AD-A077 638 UNITED TECHNOLOGIES RESEARCH CENTER EAST HARTFORD CONN F/G 11/4
PROGRAM TO STUDY SIC FIBER REINFORCED GLASS MATRIX COMPOSITES.(U)
AUG 79 J J BRENNAN N00014-78-C-0503
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PROGRAM TO STUDY SiC FIBER REINFORCED GLASS MATRIX COMPOSITES

LEVEL II

Prepared by
J.J. Brennan

ANNUAL REPORT

Contract N00014-78-C-0503

Project No. NR 032-589/5-05-78 (471)

for

Department of the Navy
Office of Naval Research
Arlington, VA 22217

August 15, 1979

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REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER
R79-914401-2 ✓

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
(6) PROGRAM TO STUDY SiC FIBER REINFORCED GLASS MATRIX COMPOSITES.

5. TYPE OF REPORT & PERIOD COVERED
(9) Annual Rep[redacted]t,
July [redacted]78 — July [redacted]79

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
(10) J. J. Brennan

(12) 36 (15)

8. CONTRACT OR GRANT NUMBER(s)
N00014-78-C-0503 new

9. PERFORMING ORGANIZATION NAME AND ADDRESS
United Technologies Research Center
East Hartford, CT 06108

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
(11) 15 Aug 79

11. CONTROLLING OFFICE NAME AND ADDRESS
Department of the Navy
Office of Naval Research
Arlington, VA 22217

12. REPORT DATE
August 15, 1979

13. NUMBER OF PAGES
31

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
(14) UTRC/R79-914401-2

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Glass-Ceramic Matrix Composites
SiC Fiber Reinforced Composites
High Temperature Composites

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

Glass-ceramic composites reinforced with SiC fibers have been fabricated that exhibit good strength properties from RT to 1000°C. In particular, a lithium-aluminum-silicate (LAS) matrix reinforced with SiC yarn has been shown to possess bend strengths of over 690 MPa (100 ksi) from RT to 800°C. However, the TiO_2 nucleating agent present in the usual LAS materials can cause matrix crystallization during hot-pressing and fiber-matrix interactions, making the Cont →

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UNCLASSIFIED 409 252

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#20. Cont'd

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fabrication of consistently high strength composites extremely difficult. The substitution of ZrO_2 for the TiO_2 appears to have eliminated this problem. Composites fabricated from SiC monofilament with a magnesium-aluminum-silicate (MAS) matrix have also exhibited high strengths from RT to 1000°C. Again, however, consistent fabrication of reproducibly high strength composites has been difficult due to lack of wetting and bonding between the SiC fibers and the matrix.

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Report R79-914401-2

Program to Study SiC Fiber Reinforced Glass Matrix Composites

ANNUAL REPORT

Contract N00014-78-C-0503

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Report R79-914401-2

Program to Study SiC Fiber Reinforced Glass Matrix Composites

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Program to Study SiC Fiber Reinforced Glass Matrix Composites

SUMMARY

Silicon carbide fiber reinforced glass-ceramic matrix composites have been investigated as a structural material for use in oxidizing environments to temperatures of 1000°C or greater. Two types of SiC fiber, a 10μ diameter yarn and a 140μ diameter monofilament, have been incorporated into matrices of both lithium aluminosilicate (LAS) and magnesium aluminosilicate (MAS) glass-ceramic by hot-pressing in the temperature range 1250-1500°C.

The results of studies dealing with the SiC yarn have shown that reactivity between the SiC yarn and the TiO_2 that is used as a nucleation agent in the commercial glass-ceramics investigated, causes degradation of the fiber reinforcement and poor composite properties for most compositions studied. The system of Corning 9617 LAS matrix with SiC yarn reinforcement can be fabricated into composite form that possesses bend strengths of over 690 MPa (100 ksi) from RT to 800°C. However, the fabrication of reproducibly high strength specimens is extremely difficult due to the aforementioned reactivity and the tendency of the 9617 glass-ceramic to crystallize during the hot-pressing cycle.

Recent tests of SiC yarn composites using a special batch of a Corning LAS material (Code 9608) that contains ZrO_2, instead of the usual TiO_2 as the nucleating agent, indicate that reproducibly high strength composites can be fabricated without reactivity or crystallization problems. This system is scheduled to be further evaluated.

Composites fabricated from SiC monofilament have, on occasion, exhibited relatively high strengths of greater than 550 MPa (80 ksi) from RT to 1000°C when fabricated with a magnesium aluminosilicate (MAS) matrix material. Fabrication difficulties in this system center on the lack of wetting and bonding between the fiber and matrix. To date, surface treatments of the SiC fiber have not been particularly successful in producing a well-bonded yet strong composite. While further fabrication studies and/or fiber surface treatments may improve this situation, it is felt that the large size of the SiC monofilament does not lend itself well to the reinforcement of a brittle matrix or to the fabrication of intricately shaped components. Thus, future work in glass-ceramic/SiC monofilament composites will be rather limited, compared to the SiC yarn composites which are felt to offer greater potential.

I. INTRODUCTION

The use of fiber reinforced resin and metal matrix composites for structural applications has, during the past 10-15 years, increased to the point where many of these systems, such as boron and graphite reinforced epoxy and boron reinforced aluminum, are now incorporated in commercially available products that range from advanced jet aircraft to sporting goods. The use of these composite materials has, in almost all cases, been restricted to applications that experience a maximum use temperature of no more than 300°C. During the past few years, however, the interest in composite materials that