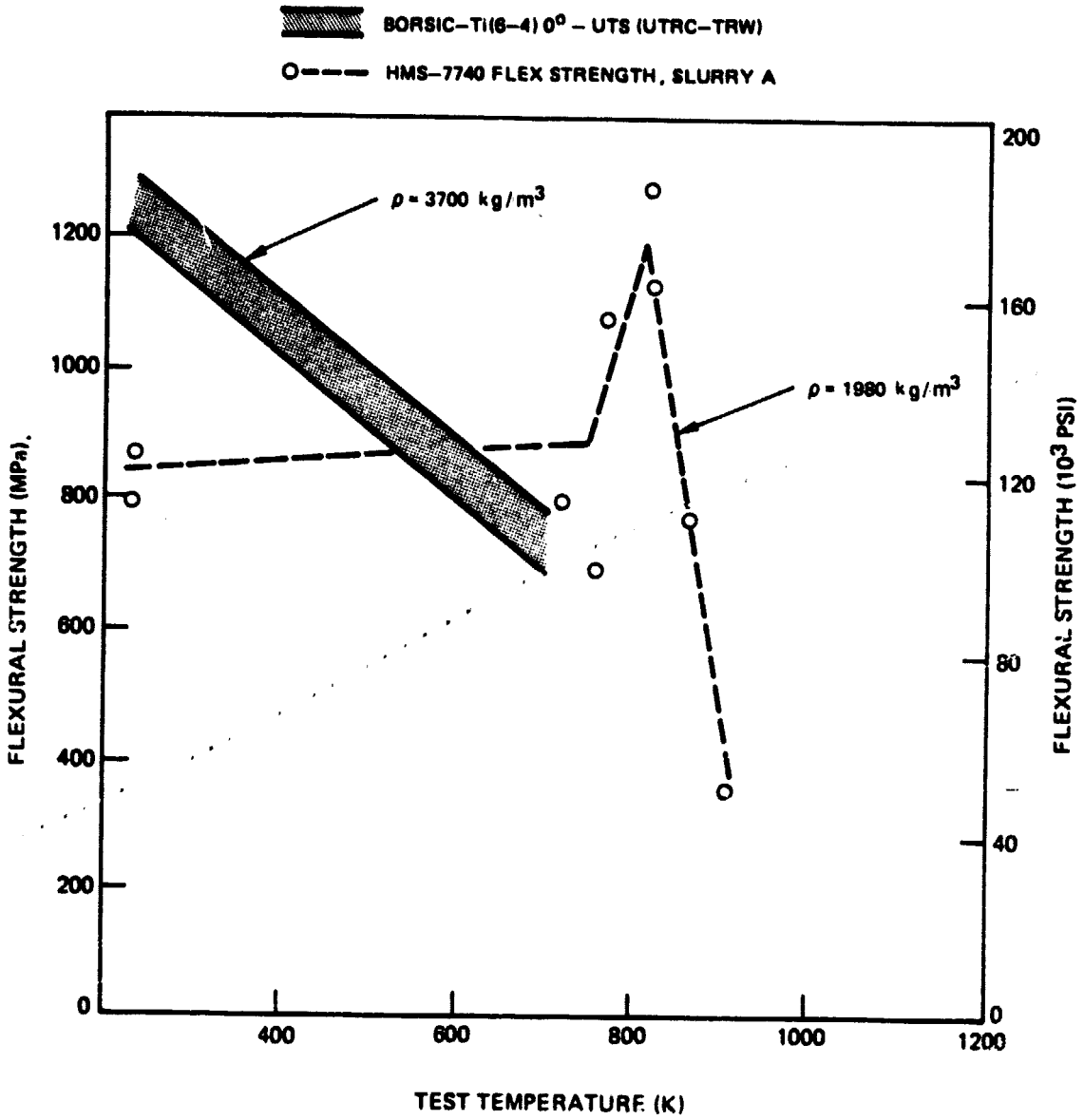

Figure 15. Flexural Strength Comparison

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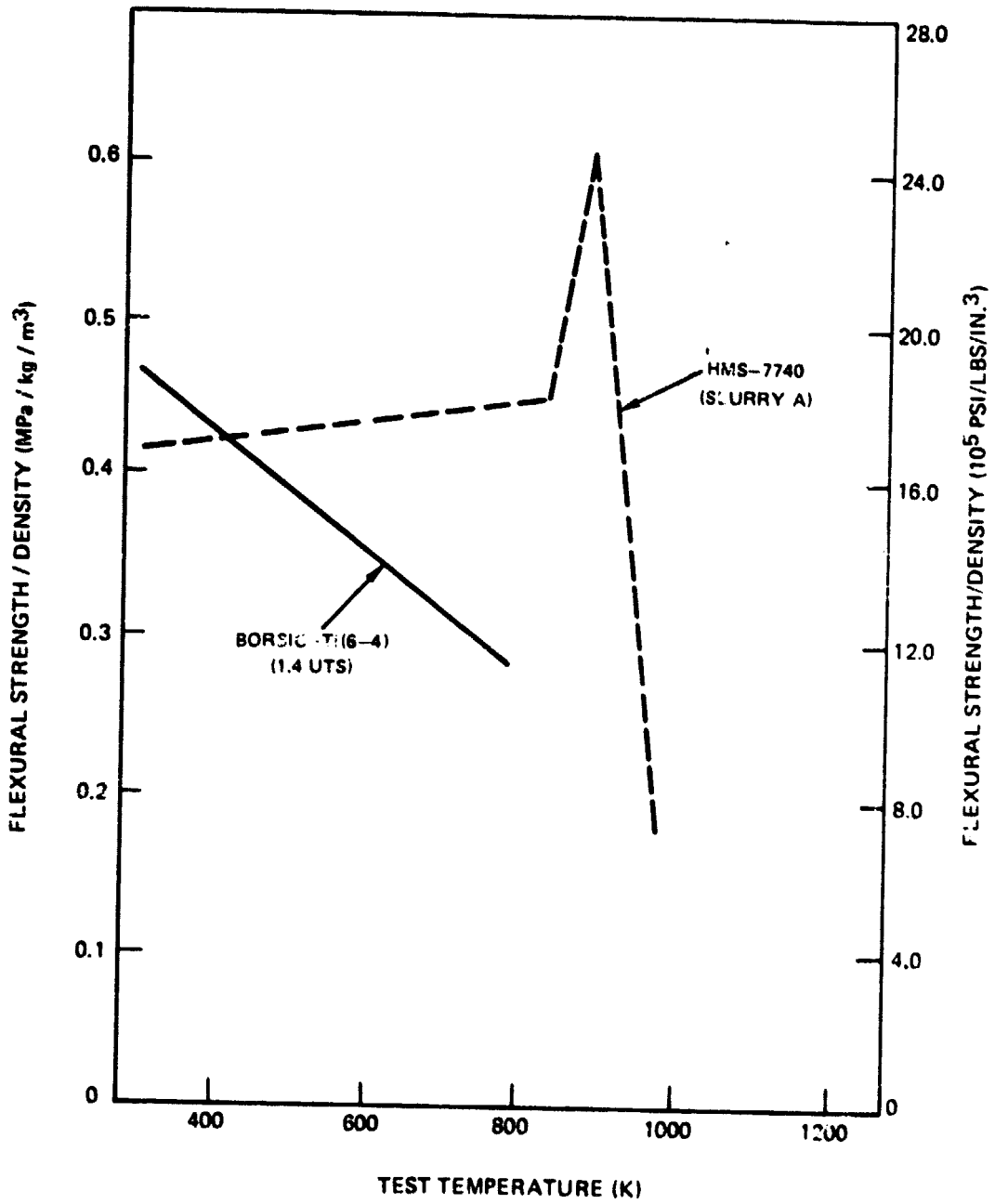


Figure 16. Specific Flexural Strength Comparison

Table VI

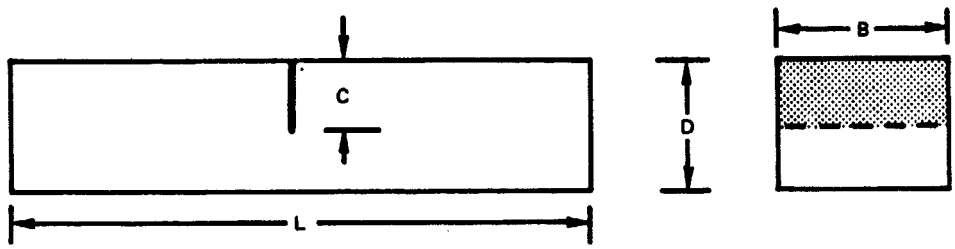
Room Temperature Elastic Modulus Comparison

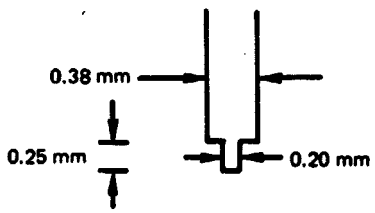
System with Calculated Fiber Contents	Density ρ (kg/m^3)	Density ρ (lb/in^3)	Elastic Modulus E GPa	Elastic Modulus E 10^6 psi	E_{11}/ρ ($GPa/kg/m^3$)
50 v/o Celanese DG-102-7740	2020	0.072	296	43	0.146
50 v/o HMS-7740	1980	0.071	193	28	0.097
42 v/o T50-Al	2300	0.083	207	30	0.090
50 v/o B-Al	2700	0.097	227	33	0.084
43 v/o B-Ti	3700	0.133	234	34	0.063

Table VII

Comparison of 3-Point Bend and 4-Point Bend Test Data for Several Graphite Fiber-Glass Composites Slurry A

Sample		3-Point Flexural Strength MPa	3-Point Flexural Strength psi	Strain Gaged 4-Point Flexural Strength MPa	Strain Gaged 4-Point Flexural Strength psi
LB 136 - 3 tests	HMS/ 7740	648	94 000		
- 6 tests				517	75 000
LB 135F - 9 tests	HMS/ 7740	977	142 000		
LB 135G - 9 tests				848	127 300
LB 97 - 9 tests	DG-102/ 7740	342	49 600		
LB 97D - 9 tests				309	44 800





NOTCH TIP CONFIGURATION

Figure 17. Fracture Toughness Specimen

76-11-107-3

Table VIII

Fracture Toughness Specimen Dimensions
Slurry A

Specimen	C (cm)	B (cm)	D (cm)	Test Span cm	L cm
LB-140-1	0.330	0.990	0.691	3.98	5.0
-2	0.305	0.990	0.691	3.80	5.0
LB-157-1	0.330	0.954	0.852	3.98	5.0
-2	0.330	0.954	0.852	3.98	5.0

Specimen Test Data
Slurry A

Specimen	Test Speed (cm/min)	Test Temp K	K_c $MN/m^{3/2}$	K_c 10^3 psi$\sqrt{in}$	Energy Per Unit Area Joules/m^2	Energy Per Unit Area ft-lbs/in^2
LB-140-1	20 000	295	21.4	19.5	23 500	11.3
-2	0.127	295	22.1	20.1		-
LB-157-1	20 000	873	15.8	14.3	10 600	5.1
-2	20 000	923	19.0	17.3	11 800	5.7

Table IX

Fracture Toughness Comparison at 295 K

Material	K_{IC} $MN/m^{3/2}$	K_{IC} 10^3 psi $\sqrt{in}$
0^o-HMS/7740, Slurry A	21.7	19.8
0/90-AS Graphite/AR 288*	14.25-1.973	13-18
Morganite II/Epoxy**		
0^o	35	32
90^o	1.75	1.6
45^o	2.52	2.3
$\pm 45^o$	19.73	18
$0/\pm 45^o/90$	24.1	22
2014-T6 Aluminum Alloy***	21.92	20
6061-T651 Aluminum Alloy***	29.6	27

*UTRC data using compact tension specimens
**H. Konish and T. Cruse, J. Comp. Materials, Vol. 6, p 114, 1972
***Damage Tolerant Design Handbook MCIC-HB-01

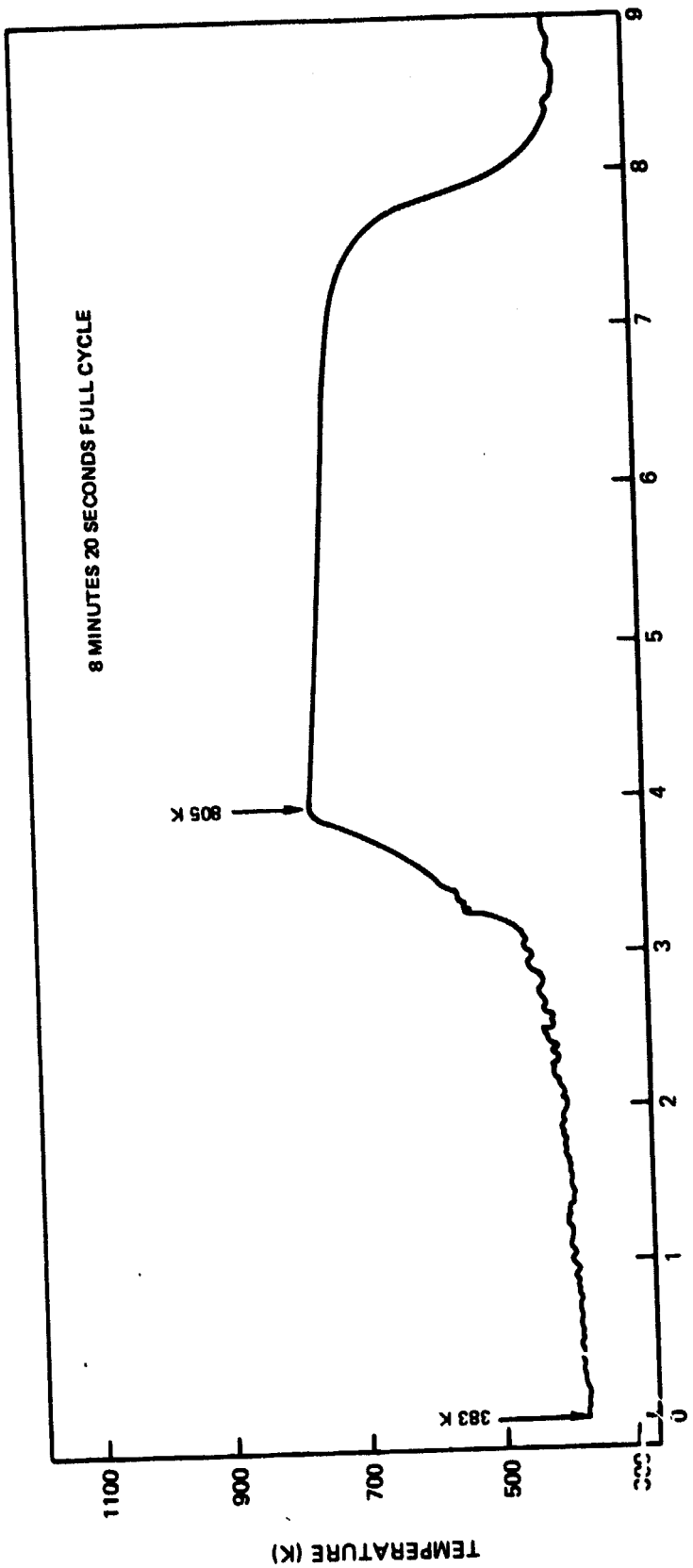


Figure 18. Temperature Cycle

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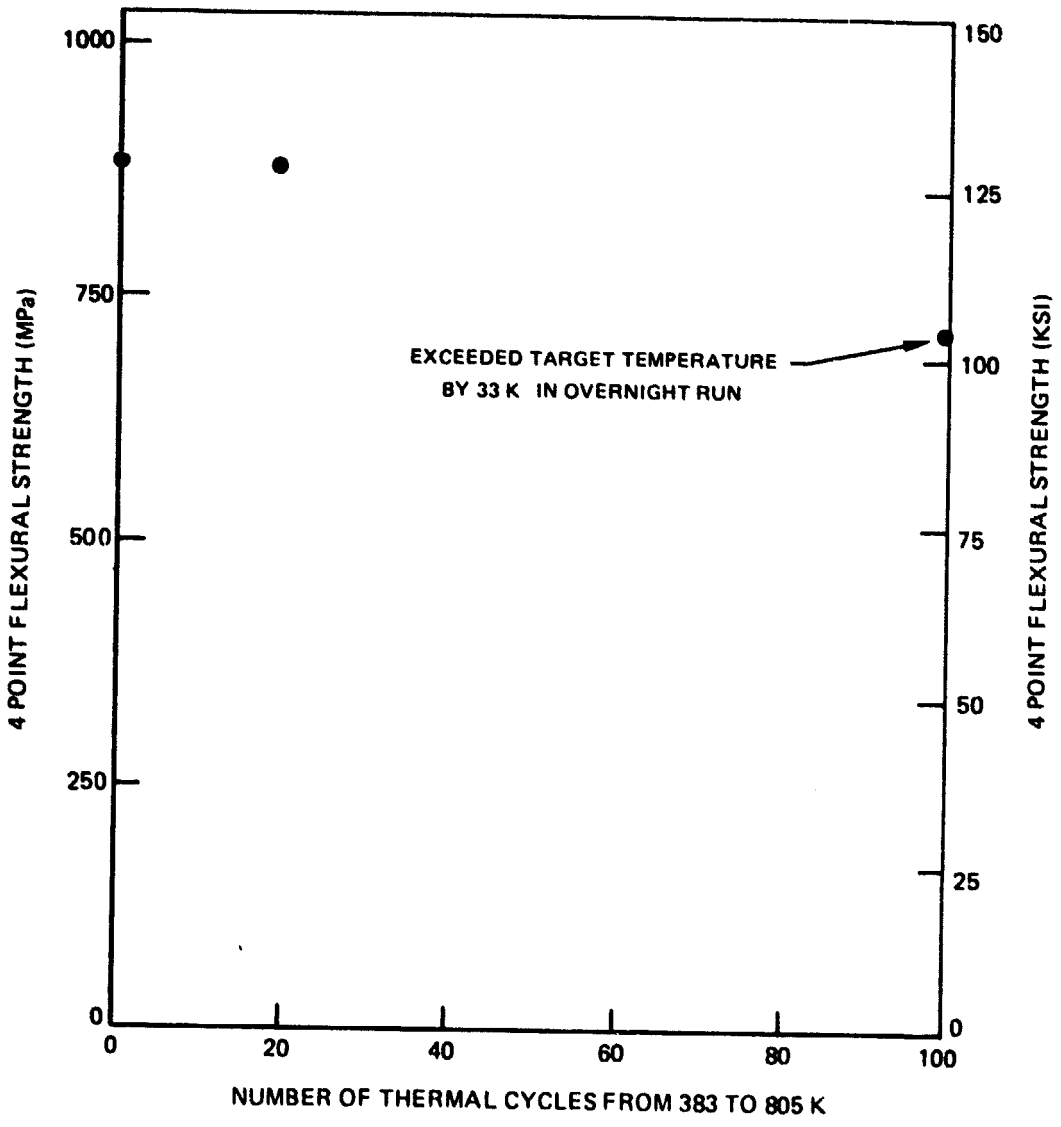

Figure 19. Flexural Strength of HMS – 7740 Glass Composite After Thermal Cycling, Slurry A

77-05-150-4

graphite reinforced 7740 glass matrix composite was unaffected by a hundred such cycles. Similarly, 100 cycles of flexural fatigue between 0.8 and 0.08 of the as-fabricated four-point bend strength left the graphite fiber glass matrix composite unaffected. Again, painting the composite specimens with six times normal sea salt concentration and thermally cycling the samples between temperatures of 383 and 833 K (encapsulated in silica tubes) left the composites unaffected.

Discussion of Recent Advances

The progress made since the last annual report is summarized below. Processing effects on the microstructural characteristics and flexural strength properties, the shear, transverse, and cross-ply strengths, the thermal expansion response and the oxidation characteristics of these composites are topics that will be discussed in turn.

Processing Effects

A positive effect of very high temperature hot pressing on the flexural properties of graphite fiber reinforced 7740 containing Ludox (slurry C) has been discovered as will be described below. In order to make a qualitative assessment of the graphite-glass composites, a comparison of the microstructures of HMS graphite fiber reinforced 7740 pressed, slurry B, at 1473 K and the Ludox containing 7740 pressed at 1723 K, slurry C, can be made by considering Figs. 20-23. In both samples the glass is seen to surround each graphite fiber. The tape maps (Figs. 22,23) of the composites suggest that there is somewhat less memory of the tows in the slurry C composite pressed at 1723 K, more intimate contact of the adjacent tows and therefore fewer glass rich areas.

The three-point flexural properties of samples processed in a fashion similar to those represented in Figs. 20-23 are shown in Tables X and XI; these data are also represented in the cumulative failure probability plot of Fig. 24. Taking the data from the samples in each curve as belonging to a single population, the average strength and standard deviations are for the composites hot-pressed at 1473 K (no silica), slurry B, 785 $\pm$ 118 MPa and at 1723 K with silica addition, slurry C, 1023 $\pm$ 104 MPa.

Specimens of HMS graphite fiber reinforced 7740 + 2% SiO_2, slurry C, hot pressed at 1723 K (GC 326), have also been flexurally tested in four-point bending. The data for these tests are listed in Appendix B, Table 8. The stress-strain behavior of one of these specimens is displayed in Fig. 25. Its ultimate strength is 1105 MPa, its modulus is 217 GPa and its failure strain is 0.53%. Although the average failure strain of HMS graphite (0.0077) is not achieved in this test, 70% of this value is achieved which is especially significant and impressive for a brittle matrix-brittle fiber composite combination.

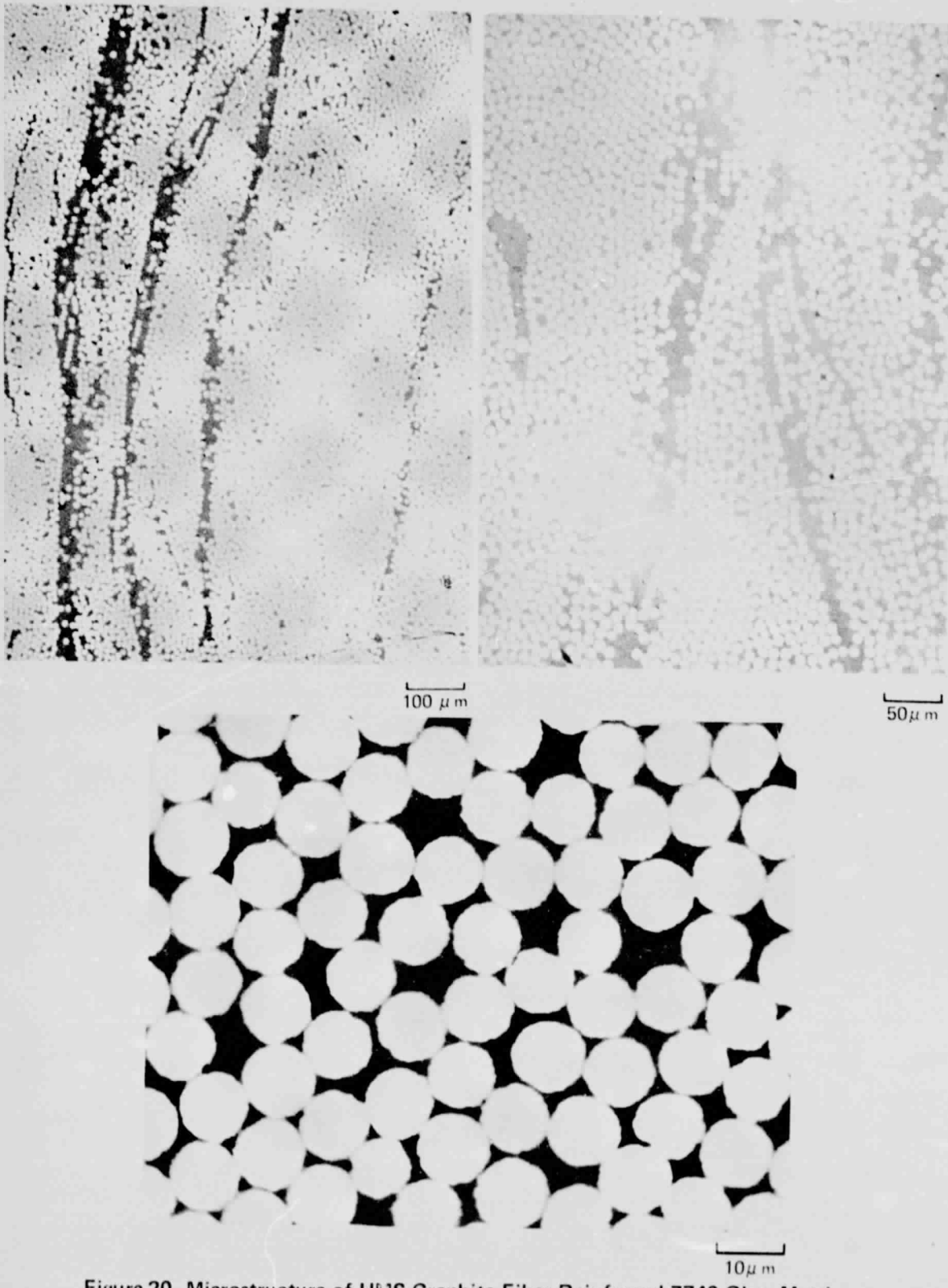

Figure 20. Microstructure of HMS Graphite Fiber Reinforced 7740 Glass Matrix (G.C. 281) Hot Pressed at 1473 K, Slurry B

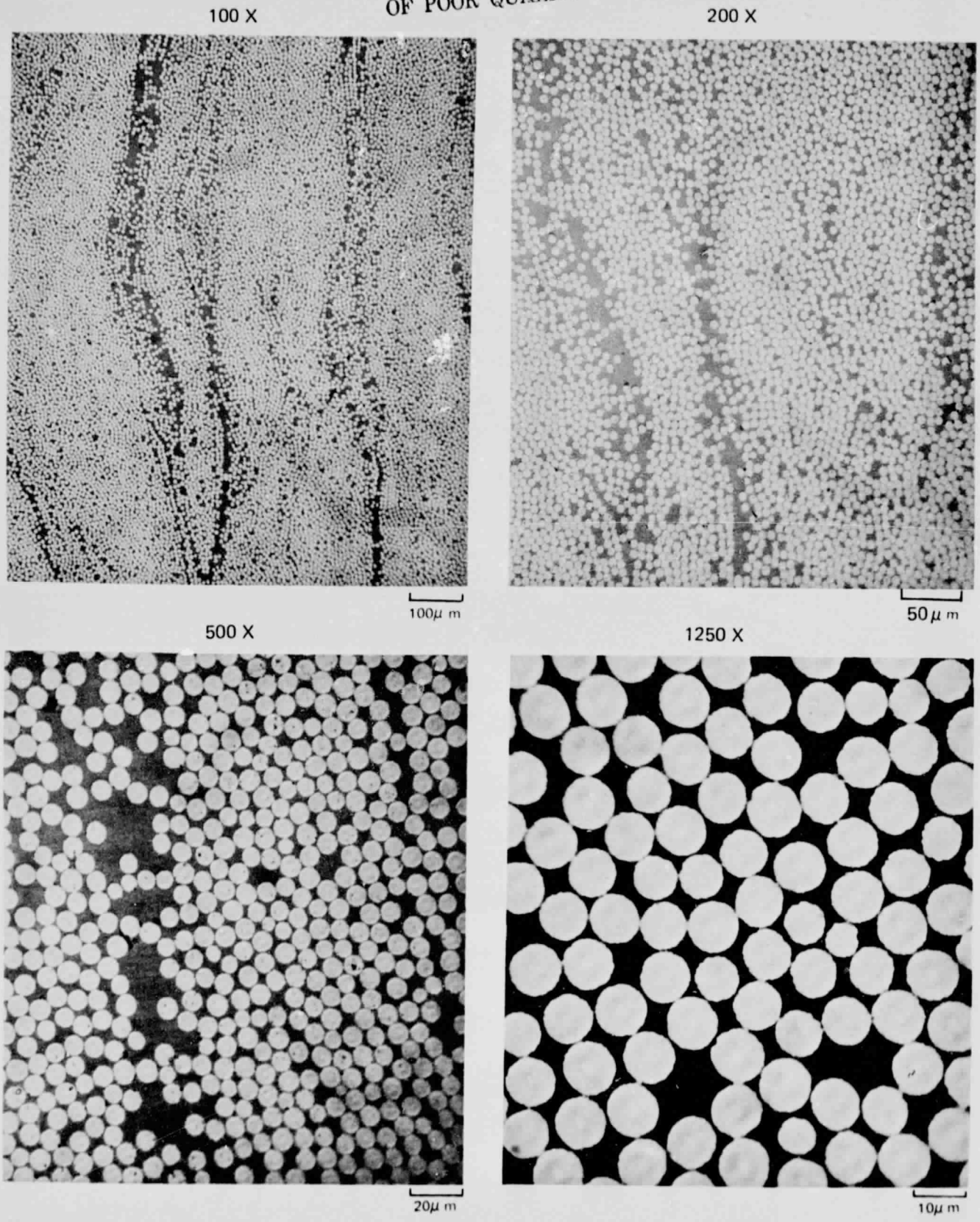

Figure 21. Microstructure of HMS Graphite Reinforced 7740 + 2% SiO_2 (GC 326) Hot Pressed at 1723 K, Slurry C

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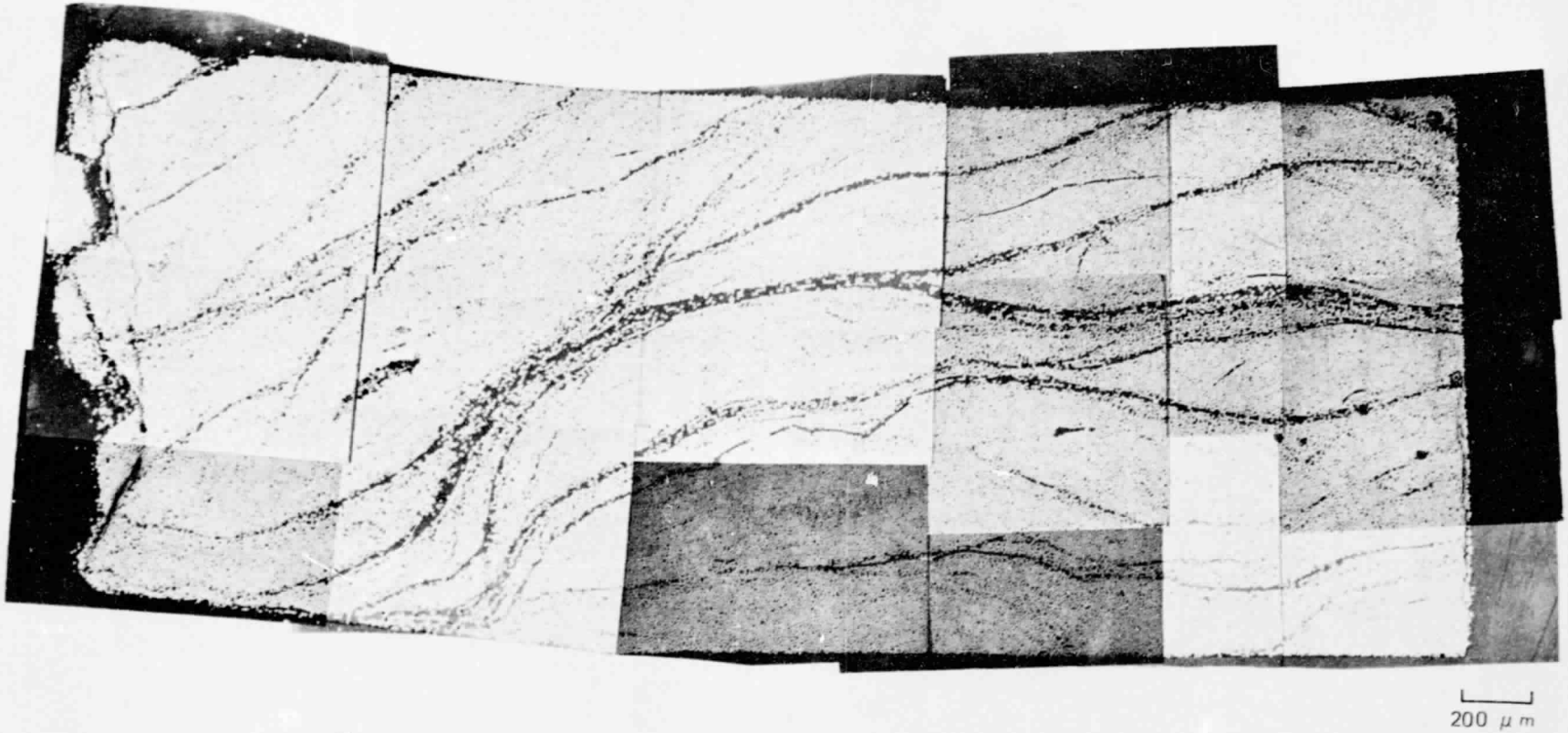

Figure 22. Tape Map of Cross Section of HMS Graphite Fiber Reinforced 7740 Glass Matrix (GC 281) Hot Pressed at 1473 K, Slurry B

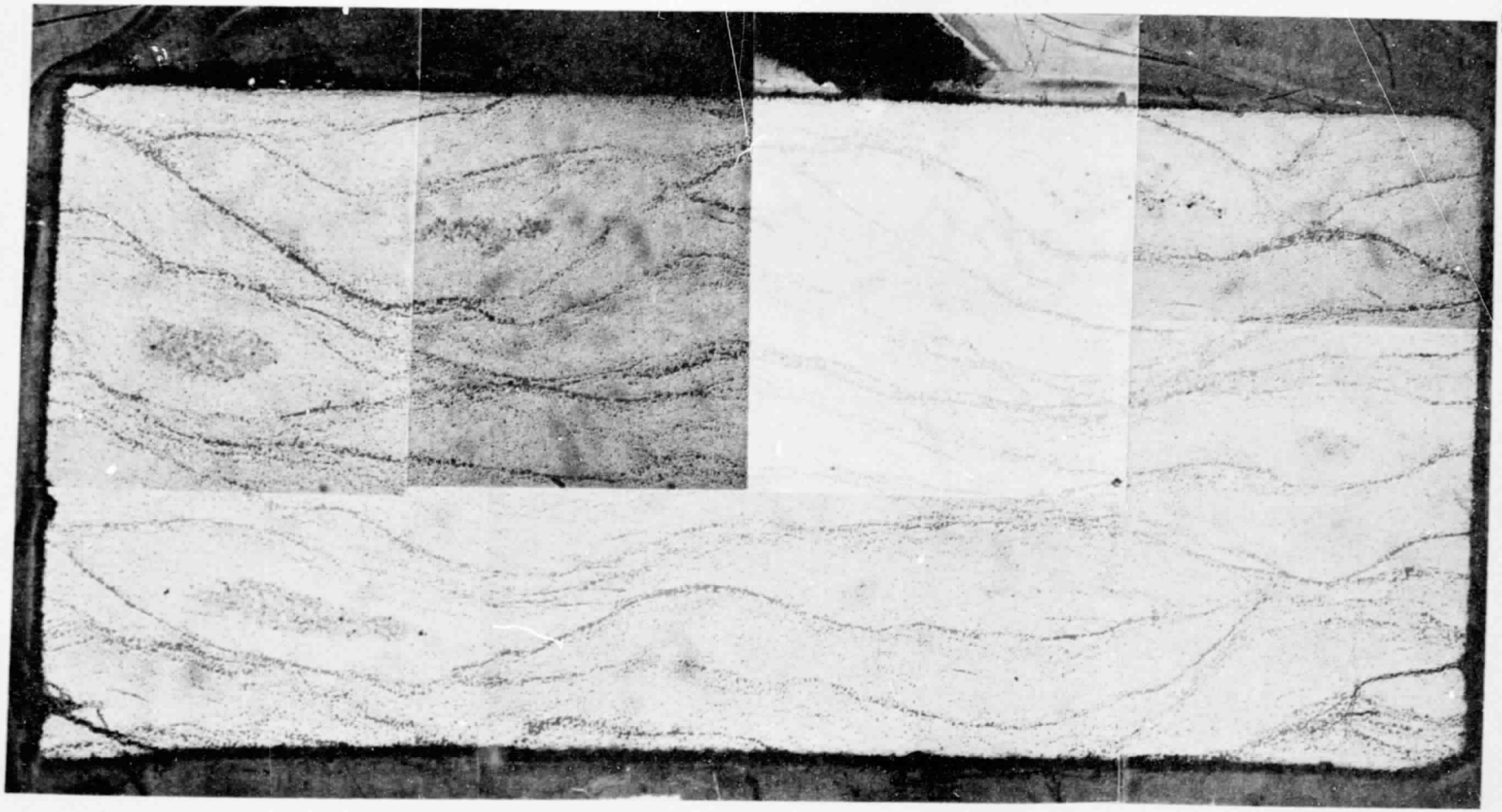

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Figure 23. Tape Map of Cross Section of HMS Graphite Reinforced 7740 + 2% SiO_2 Glass Matrix (GC326) Hot Pressed at 1723 K, Slurry A

Table X

Three Point Flexural Strengths for Several Samples of HMS Graphite Fiber Reinforced 7740 Glass Matrix (no silica), Hot Pressed at 1473 K, 13.8 MPa, Slurry B

	GC 281		GC 289 Top		GC 289 Middle		GC 289 Bottom	
	MPa	ksi	MPa	ksi	MPa	ksi	MPa	ksi
1	965	140	660	95.8	852	124	746	108
2	674	97.7	895	130	839	122	491	71.2
3	688	99.8	928	135	939	136	799	116
4	752	109	759	110	908	132	799	116
5	786	114	652	94.6	572	83.0	710	103
6	745	108	692	100	913	132	968	140
7	793	115	747	108	642	93.1	908	132
8	800	116	658	95.4	905	131	778	113
9	660	95.7	1030	149	680	98.6	774	112
10			757	110	879	127	841	123
Mean	765	111	779	113	814	118	779	113
Std. Dev.	91.7	13.3	130	18.9	131	19.0	128	18.5
Std. Error	30.6	4.44	40	5.78	41	6.00	40	5.85

Table XI

Verification of Consistency of Results Obtained with New Type Slurry,
HMS Graphite Reinforced 7740 Glass (Silica Addition) Made at 1723 K
6.9 MPa, 1 hr dwell time, argon atmosphere, slurry C

Sample	Three-Point Flexural Strength MPa	ksi	Sample	Three-Point Flexural Strength MPa	ksi	Sample	Three-Point Flexural Strength MPa	ksi
GC 326			GC 328			GC 339		
A1	1110	162	A2	866.9	125.7	A2	1102	160
A2	1150	166	A6	859.6	124.7	A5	1005	146
A3	1240	180	A8	1061.6	154.0	A7	954	138
A4	1170	170	A12	1046.1	151.7	A10	1107	161
A5	1060	153	B2	1109.9	161.0	B2	982	142
A6	931	135	B6	1199.7	174.0	B5	961	139
A7	835	121	B8	1149.8	166.8	B7	935	136
A8	942	137	B12	911.4	132.2	B10	1069	155
A9	1020	147	C2	935.0	135.6	C2	1015	147
A10	823	119	C6	999.5	144.2	C5	1020	148
A11	1040	150	C8	1140.0	165.3	C7	1015	147
A12	1070	155	C12	922.3	133.8	C10	1063	154
Avg	1034	150		1016.4	147.4		1019	148
Std Dev	130	18.9		117.7	17.1		56.7	8.34
Std Err	37.6	5.46						

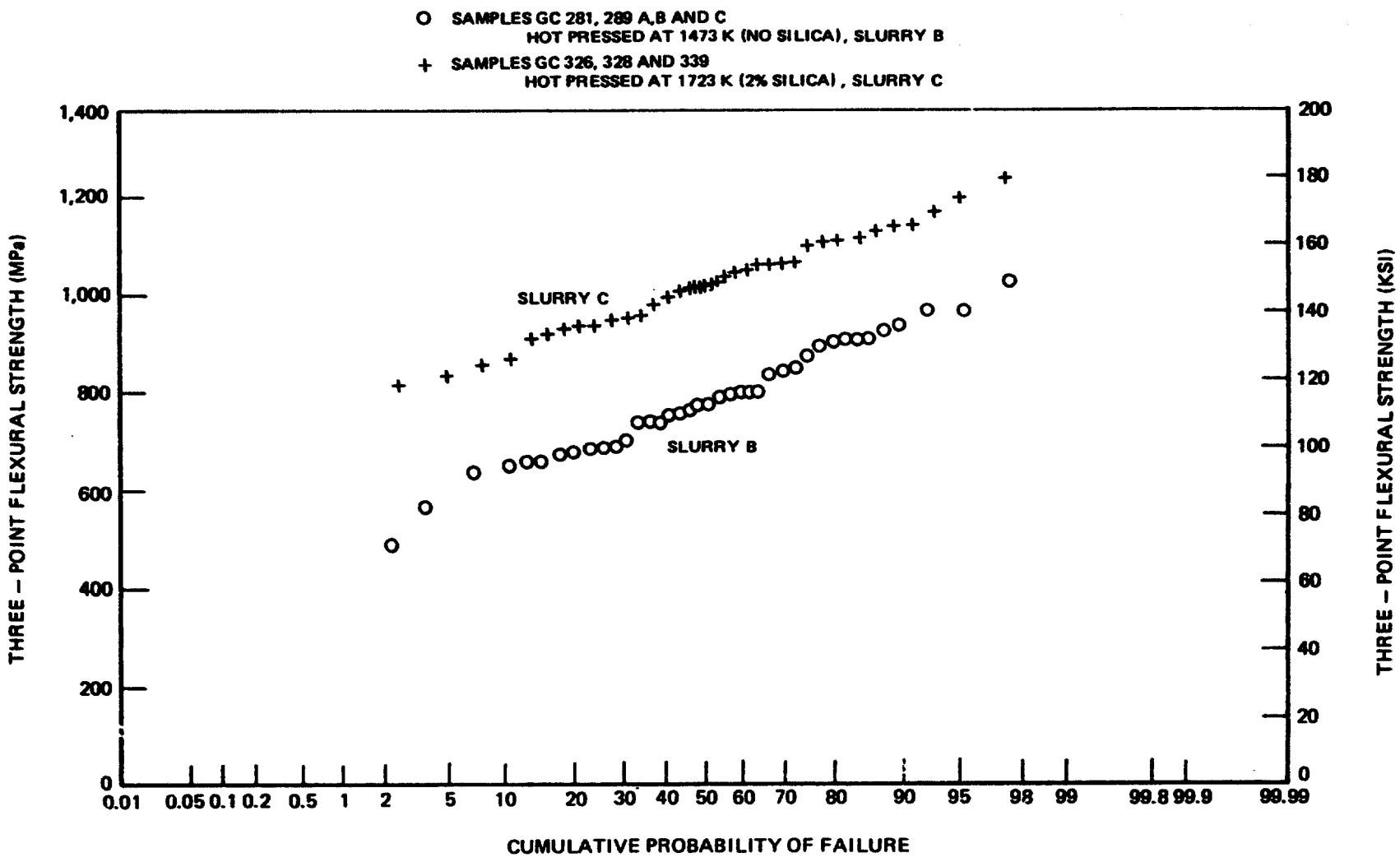

Figure 24. Failure Probability of HMS Graphite Fiber Reinforced CGW 7740 Glass with and without Silica

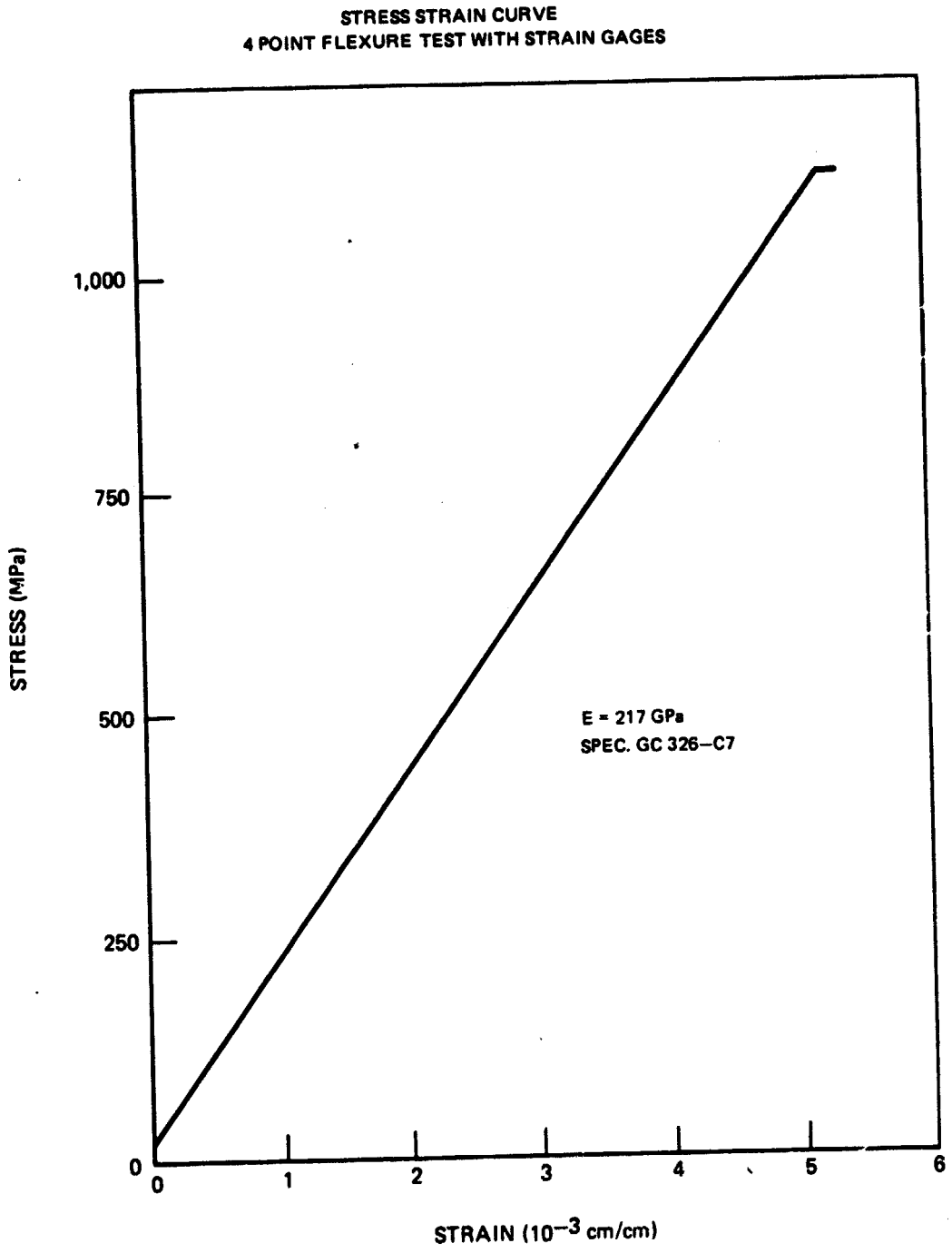

Figure 25. Stress Strain Curve of HMS Graphite Fiber Reinforced 7740 + 2% SiO_2, Slurry C, Determined by Four Point Bend Test

78-06-208-3

Prior to the discovery of the advantages of very high temperature hot pressing, other variables which might influence composite behavior were explored. One such variable was the relationship between hot pressing pressure at a temperature of 1473 K and resultant strength in HMS graphite fiber reinforced 7740 matrix composites, slurry B. The strength data from the four pressures evaluated, i.e. 4.1, 6.1, 10.1 and 13.8 MPa, are listed in Appendix B, Table 7, the average flexural strengths are plotted as a function of pressure in Fig. 26. The strength increases in a linear fashion with pressure, reaching a value of 765 MPa at a 13.8 MPa pressure.

Another variable explored was the effect of hot pressing the samples (in series) simultaneously. At a hot pressing temperature of 1473 K (slurry B) and a pressure of 13.8 MPa, the average flexural strengths from the samples were 113, 118 and 113 MPa for the top, center and bottom, respectively (Appendix B, Table 8).

After the observation was made of the positive effect of increasing the hot pressing temperature to greater than 1473 K, a study was made to determine the optimum temperature for the HMS-7740 + 2% SiO_2 composite system, slurry C. The relationship between temperature and strength, which are listed in Appendix B, Table 9 and which are plotted in Fig. 27, show an optimum temperature of 1723 K with a corresponding strength of 1034 MPa. Furthermore, the strength of the system pressed at 1473 K is only 225 MPa; in comparison, the 7740 matrix without the silica additive, pressed at 1473 K, would be expected to exhibit a strength of ~550 MPa when pressed at 6.9 MPa (Fig. 26). Therefore, not only does the colloidal silica influence the green strength of the composite, but also has a definite influence on the composite consolidation.

The consistency of strength results obtained in HMS graphite fiber reinforced 7740 + 2% SiO_2 glass matrix composites (slurry C) hot pressed at 1623 and 1723 K at a pressure of 6.9 MPa are demonstrated by comparing the data listed in Table 12 of Appendix B and Table XI of the text and the averages mentioned below. At 1623 K, the average strengths from three separate samples were 616, 639 and 651 MPa; at 1723 K, the average strengths of three separate samples were 1016, 1019 and 1034 MPa. This corresponds to an approximately 5 and 2% difference between extremes in the two cases respectively.

Holding the pressure constant, the effect of fiber type on the flexural strength properties of graphite fiber reinforced glass matrix composites made with a matrix of C.G.W. 7740 plus added silica (slurry C) was evaluated. The HTS fiber reinforced matrices had a flexural strength of 455 MPa when hot pressed at 1473 K and 731 MPa when hot pressed at 1623 K, Table XII. In comparison the average flexural strength of a similar system hot pressed at 1373 K but without silica addition (slurry B) was 370 MPa. It is evident, therefore, that the silica addition which permits hot pressing at a higher temperature by reducing fluidity of the glass is beneficial. However, the optimum temperature of hot pressing this fiber has not been achieved.

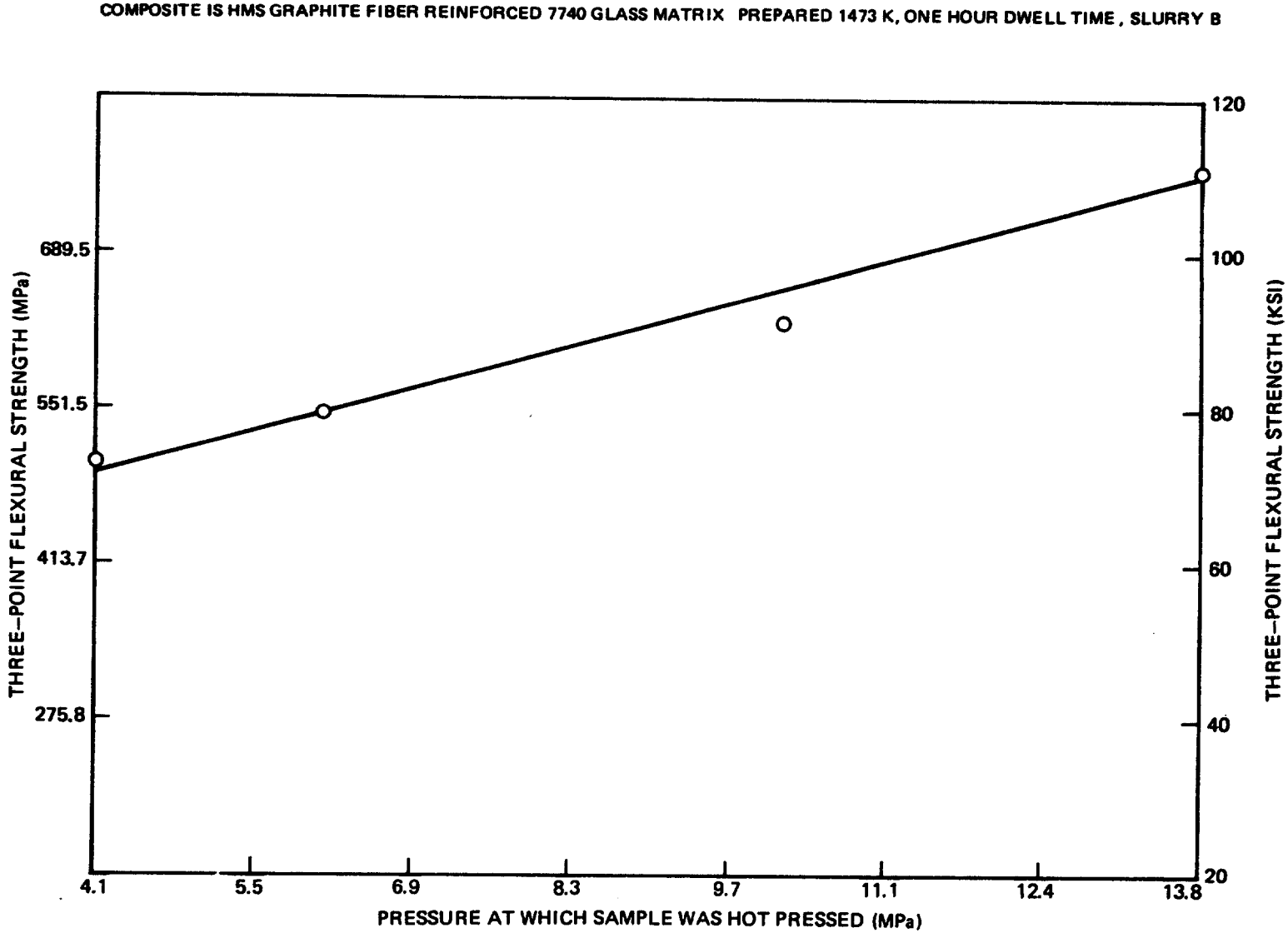

Figure 26. Relation of Hot Pressing Pressure to Three – Point Flexural Strength of Composite

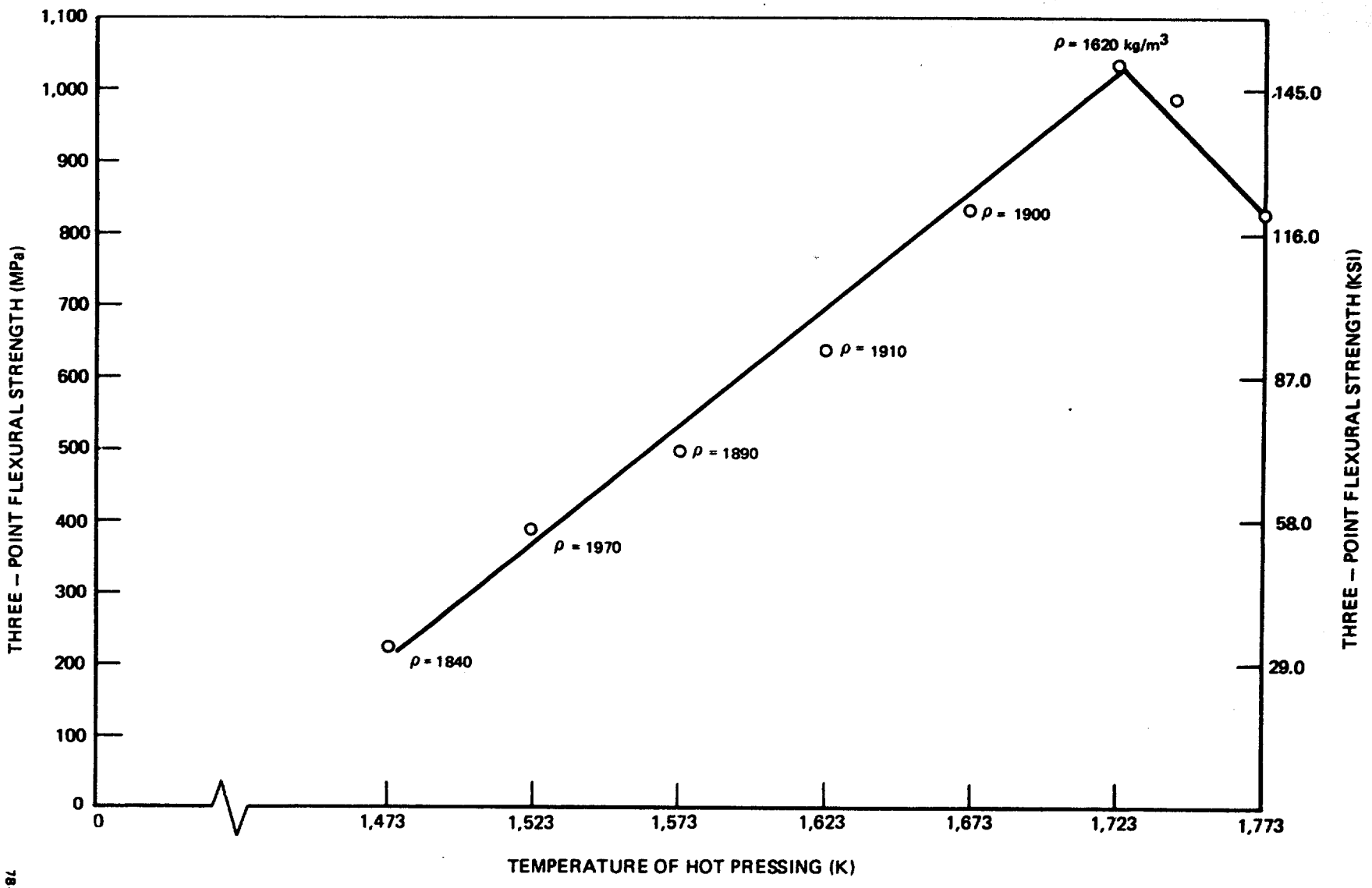

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Figure 27. Relationship of Three–Point Flexural Strength of HMS–7740 + 2% SiO_2 Composite to Temperature at which Composite is not Pressed, Slurry C

Table XII

Effect of Change in Slurry and Hot Pressing Temperature on Three-Point Flexural Strength of HTS Fiber Reinforced 7740 Composites

Sample	3-Point Flexural Strength MPa	ksi
LB 148 Old Slurry A Old Press 1373 K (13.8 MPa)		
1	338	49.0
2	408	59.2
3	341	49.5
4	357	51.7
5	410	59.4
6	389	56.4
7	408	59.2
8	379	54.9
9	456	66.1
10	354	51.4
11	343	49.8
12	407	59.1
13	319	46.3
14	297	43.0
15	348	50.4
Mean	370	63.7
Std Dev	42.4	6.15
Std Err	11.0	1.59

Sample	3-Point Flexural Strength MPa	ksi
GC 292 7740+2% SiO_2 (slurry C) New Press 1473 K (13.8 MPa)		
TR	475	68.8
CR	488	70.7
BR	405	58.8
TC	434	63.0
CC	466	67.6
CB	448	65.0
TL	476	69.1
LC	435	63.1
LC	468	67.8
	455	66.0
	26.5	3.80
	8.83	1.27

Sample	3-Point Flexural Strength MPa	ksi
GC 304 7740+2% SiO_2 (slurry C) New Press 1623 K (6.9 MPa)		
A2	766	111
A7	651	94.4
A12	681	98.7
B2	695	101
B7	698	101
B12	844	122
C2	789	114
C7	708	103
C12	749	109
	731	106
	59.8	8.67
	19.9	2.89

In the case of Celanese DG-102 fiber reinforced 7740 + 2% SiO_2 (slurry C), flexural strength data have been obtained from samples hot pressed at 1473, 1623 and 1723 K, Table XIII. The average respective strengths were 209, 417 and 460 MPa. The positive influence of higher hot pressing temperature is again apparent. The flexural strength of DG-102 reinforced 7740 prepared using the previous slurry B process method (7740 pressed at 1473 K) was 340 MPa.

An experiment was also conducted with Thornel pitch VS 0032 fiber in slurry C 7740 + 2% SiO_2. After hot pressing at 1623 K, the average flexural strength of such specimens was 448 MPa. The data are given in Table 11 of Appendix B.

For composites utilizing a matrix of 7740 + 2% SiO_2 (slurry C) and hot pressed at the nonoptimum temperature of 1623 K, the following comments with respect to fiber type are appropriate. The HTS fiber reinforced system was strongest (731 MPa) as might be expected from the nominally higher strength of this fiber. The HMS reinforced system displayed the next highest strength (635 MPa) in keeping with HMS being the next strongest fiber. The pitch and DG-102 fiber reinforced systems were weakest (448 and 417 MPa, respectively). Although the strength of both fibers is relatively low with the pitch fibers being the the weaker, the strength of the composites derived from these fibers is in reverse order.

Composites employing higher percentages of Ludox have also been prepared (GC 225 and 226). Tapes have demonstrated excellent green strength and were easily handled without the loss of glass powder. Specimens prepared from these samples which were hot pressed at 1473 K were weaker than comparison samples without Ludox. In retrospect, based on the most recent data, a much higher hot pressing temperature might provide composites from these type compositions with equivalent or superior flexural strengths to the comparison composites pressed at 1473 K.

Shear, Transverse and Cross Ply Strengths

Shear Strength

The interlaminar shear strength was determined in three-point bending using a 3.5 to 1 span-to-depth ratio. The strength for an HMS graphite fiber reinforced 7740 glass matrix hot pressed at 1473 K, slurry B, was 39.8 MPa. This low value of shear strength illustrates the poor bonding that exists between matrix and fiber. Data for specimens hot pressed at 1723 K have not, as yet, been obtained and specimens made with 2% added silica, slurry C, have not yet been evaluated.

Table XIII

Effect of Hot Pressing Temperature on Three Point Flexural Strength of Composites Formed from Celanese DG-102 Fiber Reinforced C.G.W. 7740+ 2% SiO_2 Glass Matrix Hot Pressed Using Newest Slurry, 6.9 MPa, 1 Hr Dwell Time Slurry C

GC-306 - 1473 K			GC-331 - 1623 K			GC-336 - 1723 K		
	Three Point Flexural Strength			Three Point Flexural Strength			Three Point Flexural Strength	
Specimen	MPa	ksi	Specimen	MPa	ksi	Specimen	MPa	ksi
A1	120	17.4	A1	221	32.1	A1	413.5	59.98
A6	279	40.5	A4	457	66.4	A5	379.3	55.02
A12	113	16.4	A7	533	77.4	A8	320.3	46.40
			A10	416	60.3	A11	358.6	52.01
B1	145	21.1						
B6	233	33.8	B1	351	50.9	B1	480.5	69.68
B12	267	38.8	B4	489	70.9	B5	515.8	74.81
			B7	451	65.4	B8	511.7	74.22
C1	175	25.4	B10	424	61.6	B11	576.8	83.66
C6	256	37.2						
C12	293	42.6	C1	330	47.9	C1	501.3	72.70
			C4	469	68.0	C5	543.7	78.86
			C7	409	59.4	C8	555.9	80.62
			C10	450	65.2	C11	364.1	52.81
Avg	209.4	30.37		417	60.5		460.1	66.74
Std Dev	72.4	10.5		82.7	12.0		88.12	12.78
Std Err	41.8	6.1		73.9	3.47			

Transverse Strength

Hercules HMS fiber unidirectionally reinforced 7740 glass matrix composites were fabricated from slurry B. Two composite thicknesses of 4 ply and 16 ply were used and the resultant panels were cut into 90° oriented specimens for three-point bend testing. The specimen surfaces were glass rich and this layer was not removed prior to testing since its presence simulates a surface protected against fiber oxidation.

The resultant three-point flexural strength data are listed in Appendix B, Table 12; the average flexural strengths were 9.7 and 14.8 MPa for specimens of 4 and 16 plys, respectively. In every case the specimens appeared to fracture at the tensile surface and crack propagation occurred across the specimen thickness. Fracture did not occur, however, at the mid-span in each case. This was particularly true of the 4 ply thick composite specimens (GC 208) and can be readily understood when one considers the importance of microstructure and the location of weaker and stronger material regions on transverse properties. Calculated composite strengths ranged from approximately 6.8 MPa (1000 psi) to 22.2 MPa (3240 psi) with the single high value occurring for a thicker specimen. These low levels of transverse strength are expected because of the low bond strength between the HMS graphite fiber and 7740 glass.

HTS and Celanese DG-102 fiber unidirectionally reinforced 7740 specimens were fabricated for 90° flexural strength measurement. The data for the HTS containing specimens are also presented in Table 12, Appendix B; the average transverse strength was 10.8 MPa and ranged from 4.7 to 18.0 MPa. As expected, the transverse strengths measured were quite low. The DG-102 fiber composite data were not obtained because the fabricated panels fractured during handling and cutting, thus also evidencing a very low transverse strength. As was previously noted, these data point clearly to the importance of multiaxially reinforced specimens for most applications. Furthermore, since these composites were prepared using a 7740 matrix hot pressed at 1473 K, the data should be viewed as preliminary. Improvements might be obtained from composites pressed at 1723 K, the optimum temperature for longitudinal strength.

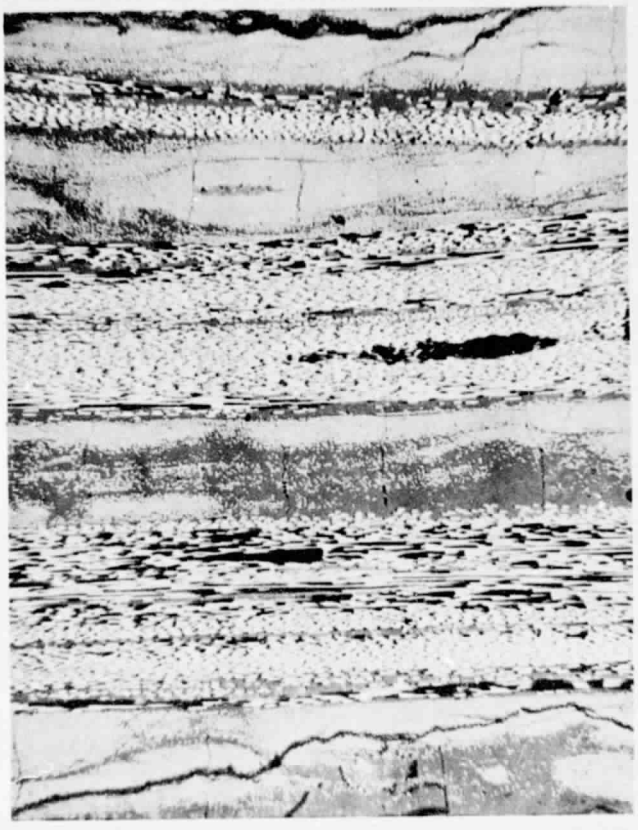
Cross-Ply Composites

Cross ply constructions of HMS and Celanese DG-102 fiber reinforced composites were fabricated by the same procedures used for uniaxially reinforced specimens (hot pressed at 1473 K). The composite lay-up consisted of a sequence of alternating 2 ply thick strata that were stacked symmetrically with respect to the composite mid plane. The abbreviated notation for this lay-up sequence is $[(90_2,0_2)_2]_s$ and consists of a total of 16 plys.

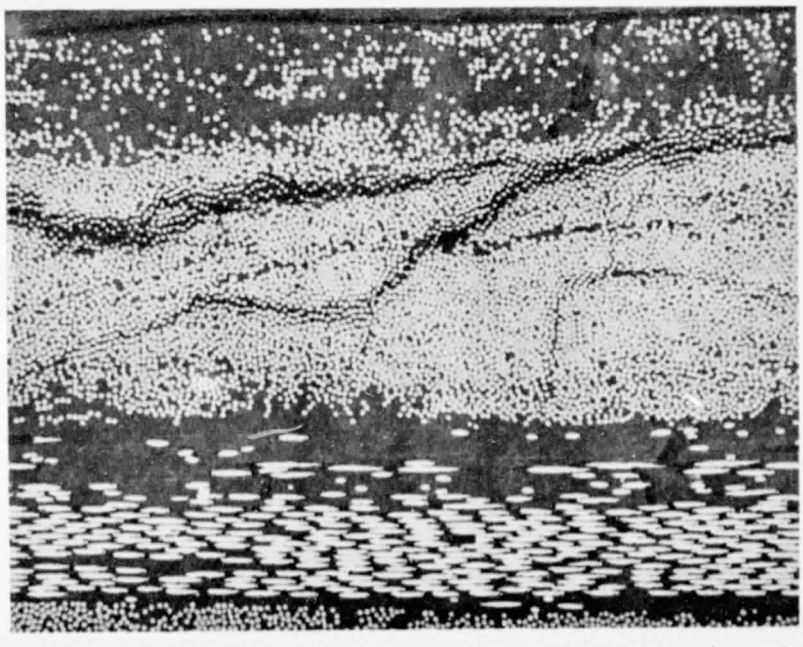
The microstructure of the composite containing DG-102 fiber is shown in Fig. 28. Besides the obvious fiber distribution, the most notable feature is the presence of many microcracks running through the plys. Many of these cracks are evenly spaced, run at 90° to the ply plane, and may be associated with the mismatch in thermal expansion between the two ply orientations. On a macro scale, however, the as-fabricated composites looked excellent and uncracked. The 90° direction has a higher coefficient of thermal expansion and thus, on cooling from the hot pressing temperature, it could crack because of the tensile stresses induced within the ply and at 90° to the fiber direction. Careful examination of composites, however, has demonstrated that any observed cracks are due more to the preparation of the metallographic sections rather than any other reason. Thus, specimens which were cut and polished by the standard technique exhibited a large population of microcracks, while those which were surface ground and polished to remove approximately 0.25 cm of material after cutting, were almost completely crack free. This is shown in the cross-ply composite, GC 215, in Fig. 29 which was prepared with a ply lay-up scheme of $[(0/90)_4]_S$. In addition, the matrix was leached out of samples of each composite and the freed fibers examined to ascertain whether any fiber fragmentation had occurred. This could conceivably occur during the application of pressure at the contact points of neighboring crossed fibers. No evidence of fiber fragmentation was found, however, and all of the extracted fibers exhibited lengths equivalent to the dimensions of the original specimens.

Mechanical testing of samples was carried out in the three-point bend mode. The specimens were cut such that the surface ply fibers were parallel to the major span of the bend test apparatus and no surface preparation was used prior to testing in order to avoid grinding through the 0° primary load bearing plys. Because of this lack of grinding, and also the fact that the as-fabricated panels were not very uniform in thickness, the bend tests were not well controlled. Nevertheless, the objective was to make a first attempt at gaining data for cross ply material, and this was achieved.

The measured strengths are given in Table XIV, along with other pertinent information. In the case of the Celanese fiber reinforced specimens, an average strength of 115 MPa (16,700 psi) is somewhat lower than that expected since the average room temperature bend strength of unidirectionally reinforced 0° specimens has been approximately 270-320 MPa (40-45,000 psi). This difference, however, may be attributable to a lower fiber content (40%) than has been typical in the past (50-60% by volume). All of these specimens fractured in a tensile mode and, as previously reported for 0° Celanese reinforced specimens, the fracture did not exhibit much fiber pull out. In contrast, the HMS fiber reinforced specimens failed by interlaminar cracking at regions generally remote from the mid-span of the specimens. These cracks then propagated along interlaminar ply bond lines toward the centers of the specimens. The specimens, however, did not separate into pieces and instead retained substantial fractions of their original



400 μ m



100 μ m

Figure 28. Microstructure of Specimen GC 30 203 Celanese DG 102 Reinforced 7740, $|(90_2\,0_2)_2|_s$, Slurry B

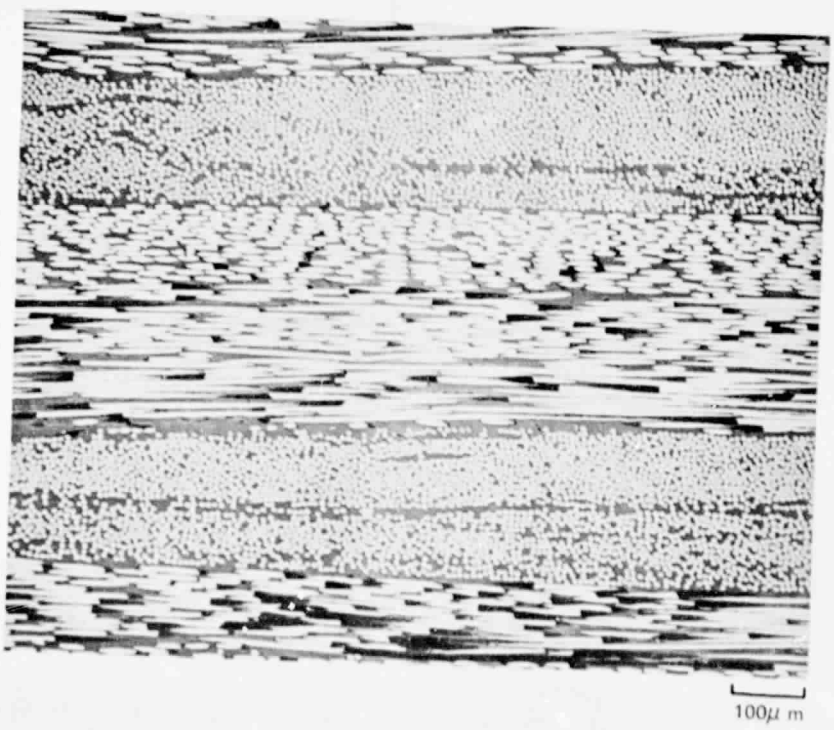


Figure 29. Microstructure of Specimen GC 215–5 HMS Reinforced 7740, $[(0/90)_4]_s$ Samples Surface Ground and Polished, Slurry B

Table XIV

Three Point Bend Data for Cross Ply Specimens
Slurry B

Specimen	Fiber	Lay-up[1]	v/o Fiber		Calc. Max. Flex. Stress 10^3 psi	MPa	S/D[2]	Fracture
GC 202-1	DG-102	$[(0_2 90_2)_2]_s$	40		24.6	170	28	Tensile[3]
-2	"				7.7	53	30	
-3	"				17.7	122	29	
				Avg	16.7	115		
GC 203-1	HMS	$[(0_2 90_2)_2]_s$	50		28.7	198	14	Interlaminar[4]
-2	"				33.1	228	15	
-3	"				32.6	225	14	
				Avg	31.5	217		
GC 210	HMS	$[(0/90)_4]_s$			35.4	244	16	Tensile[3]
					33.1	228	16	Interlaminar[4]
					25.0	172	15	"
				Avg	31.2	215		
GC 214	HMS	$[(0/90)_4]_s$			25.1	173	6.5	Interlaminar[4]
					29.6	204	6.5	
					37.6	259	10	
					36.8	253	10	
				Avg	32.3	222		
GC 215	HMS	$[(0/90)_4]_s$			32.3	223	6.4	Interlaminar[4]
					34.0	234	6.4	
					41.2	284	10	
					31.1	215	10	
				Avg	34.6	239		

[1]In these tests the outer 0° plys were oriented with fibers parallel to the major span

[2]Span-to-depth ratio for 3 point bend test

[3]Specimens separated at mid point of span into two pieces

[4]Specimens remained in tact after test. Interlaminar cracks occurred between 0° and 90° layers. These cracks started at the free ends of the specimens and propagated inward.

strength after test. This observed failure mode may have been aggravated by the use of a smaller value of span-to-depth ratio (14) than has been typical in the past (30). The tabulated specimen flexural strengths were not widely spread and averaged 217 MPa which again appears somewhat low when compared with a value of 550-700 MPa for all 0° material.

Composites GC 210, 214 and 215, slurry B, were fabricated using the $[(0/90)_4]_s$ lay-up scheme and HMS as the fiber. GC 214 was pressed in vacuum and GC 215 was slow cooled from 1473 K to minimize residual stresses. The strengths of these composites are also tabulated in Table XIV, were similar to the alternate HMS ply lay-up, and were not affected by changes in the fabrication procedures. A higher hot pressing temperature would be expected to improve the strength of the cross-plied composites.

Woven Cloth

A two dimensionally woven cloth of Thornel 300 fiber was used to fabricate cross ply specimens. The cloth contained 12 fibers per inch in both the 0° and 90° directions, woven in a simple weave, and was easily cut and handled. The fabrication procedure involved dipping the layers of cloth in a standard slurry of glass followed by stack up of plys and hot pressing. The resultant composite microstructure is shown in Fig. 30 where it can be seen that the fiber content is very high. Glass did, however, penetrate the woven cloth and this type of procedure will be pursued further in the coming months. The major difficulty is that the woven nature of the cloth prevents spreading of the individual tows and hence it is more difficult to get the glass slurry to penetrate the fiber bundle.

A specimen was also prepared wherein the PVA fiber sizing was removed prior to glass impregnation. The surface appearance of this composite is shown in Fig. 31. The fabric weave is clearly visible through the thin glass surface layer and the general appearance was excellent. The degree of internal densification and bonding was not measurably superior, however, to the specimens fabricated without a fiber precleaning step. The fiber-matrix bond was very weak, and the specimens failed by delamination at a shear stress on the order of 3 MPa. The specific data are shown in Table 13 of Appendix B.

Thermal Expansion

One of the most interesting and important aspects of graphite fiber reinforced composites is their coefficients of thermal expansion. Because of the very low axial coefficient of thermal expansion of graphite fibers, it has been possible to make resin matrix composites that are exceptionally dimensionally stable in thermal gradients. This has been accomplished despite the high thermal expansion of resin matrices. Based on this successful experience, glass matrix composites would be expected to offer superior dimensional stability due to the much lower thermal expansion of glass, as compared to resins.

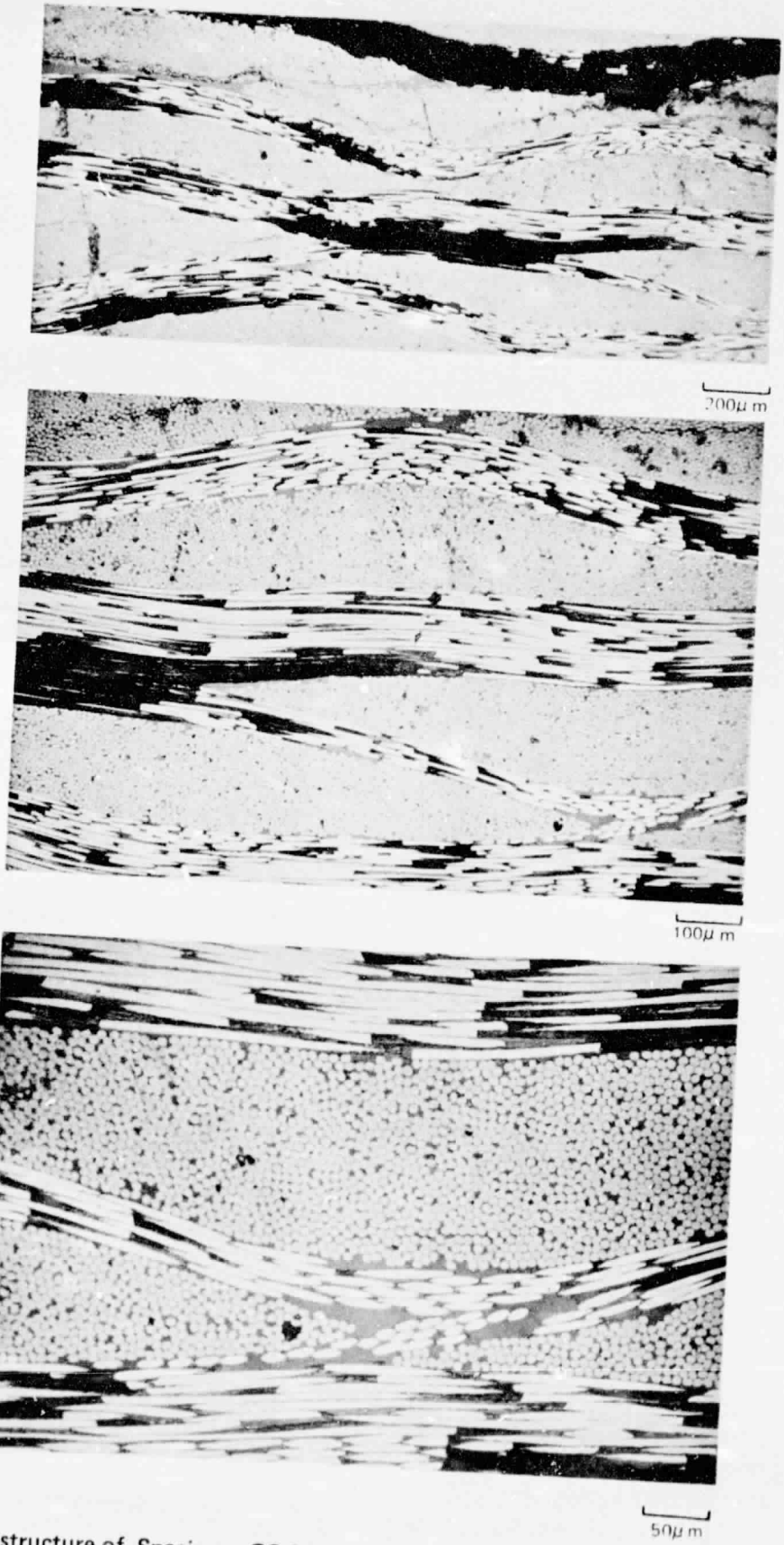
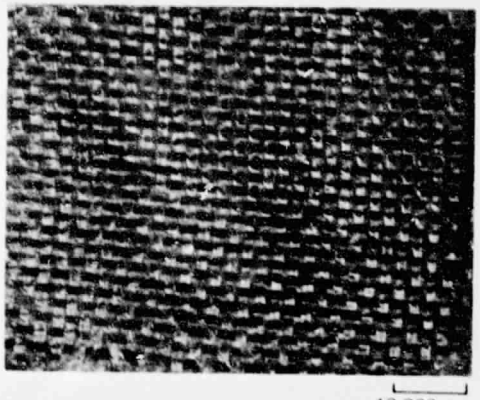


Figure 30. Microstructure of Specimen GC 218–5 Thornel 300 Cloth Reinforced 7740, Slurry B



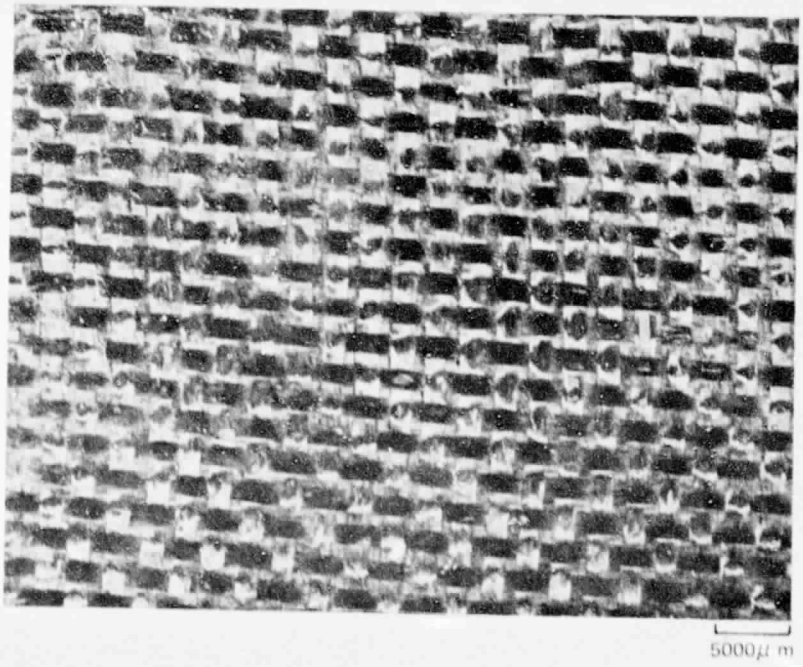


Figure 31. Transparent Glass Surface of Specimen GC 220 0° / 90 Thornel 300 Reinforced 7740 Fabricated Using Woven Cloth, Slurry B

Unidirectionally reinforced 7740 matrix composites were fabricated with Thornel 300 (LB 161E), Celanese DG-102 (LB 97L), and Hercules HMS (GC 216) reinforcements. Elongation of 0° and 90° oriented specimens was measured, and the resultant data are presented in Figs. 32-38 in the form of thermally induced specimen strain as a function of temperature. All tests were begun at room temperature and were repeatedly run up to approximately 823-848 K for at least two complete cycles. There did not appear to be any significant difference in material performance due to cycling so that the data presented, which were taken from the final cycle, are typical of stable material behavior.

The data in Figs. 32 and 33 are for 0° and 90° oriented Celanese DG-102 reinforced 7740, respectively. The 0° data are particularly interesting because they reflect the unique ability of graphite fibers to contract in the axial direction during heating. This negative expansion is reversed at about 573 K so that a net zero change in dimension is the resultant of heating to 823 K. The 90° thermal expansion is always positive and of much larger magnitude than the 0° characteristic primarily due to the glass which essentially controls the transverse expansion.

The thermal expansion of Thornel 300 reinforced glass specimens is presented in Figs. 34 and 35. The 0° data are nonlinear and small in value; however, no evidence of composite contraction was obtained illustrating the importance of fiber type in controlling expansion. As in the case of the Celanese fiber reinforced composite, the 90° expansion is considerably larger than that for the 0° orientation.

The thermal expansion data for the HMS reinforced 7740 are similar to those of the DG-102 reinforced glass. In the case of the 0° orientation, Fig. 36, the composite contracts initially on heating due to the negative thermal expansion of the fibers. The expansion is reasonably linear up to a temperature of approximately 423 K at which time the rate of contraction decreases with a complete reversal to expansion taking place between 573 and 623 K. Although the maximum temperature was 848 K, a net zero change in length would be expected at a temperature of 923 K. Because the glass is reasonably soft at this temperature, permanent deformation of the specimen would be expected, however. The transverse composite thermal expansion, Fig. 37, is much more linear, and positive at all temperatures. The value of coefficient of thermal expansion is dependent on both the radial fiber expansion, and the expansion of the matrix, with the latter having the predominant role.

Values of composite coefficients of thermal expansion were obtained from the above described data and are presented in Table XV. In the cases of nonlinearly expanding 0° specimens, the coefficient of expansion varies significantly with temperature range and each calculation was based on drawing a straight line between the low temperature and high temperature strain values.

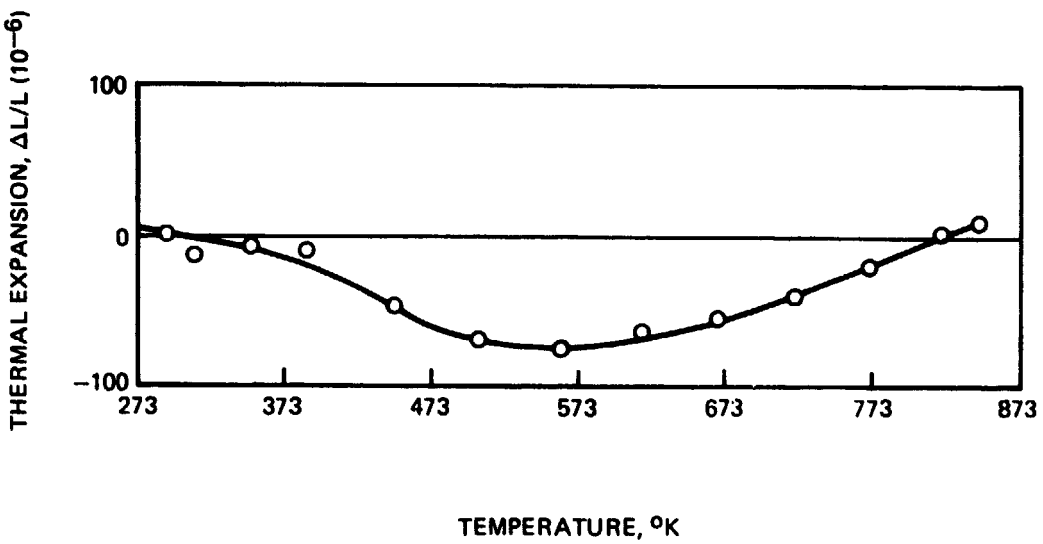


Figure 32. Thermal Expansion of 0° Celanese DG – 102 Fiber Reinforced 7740, Slurry B

77-08-157-3

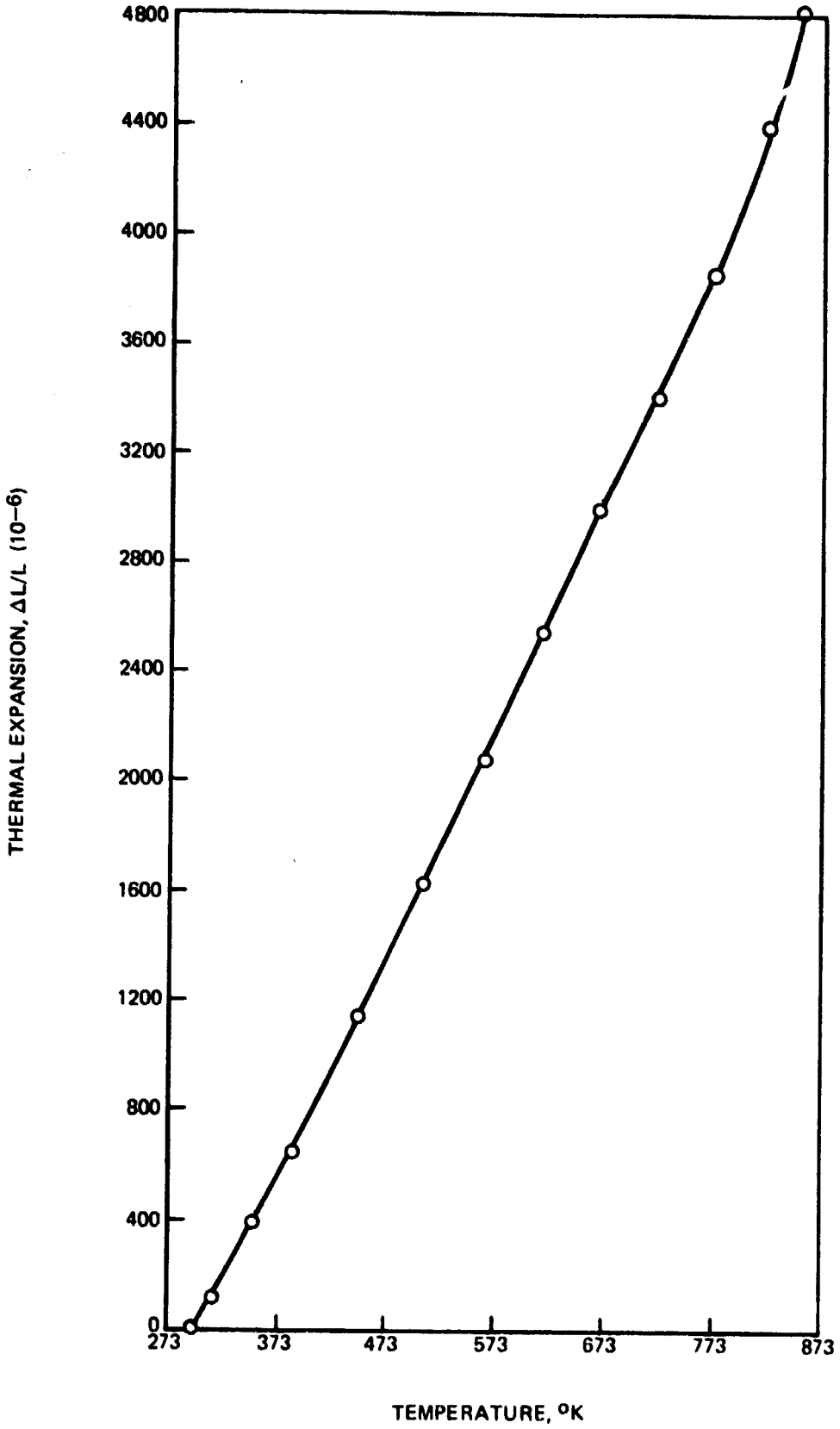


Figure 33. Thermal Expansion of 90° Celanese DG – 102 Fiber Reinforced 7740, Slurry B

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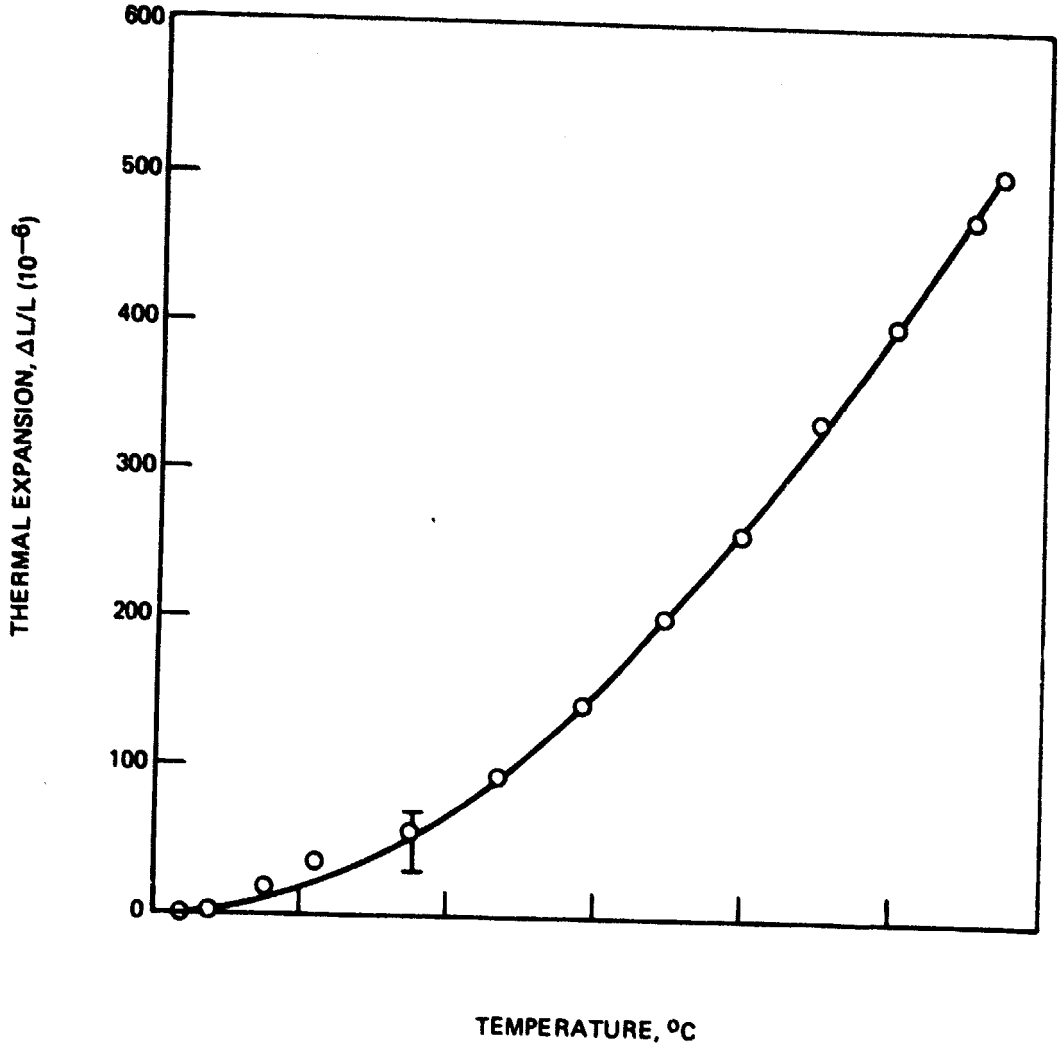

Figure 34. Thermal Expansion of 0° Thornel 300 Reinforced 7740, Slurry B

77-08-157-1

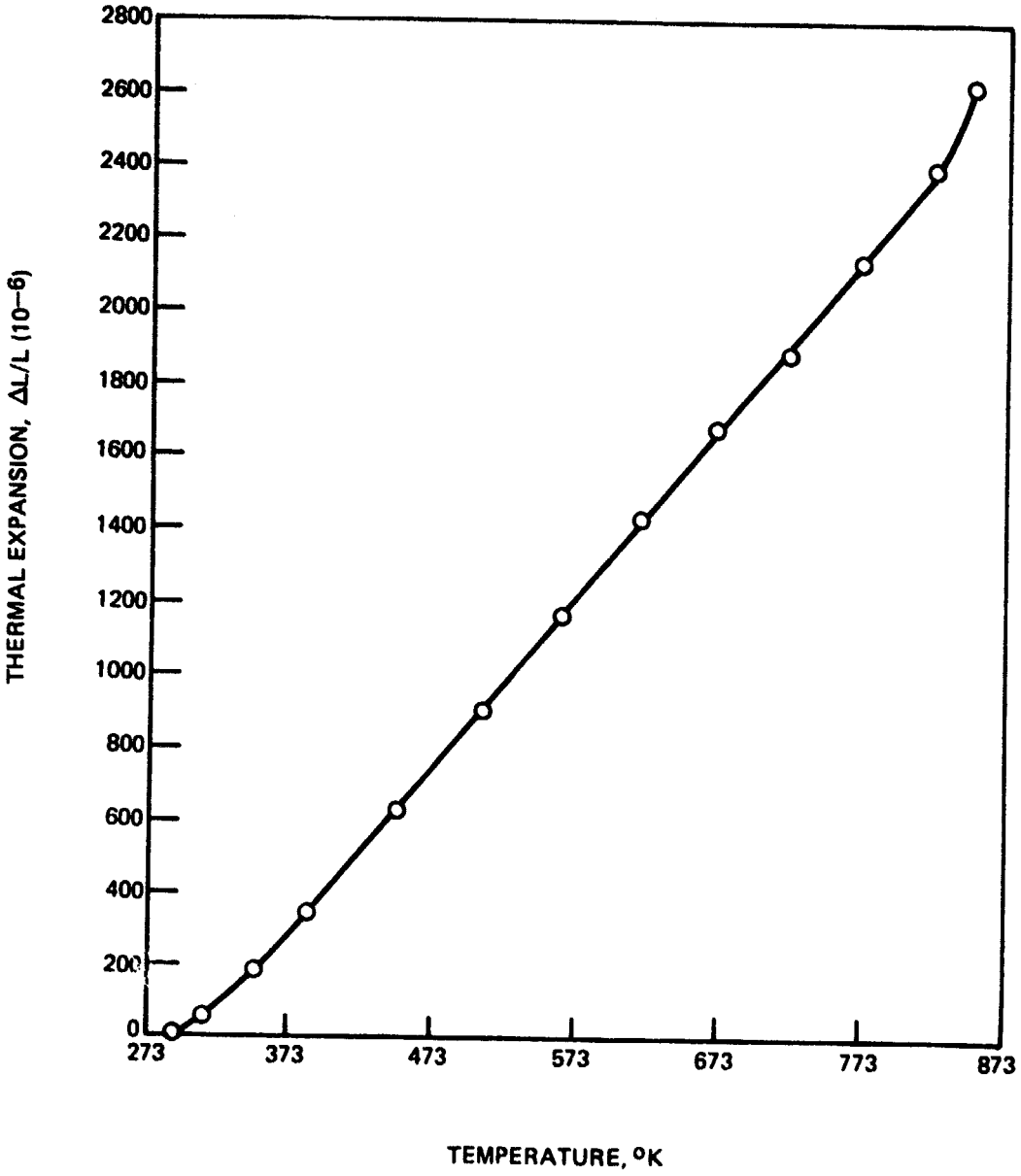

Figure 35. Thermal Expansion of 90° Thornel 300 Fiber Reinforced 7740, Slurry B

77-08-157-2

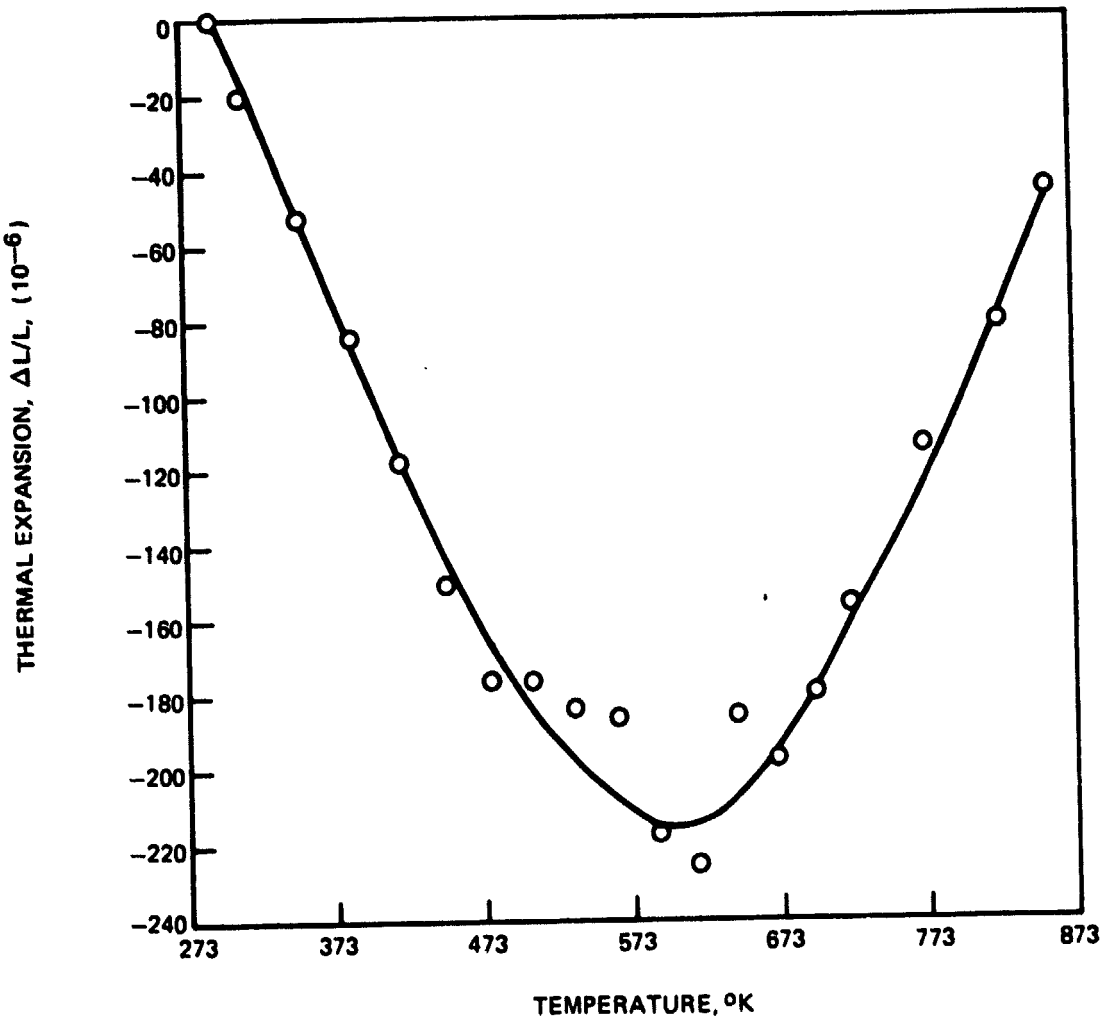

Figure 36. Thermal Expansion of 0° HMS Reinforced 7740, Slurry B

77-10-44-2

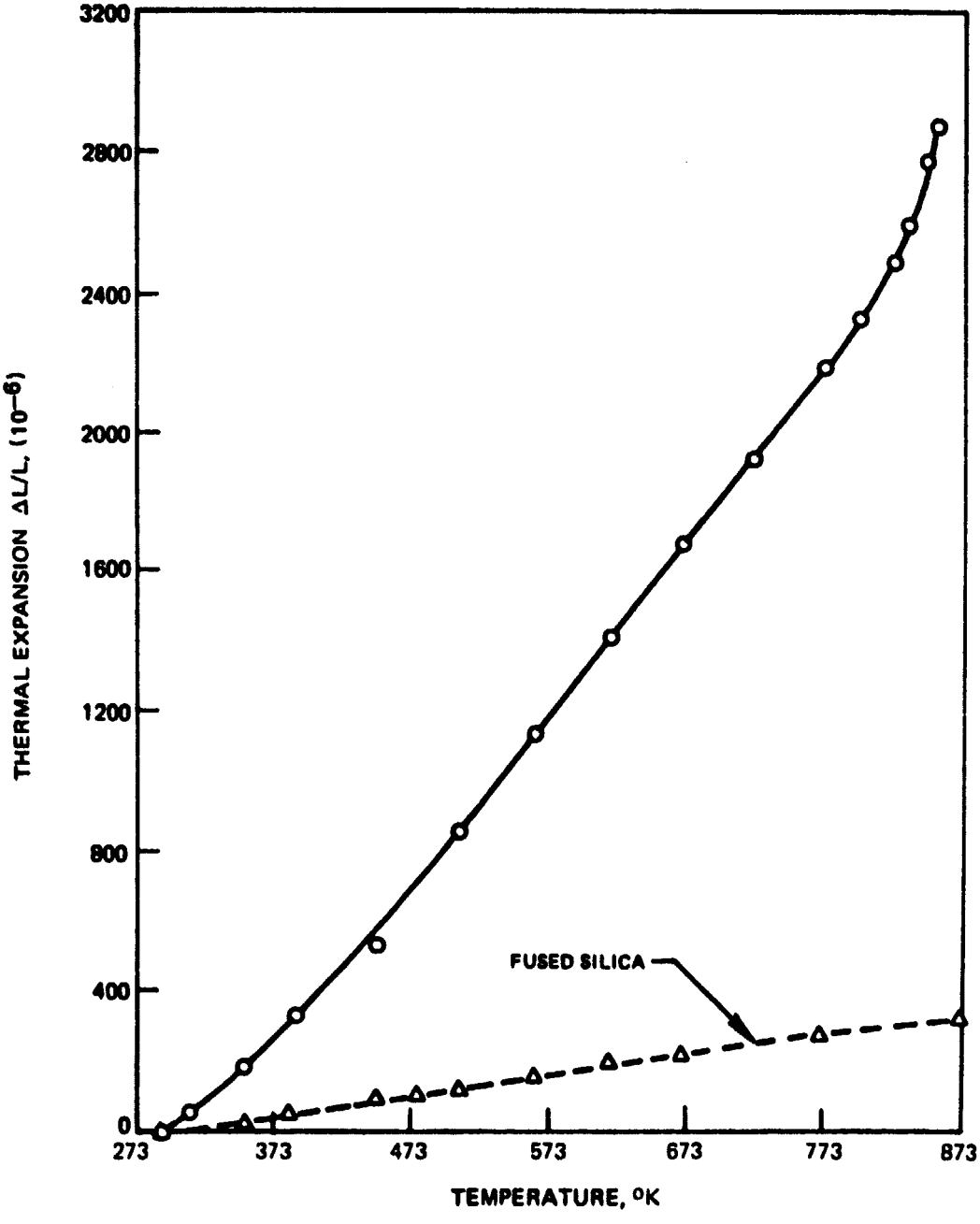

Figure 37. Thermal Expansion of 90° HMS Reinforced 7740 Spec. GC 216, Slurry B

Table XV

Comparison of Composite Coefficients of Thermal Expansion

Material	Specimen & Orientation	Temp. Range K	Coefficient of Thermal Expansion α (K^{-})
50% Thornel 300 Reinforced 7740 Slurry A	LB 161E-90°	295-823	4.3×10^{-6}
	LB 161E-0°	295-823	0.9×10^{-6}
		295-423	0.38×10^{-6}
50% Celanese DG-102 Reinforced 7740 Slurry A	LB 97-90°	295-823	7.6×10^{-6}
		295-423	7.6×10^{-6}
	LB 97-0°	295-823	0
		295-423	-0.29×10^{-6}
		295-573	-0.29×10^{-6}
		295-673	-0.14×10^{-6}
60% Hercules HTS Reinforced 3002 Resin	90°	295-423	30×10^{-6}*
	0°	295-423	-0.4×10^{-6}*
50% Hercules HTS Reinforced ERLA 4617 Resin	90°	-	33.9×10^{-6}**
	0°	-	-0.06×10^{-6}**
50% Hercules HMS Reinforced ERLA 4617 Resin	90°	-	33.9×10^{-6}**
	0°	-	-0.5×10^{-6}**
50-60% HMS Reinforced 7740 Slurry B	GC 216-90°	295-823	4.7×10^{-6}
		295-423	3.6×10^{-6}
	GC 216-0°	295-823	-0.2×10^{-6}
		295-423	-1.0×10^{-6}
		295-573	-0.8×10^{-6}
		295-673	-0.5×10^{-6}
50% HMS Reinforced ERLA 4617 Resin	90°	-	33.9×10^{-6}*
	0°	-	-0.5×10^{-6}*

*Freeman & Campbell, ASTM-STP 497, p 121, 1972
**Rogers, et al, J. Mat. Sci., Vol. 12, p 718, 1977

Also presented in the table are data for several resin matrix systems. A comparison between resin and glass matrix composites reveals a major difference in 90° values of α, with a factor of up to eight decrease in expansion ascribable to the 7740 matrix composites. In all cases the 0° values are quite low. Another important point is that the glass matrix data extend up to a temperature of 823 K while resin matrix composite data are limited (by matrix properties) to a maximum temperature of about 423 K.

The above described data have confirmed the unique qualities of graphite reinforced glass matrix composites for use in the construction of dimensionally stable structures. They also confirm the major anisotropy of expansion which can cause microcracking in cross ply composites.

The thermal expansion of a cross ply (0/90°) HMS reinforced 7740 composite was measured; the results are displayed in Fig. 38. The measurement was repeated several times, and in no case was there any permanent change in dimension after a full heating and cooling cycle. The measured thermal expansion of the cross ply material is quite low over the entire temperature range and particularly between 295 and 573 K. In this range, a hysteresis effect is also maximized. The hysteresis arises from the significant thermal expansion mismatch of the 0° and 90° directions.

Oxidation Properties

The effect of oxidation on the strength of graphite fiber reinforced glass matrix composites is summarized in Fig. 39. The specimens from which these data were collected were nominally 0.2 x 0.5 x 6.4 cm in size. After oxidation exposure the surfaces of the specimens assumed a whitish color. Nonetheless, the most important path for oxidation is along the fiber direction. This accounts for the majority of the weight loss experienced by the composites. Therefore any application which minimizes edge exposure should exhibit superior oxidation resistance.

Specific data on the oxidation properties of the graphite fibers at 823 K, the flexural strength and weight loss in HTS and HMS graphite fiber reinforced 7740 and the flexural strengths of DG-102 and pitch type graphite fiber reinforced 7740 are tabulated in Appendix B, Tables 19-31.

As shown in Fig. 39 and the tabulated data, the HMS graphite fiber reinforced 7740 + 2% silica, hot pressed at 1723 K, exhibits superior resistance to oxidation. After 24 hrs at 813 K, the percentage weight loss is 5.6; after 100 hrs, 12.6. In comparison, this matrix reinforced by HTS fiber and hot pressed at 1623 K exhibits a weight loss of 9.7% after 24 hrs and 28.8% after 100 hrs. At an oxidation temperature of 723 K, the weight loss is accordingly much less for the HMS fiber reinforced composite. After 24 hrs, the loss is 0.6% and after 100 hrs, 1.8%.

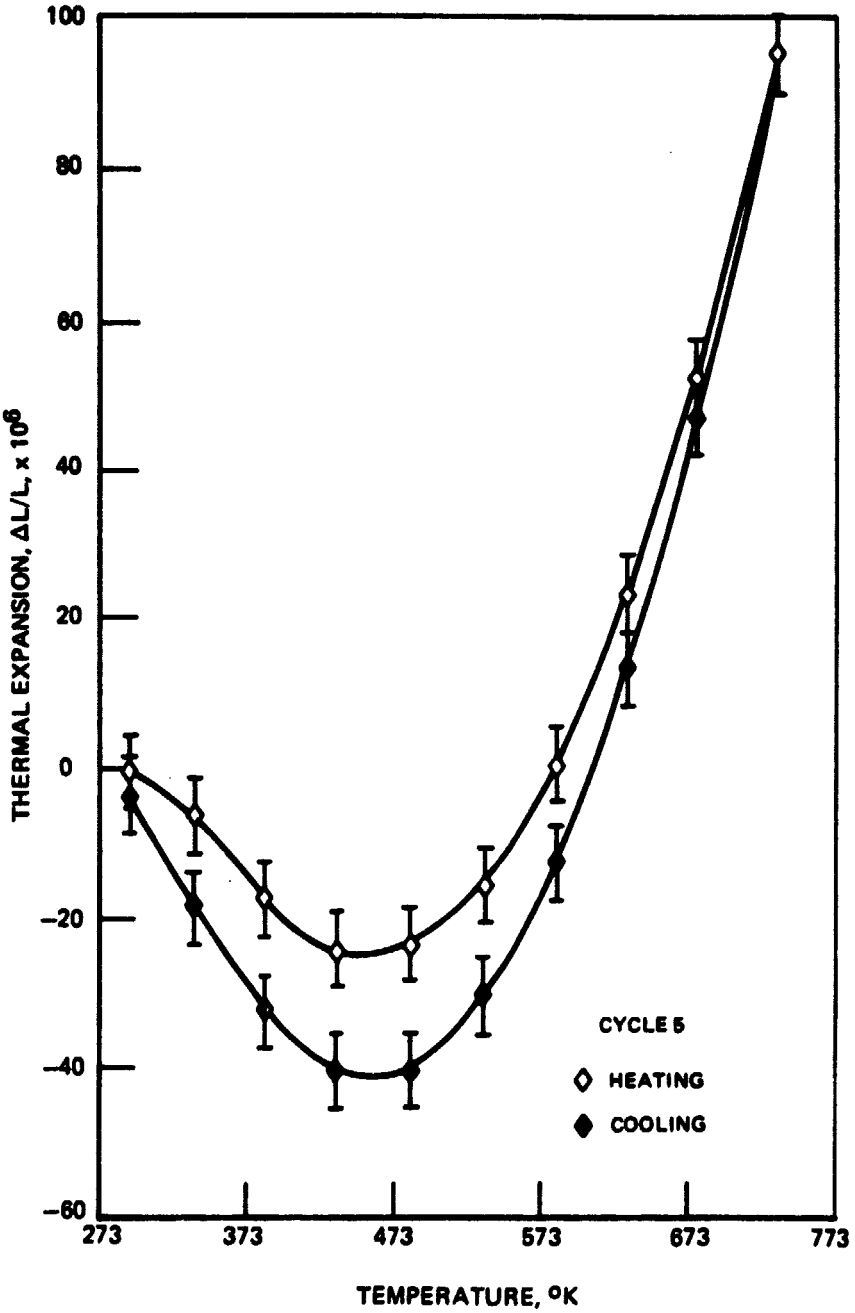

Figure 38. Thermal Expansion of 0° / 90° HMS Reinforced 7740, Bars Represent Confidence in these Data Points for this Cycle

77-12-111-2

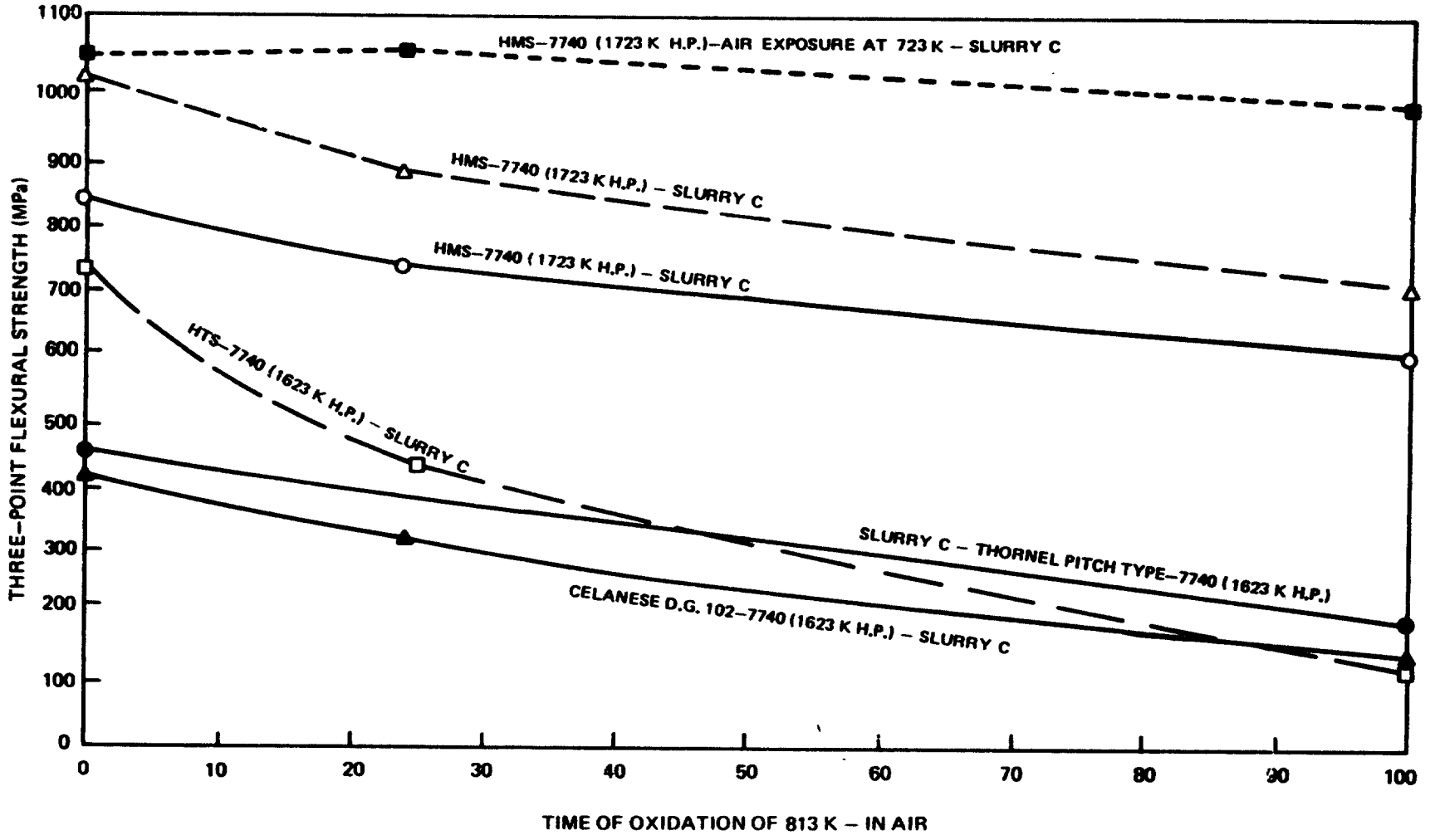

Figure 39. Effect of Oxidation on Three – Point Flexural Strength of Graphite Fiber – 7740 Glass Matrix Composites with added Silica, Slurry C

In the case of composites fabricated with fibers of the Thornel pitch and Celanese DG-102 types, strength losses of 57 and 68% were suffered after 100 hrs at 813 K. In both cases these results are disappointing since, based on oxidation studies of the bare graphite fibers (Appendix B, Tables 19 and 20), these materials were expected to yield better, not worse, oxidation resistance than found for the HMS graphite reinforced glass composites. These results are not conclusive, however, since composites pressed at 1723 K, found optimum for the HMS composites, need to be evaluated.

In comparing the data in Table 27 of Appendix B which represents recently made samples of HMS graphite fiber reinforced C.G.W. 7740 glass + 2% silica with that of Table 28 of Appendix B for similar samples made a year ago and with a slurry without added silica, two facts must be considered. First, the making of strong graphite fiber reinforced C.G.W. 7740 + 2% SiO_2 has been a gradual learning process and secondly, not only did the older samples lack the beneficial effect of the 2% added silica but they were also hot pressed at 200 K higher temperature. These same two factors must also be considered in comparing Tables 29 and 30, Appendix B, for Celanese graphite fiber reinforced glass matrix composites where Table 29 represents year old data and here the 4 hr data of Table 29 is certainly less accurate than the 24 and 100 hr data of Table 30.

CONCLUSIONS

High strength graphite fiber reinforced borosilicate glass matrix composites can be prepared by hot pressing tapes of powdered glass which has been introduced into graphite yarn from a slurry. By employing colloidal silica as part of the slurry vehicle, a modified borosilicate glass which contains an additional 2% silica has been identified as a composite matrix. With such a matrix, Hercules HMS graphite fiber and a very high hot pressing temperature (i.e. 1723 K), uniaxially reinforced composites have exhibited room temperature flexural strengths on the order of 1000 MPa, elastic moduli of 200 GPa and failure strains of 0.005; furthermore, strengths have been retained after 100 hrs of air exposure at 723 K. These results represent substantial improvements over what has been previously accomplished with graphite fiber reinforced glass matrix composites.

From other data which have been obtained on graphite fiber reinforced glass matrix composites, the following conclusions can be made:

- the flexural strength of borosilicate glass matrix composites increases with temperature up to 875 K which is the softening point of the glass;
- the uniaxially reinforced composites exhibit surprisingly high values of fracture toughness only 40% less than that of a graphite reinforced epoxy composite;
- the composite strength is not reduced by flexural fatigue cycling or by short term thermal cycling between 383 and 833 K; and
- extremely low values of thermal expansion and attendant dimensional stability result from the properties of the composite components.

By suitable orientation of tapes, uniaxial, biaxial and multiaxially reinforced composites can be prepared in the graphite fiber reinforced glass matrix system.

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APPENDIX A

Summary of Graphite Fiber Reinforced Glass Matrix Composites Made

Table A1

Summary of Graphite Fiber Reinforced Glass Matrix Composites

Sample No.	Glass Type	Fiber Type	Hot Pressing Conditions Pressure (MPa)	Hot Pressing Conditions Temp. (K)	Density (kg/m^3)	Highest Density Achieved in Similar Composite (kg/m^3)
GL 10	7913	Thornel 75	13.8	1823	1585	2138
LB 11	↓	↓	↓	1873	1695	↓
12				1923	1605	
13				1823	1585	
53	7913+7740			1873	2138	
53B	7913			1873	1732	
90	7740	Celanese DG-102	13.8	1393	2011	2060
91	↓	↓	↓	1393	2046	↓
92				1388	2060	
93				1383	2043	
94				1298	1936	
95				1323	1997	
96				1348	1911	
97				1373	1969	
97B				1373	1980	
97C				1373	1969	
97D				1473	2025	
97E				↓	2049	
97F					Cracked	
97G					↓	
97H						
97I						
97J						
98	↓			1393	1969	
107	7913			1873		
108	7913			1923		
112	7913			2123	1375	
131	7740			1373	1952	2060
132	7740	↓	↓	1373	2000	2060
135	7740	Hercules HMS	13.8	1373	1960	1976
135B	↓	↓	↓	↓		↓
135C					1972	
135D						
135E					1976	
135F					1920	
135G					1939	
135H					1957	
135I					1955	
135J					1949	
135K					1943	
135L					1937	
135M					1955	
135N					1951	
135O	↓	↓	↓	↓	1958	↓

All samples with numbers lower than GC 175 are slurry A. Samples GC 175 through GC 294 are slurry B, higher numbered samples are slurry C. Exceptions are noted.

Table A1 (Cont'd).

Sample No.	Glass Type	Fiber Type	Hot Pressing Conditions Pressure (MPa)	Hot Pressing Conditions Temp. (K)	Density (kg/m^3)	Highest Density Achieved in Similar Composite (kg/m^3)
LB 136	7740	Hercules HMS	13.8	1373	1960	1977
137					1957	
138					1952	
139						
140						
157						
158					1977	
159						
171	1723			1393	1963.7	
172						
173					1948.9	
174						
147	7740	Hercules HTS	13.8	1373	1902	1902
148					1597	
148B					1858	
148C					1886	
148D					1865	
148E				1473	1800	
148F				1473		
149				1373		
150						
151						
152						
C2639-23	7740	Thornel 300	13.8	1373		2013
C2658-1,2				1373	1931	
GL 1-1,2				1498	1603	
2a,b				1873	1955	
3a,b				1923	2013	
4a,b				1823		
5a,b				1423		
6a,b				1323		
LB 75					1757	
78		Thornel 300S			1829	
79		Thornel 300	27.6			
80				1373		
81					1780	
82						
133		Thornel 300S	13.8		1566	
160				1393		
161						
161B					1700	
161C					1674	
161D					1640	
161E					1675	
161F					1673	
162					1823	
163					1829	
134				1373		

Table A1 (Cont'd)

Sample No.	Glass Type	Fiber Type	Hot Pressing Conditions Pressure (MPa)	Hot Pressing Conditions Temp. (K)	Density (kg/m^3)	Remarks
GC 200	7740	DG-102	13.8	1473		
201	↓	HMS	↓	↓		Biaxial
202		DG-102				
203		HMS				
204		HMS				
205	7740	DG-102	13.8	1473		Biaxial (Die Broke)
206	↓	HMS	↓	↓		↓
207		↓				
208						
209						Biaxial
210	7740	HMS	13.8	1473	1926	
211	↓	DG-102	↓	↓	1840	
212		300S				
213		300			1970	Biaxial
214		HMS				
215	7740	HMS	13.8	1473	1990	Biaxial, Annealed
216	↓	HMS	↓	↓	1980	
217		300 cloth				Failure
218		↓			1660	Biaxial
219					1689,1618	Biaxial
220					1638	Biaxial
221	7740	HTS	13.8	1473	1700	
222	↓	HTS	6.9	↓	1800	
223		DG-102	13.8			Failure
224		DG-102	13.8			Failure
225	7740+50% Ludox	HTS	13.8	1473	1840	
226	"	HTS	13.8	↓	1858	
227	7740	HMS	6.9		1950	Biaxial
228	↓	HTS	13.8		1890	
229a		HTS	13.8		1790	
229b		HTS	13.8		1820	
230a	7740	Ni Coated C	13.8	1473		
230b	↓	Ni Coated C	↓	↓		
231		Pitch		1523		
232	7940+25% Pyrex	HMS		1623	1733	
233	Vycor+20% Pyrex	HMS				
234	7740	HMS	6.9	1473		
235	7940+25% Pyrex	↓	13.8	1573		
236	7940+25% Pyrex		↓	1623	1684	
237	7940+4% Pyrex			1623	1173	
238	100 ml Ludox, 12.9 gm Pyrex			1673	1786	

Table A1 (Cont'd)

Sample No.	Glass Type	Fiber Type	Hot Pressing Conditions: Pressure (MPa)	Hot Pressing Conditions: Temp. (K)	Density (kg/m^3)	Remarks
GC 239	100 ml Ludox, 12.9 gm Pyrex	HMS	13.8	1673	2249	
241	"			1723	1996	
242	7940+5% Pyrex			1723	1575	
243	Vycor+5% Pyrex			1673		
244	Vycor+25% Pyrex			1673	1885	
247	"			1723	1902	
248	Vycor+10% Pyrex				1796	
249	"				1878	
250	"				1866	Not useful
251	7740					
252A					1582	
252B					2133	
254A	Ludox+5% Pyrex					
254B	"					
255	"					
256	7740			1473		53.7 v/o graphite
GC 257a	7740	HMS	6.1	1473		
b						
c						
258					2000	
259a						49.1 v/o graphite
b					1940	
c					1920	
271			13.8		1900	
272a			13.8			
b			13.8			
273	7740	HMS	13.8	1773		Die Broke
274				1773		
275				1473	1989	
277				1473	1989	
278			10.3	1473	1932	64.9 v/o graphite
279	7740	HMS	10.3	1473	1920	64.4 v/o graphite
280			4.1	1473	1918	60 v/o graphite
281			13.8	1473	1950	
282			13.8	1823		
283			13.8	1473	1977	
284	7740	HMS	13.8	1473		
285			13.8			
286			13.8			
287a			6.9			Biaxial
b			6.9			Biaxial
288	7740	HMS	13.8	1473	1970	Biaxial
289a					1978	
289b					1968	
289c					1966	
290						
291					1780	
292	7740+2% SiO_2	HTS				
293A	7740	HMS			1800	
293B					1690	
294A						
294B						

Table A1 (Cont'd)

Sample No.	Glass Type	Fiber Type	Hot Pressing Conditions Pressure (MPa)	Hot Pressing Conditions Temp. (K)	Density (kg/m^3)	Remarks
GC 295A	7740+2% SiO_2	HTS	13.8	1473	1760	
B					1770	
C					1790	
296A					1800	
B					1830	
C					1820	
297A					1814	
B					1820	
C					1790	
298A					1810	
B					1800	
C					1830	
299A					1790	
B					1830	
C					1800	
300A					1670	
B					1820	
C					1820	
301A			6.9		Broken	
B			6.9		Broken	
C			6.9		Broken	
302A			13.8		1660	
B			13.8		1540	
C			13.8		1720	
303A			6.9		1820	
B+					1829	
C					1828	
304A				1623	1820	
B				1623	1800	
C				1623	1820	
305A				1473	Broken	
B				1473	Broken	
C				1473	Broken	
306A	7740+2% SiO_2	Celanese	6.9	1473	1910	
B					1870	
C					1920	
307A					1780	
B					1840	
C					1820	
308A					1990	
B					1960	
C					1970	
309A	7740+2% SiO_2	Thornel Pitch	6.9	1623	2050	
B					2090	
C					2060	
310A					2100	
B					2100	
C					2050	

Table A1 (Cont'd)

Sample No.	Glass Type	Fiber Type	Hot Pressing Conditions Pressure (MPa)	Hot Pressing Conditions Temp. (K)	Density (kg/m^3)	Remarks
GC 311	7740+2% SiO_2	HMS	6.9	1623		
312B						
C						
313A						
B						
C						
314A						
B					1930	
C					1910	
315A					1880	
B					1850	
C					1890	
316A					1900	
B					1930	
C					1900	
317A					1920	
B				1673	1900	
C				1673	1920	
318A				1673	1890	
B				1623	1910	
C				1623	1900	
319A				1623	1930	
B				1573	1888	
C				1573	1900	
320A				1573	1860	
B				1523	1870	
C				1523	1860	
321A				1523	1860	
B				1473	1840	
C				1473	1840	
				1473	1850	
323A	7740+2% SiO_2	HMS	6.9	1623		No composite
B				1623		"
C				1623		"
326A				1723	1910	
B				1723	1920	
C				1723	1920	
327A				1773	1870	
B				1773	1870	
C				1773	1880	
328A				1723	1910	
B				1723	1900	
C				1723	1890	
329A				1743	1910	
B				1743	1850	
C				1743	1890	
330A	7740+2% SiO_2	Celanese Multi	6.9	1623	1990	
B					1940	
C					2000	
331A					1970	
B					1960	
C					1960	

Table A1 (Cont'd)

Sample No.	Glass Type	Fiber Type	Hot Pressing Conditions Pressure (MPa)	Hot Pressing Conditions Temp. (K)	Density (kg/m^3)	Remarks
GC 332A	9608	HMS	6.9	1623		Lost most glass
B	↓	↓	↓	1623		"
C				1623		"
333A				1548		Lacked glass
B				1548		Reacted with Mo
C				1548		"
336A	7740+2% SiO_2	Celanese Multi	6.9	1723	2010	
B	↓	↓	↓	↓	2020	
C					2030	
337A						
B					1870	
C					1970	
338A	7740+2% SiO_2	HMS	6.9	1723	1880	
B	↓	↓	↓	↓	1880	
C					1890	
339A					1890	
B					1880	
C					1890	
340A					1880	
B					1900	
C					1900	
341A	7740+2% SiO_2	HMS	6.9	1723	1900	
B	↓	↓	↓	↓	1890	
C					1850	
342A					1910	
B					1920	
C					1930	
343A					1910	
B					1920	
C					1930	
344A					1880	
B					1890	
C					1900	
356A	S	HMS	6.9	1723		Insufficient glass
B	↓	↓	↓	↓		"
C						"
357A					1850	
B					1860	
C					1900	
358A	1723	HMS	6.9	1723	1910	Much flash,
B	↓	↓	↓	↓	1910	samples
C					1930	unusable
359A					1940	Composite not
B					1910	fully infiltrated
C					2140	with glass
360A	7740+2% SiO_2	HMS	6.9	1623	1950	Biaxial
B	↓	↓	↓	↓	1950	"
C					1960	"

APPENDIX B

Properties of Selected Graphite Fiber Reinforced Glass Matrix Composites

Table B1

Flexural Strength of HMS Reinforced 7740
Slurry A

Sample Number	Thickness cm	Hot Pressing Temperature K	Type of Load Curve	Three-Point Flexural Strength MPa	psi x 10^3
LB 135 RC	0.152	1373		673	97.7
CB	0.142			663	96.2
LC	0.150			705	102.0
CC	0.124			734	106.0
TC	0.081			640	92.9
TR	0.084			705	102.0
TL	0.086			733	106.0
LB	0.084			746	108.0
RB	0.137			614	89.0
			Average	689	99.98
LB 135FRC	0.150	1473		1070	155.0
CB	0.150			1010	146.0
LC	0.173			1050	152.0
CC	0.150			1140	165.0
TC	0.152			903	131.0
TR	0.157			946	137.0
TL	0.160			698	101.0
LB	0.152			1050	152.0
RB	0.155			983	143.0
			Average	977	142.0

Table B2

Hercules HMS-10K Reinforced 7740 LB 139
Slurry A
3 Point Flexural Strength Tested at Temperature in Argon

Test Temperature (K)	Flexural Strength MPa	10^3 psi
295	863	125
295	785	114
773	793	115
823	1081	157
873	706	102
873	1292	187
923	1134	164
973	772	112
	347*	50.3*

*Specimen highly deformed so that this number is not strictly valid

C-2

Table B3

Flexural Strength of Celanese Graphite Fiber DG-102 Reinforced C.G.W. 7740 Glass Composite at Elevated Temperatures
Slurry A

Specimen	Temperature at Which Flexural Strength was Measured (K)	3-Point Flexural Strength Span 5.0 cm MPa	ksi
LB 98 BL	295	374	54.2
CR	295	250	36.2
TL	773	515	74.7
BR	773	481	69.7
CL	823	565	82
TR	873	196	28.4
TC	973	292	42.3
CC	973-908	305	44.3

Table B4

Thermal Cycling

HMS Reinforced 7740 Spec LB 135 G
Slurry A

Condition		4 Point Bend Strength MPa	10^3 psi	*Elastic Modulus GPa	10^6 psi
As Fabricated		896	130	185	26.8
		938	136	196	28.5
		800	116	201	29.2
	Average	876	127	194	28.2
After 20 Cycles**		917	133	196	28.5
		910	132	203	29.4
		834	121	189	27.4
	Average	889	129	196	28.4
After 100 Cycles***		786	114	174	25.2
		614	89	167	24.2
		758	110	185	26.9
	Average	717	104	175	25.4

*Tested with major and minor spans of 5 cm and 1.27 cm

**Cycled while in argon containing glass tube between 863-903 K and 383 K
Target temperature 833 K or annealing point of glass matrix

***The 100 cycles extended overnight with result that temperature exceeded target temperature (annealing point of glass matrix is 833 K or 1040°F) by 33K

Table B5

Four Point Flexural Fatigue
(Major and minor spans of 5 cm and 1.27 cm)
HMS Reinforced 7740 Spec LB 135 H
Slurry A

Condition	4 Point Bend Strength		Elastic Modulus	
	MPa	10^3 psi	GPa	10^6 psi
As Fabricated	548	79	200	29.0
	532	77	195	28.3
After 3 cycles between 484 and 48 MPa	325	47	185	26.8
After 20 cycles between 337 and 34 MPa	519	75	186	26.9
After 20 cycles between 390 and 39 MPa	658	95	194	28.1
After 20 cycles between 450 and 45 MPa	574	83	210	30.5
After 20 cycles between 520 and 52 MPa	638	92	208	30.1
After 100 cycles between 430 and 43 MPa	575	84	207	30.0
After 100 cycles between 445 and 44 MPa	573	83	201	29.1

Table B6

Four Point Flexural Strength Data for HMS Graphite Fiber Reinforced Glass Matrix Composite* (C.G.W. 7740 + SiO_2) Made from New Slurry C
Span 6.35 cm to 1.90 cm

Sample	Four Point Flexural Strength MPa	ksi	Flexural Modulus GPa	10^6 psi	% ε_f
GC 326 B3	896	130	195	28.3	0.43
B6	1131	164	144	21.0	0.62
B9	803	116	213	30.8	0.46
B11	931	135	207	30.0	0.48
C2	853	124	202	29.3	0.50
C5	950	138	211	30.6	0.45
C7	1105	160	217	31.5	0.53
C10	1041	151	206	29.9	0.67
Mean	964	140	199	28.9	0.52
Std Dev	118	17.1	23	3.3	0.085

*Hot pressed at 1723 K, 6.9 MPa pressure, 1 hr dwell time in argon

Table B7

Relation of Hot Pressing Pressure to Three Point Flexural Strength of HMS Graphite Fiber Reinforced 7740 Glass Matrix Composites
All Samples Made at 1473 K
Slurry B

GC-280 - 4.1 MPa

Sample	Three Point Flexural Strength MPa	ksi
TL	595	86.4
LC	553	80.2
LB	481	69.8
TC	387	56.5
CC	507	73.5
CB	471	68.3
RB	513	74.3
RC	489	70.9
TR	563	81.6
Avg	507	73.5

GC-257 - 6.1 MPa

Sample	Three Point Flexural Strength MPa	ksi
1	558	80.9
2	646	93.7
3	473	68.6
4	674	97.8
5	474	68.8
6	753	109
7	407	59.1
8	496	72.0
9	471	68.3
10	513	74.4
	548	79.5

GC-278 - 10.1 MPa

Sample	Three Point Flexural Strength MPa	ksi
LC	644	93.4
TR	585	84.8
RC	553	80.2
RB	644	93.5
TL	633	91.8
CB	785	114
TC	690	100
CC	552	80.0
LB	582	84.4
Avg	630	91.3

GC-281 - 13.8 MPa

Sample	Three Point Flexural Strength MPa	ksi
RB	965	140
RC	674	97.7
TR	688	99.8
CB	752	109
CC	786	114
TC	745	108
LB	793	115
LC	800	116
TL	660	95.7
	765	111

Table B8

Properties of Three Composite Samples of HMS-7740 Produced Simultaneously
(Hot Pressed at 1473 K, 13.8 MPa)
Slurry B

GC-289 - Top Sample			GC-289 - Center Sample			GC-289 - Bottom Sample		
	Three Point Flexural Strength			Three Point Flexural Strength			Three Point Flexural Strength	
Specimen	MPa	ksi	Specimen	MPa	ksi	Specimen	MPa	ksi
1	660	95.8	1	852	124	1	746	108
2	895	130	2	839	122	2	491	91.2
3	928	135	3	939	136	3	799	1.6
4	759	110	4	908	132	4	799	1.6
5	652	94.6	5	572	83.0	5	710	103
6	692	100	6	913	132	6	968	140
7	747	108	7	642	93.1	7	908	132
8	658	95.4	8	905	131	8	778	113
9	1030	149	9	680	98.6	9	774	112
10	757	110	10	819	127	10	841	123
Avg		113			118			113
Std Dev		18.9			19.0			18.5
Std Err		5.78			6.00			5.85

Effect of Hot Pressing Temperature on Three-Point Flexural Strength of HMS Fiber Reinforced-7740 Composites Made with New Slurry C at a Pressure of 6.9 MPa

GC 321 - 1473 K Hot Press
Three-Point
Flexural Strength

	MPa	ksi
A1	284	41.1
A2	284	41.2
A3	205	29.8
A4	203	29.5
A5	174	25.3
A6	227	32.9
A7	228	33.1
A8	267	39.1
A9	223	32.3
A10	278	40.3
A11	176	25.5
A12	148	21.4
Avg	225	32.6
Std Dev	46.3	6.71
Std Err	13.4	1.94

GC 320 - 1523 K Hot Press
Three-Point
Flexural Strength

	MPa	ksi
A1	372	54.0
A2	365	53.0
A3	419	60.7
A4	372	54.0
A5	509	73.8
A6	467	67.8
A7	391	56.7
A8	332	48.2
A9	441	63.9
A10	404	58.6
A11	302	43.7
A12	293	42.6
Avg	389	56.4
Std Dev	64.2	9.31
Std Err	18.5	2.69

GC 319 - 1573 K Hot Press
Three-Point
Flexural Strength

	MPa	ksi
C1	352	51.1
C2	381	55.3
C3	446	64.7
C4	350	50.7
C5	658	95.5
C6	609	88.3
C7	578	83.9
C8	615	89.1
C9	496	72.0
C10	417	60.5
C11	524	76.0
C12	508	73.7
Avg	494	71.7
Std Dev	106	15.4
Std Err	30.8	4.46

GC 318 - 1623 K Hot Press
Three-Point
Flexural Strength

	MPa	ksi
A1	767	111
A2	746	108
A3	628	91.0
A4	615	89.2
A5	515	74.7
A6	630	91.4
A7	637	92.5
A8	667	96.8
A9	456	66.1
A10	622	90.1
A11	682	98.9
A12	712	103
Avg	639	92.7
Std Dev	87.6	12.7
Std Err	18.5	2.68

GC 317 - 1673 K Hot Press
Three-Point
Flexural Strength

	MPa	ksi
A1	no result	
A2	873	127
A3	944	137
A4	1048	152
A5	903	131
A6	806	117
A7	812	118
A8	762	110
A9	782	113
A10	645	93.5
A11	778	113
A12	806	117
Avg	834	121
Std Dev	107	15.5
Std Err	32.2	4.67

GC 326 - 1723 K Hot Press
Three-Point
Flexural Strength

	MPa	ksi
A1	1110	162
A2	1150	166
A3	1240	180
A4	1170	170
A5	1060	153
A6	931	135
A7	835	121
A8	942	137
A9	1020	147
A10	823	119
A11	1040	150
A12	1070	155
Avg	1034	150
Std Dev	130	18.9
Std Err	37.6	5.46

GC 329 - 1743 K Hot Press
Three-Point
Flexural Strength

	MPa	ksi
A2	1097	159
A6	923	134
A8	737	107
A11	910	132
B2	1019	148
B6	1153	167
B8	1026	149
B11	1115	162
C2	706	102
C6	1061	154
C8	957	139
C11	1161	168
Avg	989	143
Std Dev	150	21.7
Std Err	43.2	6.27

GC 327 - 1773 K Hot Press
Three-Point Fl
Flexural Strength

	MPa	ksi
A4	644	93.5
A6	786	114
A8	644	93.5
A10	666	96.6
B4	702	102
B6	672	97.5
B8	813	118
B10	684	99.2
C4	978	142
C6	1236	179
C8	1085	157
C10	1000	145
Avg	825	120
Std Dev	200	289
Std Err	57.8	8.35

Table B10

Check of Consistency of Test Results Obtainable in Measuring the Three-Point Flexural Strength of HMS Fiber Reinforced-774- Composites Made With 7740 + 2% Silica Slurry C at a Temperature of 1623 K, 6.9 MPa Pressure

	GC 318			GC 312			GC 311	
	Three-Point Flexural Strength			Three-Point Flexural Strength			Three-Point Flexural Strength	
	MPa	ksi		MPa	ksi		MPa	ksi
A1	767	111	B1	565	81.9	A1	700	102
A2	746	108	B2	689	99.9	A2	755	110
A3	628	91.0	B3	623	90.4	A3	521	75.5
A4	615	89.2	B4	727	105	A4	563	81.7
A5	515	74.7	B5	668	96.9	A5	563	81.7
A6	630	91.4	B6	774	112	A6	691	100
A7	637	92.5	B7	466	67.7	A7	538	78.0
A8	667	96.8	B8	586	84.9	A8	642	93.1
A9	456	66.1	B9	818	119	A9	720	104
A10	622	90.1	B10	536	77.7	A10	556	80.6
A11	682	98.9	B11	635	92.1	A11	547	72.3
A12	712	103	B12	733	106	A12	642	93.1
Avg	639	92.7		651	94.5		616	89.3
Std Dev	87.6	12.7		103	14.9		87.9	12.6
Std Err	18.5	2.68		29.8	4.32		25.1	3.64

Table B11

Three Point Flexural Strength of Thornel Pitch VS 0032
Fiber Reinforced 7740 + 2% SiO_2 Glass Composite (GC-209)
Hot Pressed at 1623 K, 6.9 MPa, 1 Hr Dwell Time
Slurry B

Specimen	Three Point Flexural Strength	
	MPa	ksi
A1	539	78.2
A3	465	67.6
A5	491	71.2
A7	579	84.0
A9	399	57.8
A11	335	48.6
B1a	574	74.5
B3	396	57.4
B5	489	70.9
B7	523	75.8
B9	294	42.7
B11	349	50.6
Avg	448	65.0
Std Dev	95	13.8
Std Err	39	5.6

Table B12

Three Point Bend Data for Transversely Oriented Specimens

Specimen	Fiber	Lay-up	Max. Flex. Stress 10^3 psi	MPa	S/D*	Fracture
GC 208	HMS	90°	1.4	9.3	40	Tensile
	(4 plys in thickness)		1.3	9.1	40	"
	13.8 MPa		1.0	6.8	40	"
			2.0	13.6	40	"
		Avg	1.4	9.7		
GC 209	HMS	90°	1.8	12.7	10	Tensile
	(16 plys in thickness)		3.2	22.2	10	"
	13.8 MPa		1.4	9.5	10	"
		Avg	2.15	14.8		
GC 221**	HTS	90°	1.8	12.6	14	Tensile
	10 plys thick		0.7	4.7	14	"
			1.3	9.1	14	"
			1.6	11.2	14	"
			1.4	9.8	14	"
		Avg	1.4	9.5		
GC 222***	HTS	90°	2.1	14.7	12	Tensile
	10 plys thick		1.4	9.3	12	"
			1.8	12.1	12	"
			1.0	6.9	12	"
			2.6	18.0	12	"
		Avg	1.8	12.0		

*span-to-depth ratio for 3 point bend test
**fabricated using 13.8 MPa pressure
***fabricated using 6.9 MPa pressure

Table B13

Three Point Bend Data for
Thornel 300 Fabric Reinforced 7740 Glass
Slurry B

Specimen	Precleaned Fiber	Flexural Strength MPa	Flexural Strength ksi	Shear Strength MPa	Shear Strength ksi	S/D*
GC 218	No	99.6	14.4	2.24	0.32	5
		93.1	13.5	2.05	0.30	5
		80.4	11.7	1.81	0.26	5
		108.0	15.7	2.32	0.34	5
GC 219	No	94.8	13.8	5.6	0.81	8
		87.1	12.6	6.1	0.75	8
		48.4	7.0	3.0	0.44	8
		43.0	6.2	2.7	0.39	8
GC 220	Yes	105.0	15.2	3.3	0.48	16
		106.0	15.4	3.3	0.48	16
		102.0	14.8	1.6	0.23	16

*Span-to-depth ratio of test

Table B14

Oxidized Fiber Strength Loss

	HMS	HTS	Celanese DG-102
Vendor supplied fiber Average UTS (MPa)	2446	2873	1723
As-received average fiber UTS measured at UTRC (MPa)	2956	2777	2074
Average fiber strength after exposure to air at 823 K for 1 hr (MPa)	1550*	792*	1054*
% of fiber UTS lost based on UTRC measurements	48%	71%	49%
% weight loss of fiber after exposure to air at 823 K for 1 hr	20%	84%	16%

*Strength calculated based on original unexposed average fiber diameter

Table B15

Air Exposure of Graphite Fibers at 823 K for Several Lengths of Time (% Weight Loss)

Fiber	1 hour	2 hours	6 hours	Delivered Modulus & Strength GPa	MPa	Precursor
Hercules HTS	83.8	96.9	100	255	2873	PAN
Hercules HMS	19.8	no data	no data	351	2446	PAN
Celanese DG-102	16.5	32.3	85.2	530	1723	PAN
Thornel 50	15.5	26.4	56.1	393	2170	Rayon
Thornel Pitch Type	10.0	17.3	47.3	413	*944	Pitch

*Material currently shipped has strength greater than 1378 MPa

Table B16

Effect of Exposure to Air for 4 hrs at 833 K on the 3 Point Flexural Strength of HTS Graphite Fiber Reinforced 7740, Hot Pressed at 1473 K Slurry B

Specimen	Specimen Surface Condition	Specimen Condition		Three Point Flexural Strength MPa	ksi
GC 228	Exposed Fibers	As Fabricated		254	36.8
				214	31.1
				272	39.5
				274	39.7
			Avg	250	36.2
GC 228	Exposed Fibers	Oxidized		195	28.3
				211	30.7
				198	28.8
				299	43.3
				274	39.8
			Avg	236	34.2
GC 229	Glazed on Two Surfaces	As Fabricated		342	49.5
				254	36.8
				466	67.5
			Avg	354	51.3
GC 229	Glazed on Two Surfaces	Oxidized		382	55.4
				264	38.3
				303	44.0
			Afg	317	45.9

Table B17

Effect of Heat Treatment in Argon and Air on 3 Point Strength of Hercules HTS Graphite Fiber in 7740 Glass Matrix Hot Pressed at 1473 K
Slurry C

Specimen	Heat Treatment		3 Point Flexural Strength MPa	ksi
LB 148E-RB	none		344	49.9
-CB	none		338	49.0
-LC	none		384	55.7
		Avg	355	51.5
LB 148E-TR	4 hrs, 833 K, argon		396	57.5
-CC	4 hrs, 833 K, argon		337	48.8
-TL	4 hrs, 833 K, argon		438	63.5
		Avg	390	56.6
LB 148E-LB	4 hrs, 833 K, air		370	53.6
-RC	4 hrs, 833 K, air		318	46.2
-TC	4 hrs, 833 K, air		315	45.7
		Avg	334	48.5

Table B18

Effect of Heat Treatment in Vacuum and in Air on 3 Point Flexural Strength of Hercules HTS Graphite Fiber in C.G.W. 7740 (Pyrex) Glass Matrix 1473 K - Hot Pressed, Slurry B

Specimen	Heat Treatment		Three Point Flexural Strength MPa	ksi
GC 293A				
1	none		368	53.3
2	↓		311	45.0
3			408	59.2
4			339	49.1
		Avg	356	51.7
GC 293A				
1	4 hrs @ 833 K in air		345	50.0
2	↓		321	46.6
3			342	49.7
4			343	49.7
		Avg	338	49.0
GC 293A				
1	4 hrs @ 833 K in air		336	48.8
2	↓		361	52.3
3			448	65.0
4			302	43.8
		Avg	362	52.5
GC 293B				
1	none		412	59.7
2	↓		432	62.6
3			287	41.6
4			330	47.9
		Avg	365	53.0
GC 293B				
1	4 hrs @ 833 K in air		377	54.6
2	↓		322	46.6
3			300	43.6
4			272	39.4
		Avg	318	46.1
GC 293C				
1	4 hrs @ 833 K in vacuum		424	61.4
2	↓		333	48.3
3			271	39.2
		Avg	343	49.6

Table B19

Effect of Air Exposure at 813 K on the Three Point Flexural Strength and Weight Loss of HTS Graphite Fiber Reinforced 7740, GC 304, Pressed at 1623 K, Slurry C

Sample	Time in Air at 813 K hrs	Initial Weight gms	Final Weight gms	3 Point Flexural Strength After Exposure MPa	ksi
A2	0			766	111
A7				651	94.4
A12				681	98.7
B2				695	101
B7				695	101
B12				844	122
C2				789	114
C7				708	103
C12				749	109
			Avg	730	106
A1	24	1.920	1.745	530	76.9
A6		1.950	1.797	438	63.6
A11		1.900	1.736	514	74.5
*B1		1.747	1.558	435	63.1
B6		1.816	1.682	448	65.0
B11		1.799	1.644	492	71.3
*C1		2.018	1.737	304	44.0
C6		2.152	1.950	343	49.7
C11		2.136	1.903	357	51.9
	Avg	1.938	1.750	429	62.2
A4	100	1.923	1.401	137	19.9
A5		1.942	1.461	160	23.2
A9		1.915	1.409	120	17.4
B4		1.802	1.341	171	24.8
B5		1.784	1.296	93.2	13.5
B9		1.814	1.334	165	23.9
C4		2.130	1.500	88.4	12.8
C5		2.146	1.448	78.5	11.4
C9		2.137	1.340	42.1	6.1
	Avg	1.955	1.392	117	17

*Damaged sample. Damaged side closer to compression surface. All samples tested with 6.4 cm test span

Table B20

Effect of Air Exposure at 723 K on the Three Point Flexural Strength of HMS Graphite Fiber Reinforced 7740 + 2% Silica, GC 328, Pressed at 1723 K
Slurry C

Sample	Time in Air at 723 K hrs	Initial Weight gms	Final Weight gms	3 Point Flexural Strength After Exposure MPa	ksi
A2	0	-	-	867	125.7
A6				860	124.7
A8				1062	154.0
A12				1046	151.7
B2				1110	161.0
B6				1200	174.0
B8				1150	166.8
B12				911	132.2
C2				935	135.6
C6				995	144.2
C8				1140	165.3
C12				923	133.8
Avg				1016	147.4
A3	24	1.6885	1.678	956	139
A7		1.7125	1.7025	930	135
A9		1.7195	1.706	859	125
A11		-	-	1021	148
B3		1.852	1.8405	1074	156
B7		1.831	1.820	1237	179
B9		1.823	1.809	1230	178
B11		1.850	1.836	1039	151
C3		1.651	1.638	910	132
C7		1.651	1.6425	1096	159
C9		1.6475	1.638	1220	177
C11		1.663	1.654	973	141
Avg		1.735	1.725	1045	152
A1	100	1.7000	1.6565	1150	167
A4		1.6875	1.655	824	120
A5		1.7015	1.6715	757	110
A10		1.7365	1.710	1020	148
B1		1.849	1.806	840	122
B4		1.8315	1.801	796	115
B5		1.820	1.789	971	141
B10		1.835	1.8025	1070	155
C1		1.6515	1.6065	856	124
C4		1.650	1.6275	987	143
C5		1.646	1.622	971	141
C10		1.653	1.6255	1050	153
Avg		1.730	1.698	941	124

Table B21

Effect of Air Exposure at 813 K on Weight Loss and Flexural Strength of HMS Graphite Fiber Reinforced 7740 + 2% Silica, GC 326, Pressed at 1723 K and GC 327, Pressed at 1773 K Slurry C

Sample	Time in Air at 813 K hrs	Initial Weight gms	Final Weight gms	Three Point Flexural Strength MPa	ksi
GC 326					
Avg	0			1034	150
B1	24	1.687	1.590	867	126
B4		1.693	1.6155	982	142
B8		1.691	1.5685	748	109
B12		1.685	1.5755	818	119
C1		1.437	1.3575	925	134
C4		1.445	1.3775	986	143
C8		1.435	1.366	859	125
C12		1.4475	1.369	920	133
Avg		1.565	1.477	888	129
B2	100	1.6905	1.4825	698	101
B5		1.704	1.5165	610	88
B7		1.698	1.500	820	119
B10		1.706	1.458	674	98
C3		1.431	1.248	617	89
C6		1.431	1.262	754	109
C9		1.4365	1.242	703	102
C11		1.4495	1.252	703	102
Avg		1.568	1.370	697	101
GC 327					
Avg	0			825	120
A2	100	1.4525	1.170		
A3		1.534	1.282		
A9		1.501	1.248		
A11		1.502	1.255		
B2		1.722	1.417		
B3		1.731	1.478		
B9		1.724	1.480		
B11		1.715	1.453		
C2		1.7355	1.524		
C3		1.7475	1.5155		
C9		1.725	1.499		
C11		1.7175	1.496		
Avg		1.651	1.401		

Table B22

Improved Oxidation Resistance of HMS Fiber-7740 Composites
Made by Slurry C at 1673 K and 6.9 MPa
Compare Table B23

	As Made		After 24 hrs in Air @ 813 K			After 100 hrs in Air @ 813 K		
	GC 317 Three Point Flexural Strength		GC 317 Three Point Flexural Strength			GC 317 Three Point Flexural Strength		
	MPa	ksi		MPa	ksi		MPa	ksi
A1	no test data		C1	708	103	B1	511	74.2
A2	873	127	C2	677	98.2	B2	619	89.8
A3	944	137	C3	719	104	B3	544	78.9
A4	1048	152	C4	811	118	B4	605	87.7
A5	903	131	C5	820	119	B5	589	85.4
A6	806	117	C6	878	127	B6	635	92.1
A7	812	118	C7	798	116	B7	657	95.3
A8	762	110	C8	777	113	B8	672	97.4
A9	782	113	C9	705	102	B9	582	84.5
A10	645	93.5	C10	647	93.8	B10	642	93.1
A11	778	113	C11	625	90.6	B11	650	94.2
A12	806	117	C12	663	96.2	B12	559	81.1
Avg	834	121		738	107		605	87.8
Std Dev	107	15.5		80.0	11.6		49.4	7.17
Std Err	32.2	4.67		23.0	3.34		14.3	2.07

Table B23

Effect of Air Heat Treatment on 4 Point Flexural Strength
of Hercules HMS Graphite Fiber in 7740 Glass Matrix
Spans 1.25 cm and 5.0 cm
Slurry A

Specimen	Heat Treatment		4 Point Flexural Strength MPa	ksi	Modulus GPa	10^6 psi
LB 135T-LC	none		596	86.5	176	25.6
-BC	↓		699	101	187	27.1
-CC			594	86.1	168	24.4
-TC			487	70.7	186	27.0
-RB			475	66.3	178	25.8
		Avg	566	82.2	179	26.0
-LB	4 hrs, 833 K, air		345	50.0	175	25.4
-RC	↓		286	41.5	167	24.2
-TL			413	59.9	175	25.3
-TR			476	69.1	174	25.2
		Avg	380	55.3	173	25.0

Table B24

Effect of Heat Treatment in Argon on 4 Point Flexural Strength of Celanese DG-102 Graphite Fiber in 7740 Glass Matrix

Specimen	Heat Treatment		4 Point Flexural Strength MPa	ksi	Modulus GPa	10^6 psi
LB 97E-TL	none		239	34.7	354	51.4
-LC	↓		258	37.5	327	47.5
-LB			262	38.0	285	41.4
		Avg	253	36.7	322	46.8
LB 97E-TR	4 hrs, 833K, argon		289	41.9	277	40.2
-CR	↓		301	43.7	269	39.0
-BR			336	48.7	271	39.3
		Avg	308.7	44.8	272	39.5

Table B25

Apparent Failure to Improve Oxidation Resistance of Celanese DG-102 Graphite Fiber-7740 Glass Composites Made by Slurry C at 1623 K and 6.9 MPa
Compare Table B24

	As Made		After 24 hrs in Air @ 813 K		After 100 hrs in Air @ 813 K	
	GC 331 Three Point Flexural Strength		GC 331 Three Point Flexural Strength		GC 331 Three Point Flexural Strength	
	MPa	ksi	MPa	ksi	MPa	ksi
A1	221	32.1				
A2					112	16.2
A3			327	47.8		
A4	457	66.4				
A5					150	21.7
A6			277	40.2		
A7	533	77.4				
A8					164	23.7
A9			375	54.3		
A10	416	60.3				
A11					no test	
A12			117	16.9		
B1	351	50.9				
B2					28.0	4.06
B3			306	44.3		
B4	489	70.9				
B5					140	20.3
B6			284	41.2		
B7	451	65.4				
B8					129	18.6
B9			326	47.3		
B10	424	61.6				
B11					119	17.2
B12			291	42.2		
C1	330	47.9				
C2					254	36.8
C3			313	45.4		
C4	469	68.0				
C5					180	26.1
C6			330	47.8		
C7	409	59.4				
C8					148	21.4
C9			285	41.3		
C10	450	65.2				
C11					15.3	2.22
C12			340	49.4		
Avg	417	60.5	314	45.6	131	19.0
Std Dev	82.7	12.0	29.5	4.28	66.1	9.59
Std Err	23.9	3.47	8.89	1.29	19.9	2.89

Table B26

Apparent Failure to Improve Oxidation Resistance of Pitch Type Fiber-7740 Composites Made by New Process at 1623 K and 6.9 MPa
Slurry C

	As Made GC 309 - Thornel Pitch Type Graphite Fibers Three Point Flexural Strength		As Made GC 310 - Thornel Pitch Type Graphite Fibers Three Point Flexural Strength		After 100 hrs in Air @ 813 K GC 310 - Thornel Pitch Type Graphite Fibers Three Point Flexural Strength	
	MPa	ksi	MPa	ksi	MPa	ksi
B1	490	71.0	A1	539	78.2	A2	200	29.1
B3	520	75.4	A3	465	67.6	A4	248	36.0
B5	449	65.2	A5	491	71.2	A6	180	26.2
B7	431	62.6	A7	579	84.0	A8	295	42.9
B9	394	57.2	A9	399	57.8	A10	206	29.9
B11	327	47.5	A11	335	48.6	B2	146	21.1
C1	661	95.9	B1a	514	74.5	B4	32.6	4.74
C3	555	80.6	B3	396	57.4	B6	261	37.9
C5	546	79.2	B5	489	70.9	B8	196	28.4
C7	482	69.9	B7	523	75.8	B10	113	16.4
C9	245	35.6	B9	294	42.7	B12	200	29.0
C11	214	31.0	B11	349	50.6			
Avg	443	64.3		448	65.0		192	27.9
Std Dev	131	19.0		95.0	13.8		72.3	10.5
Std Err	37.7	5.47		38.8	5.63		21.9	3.18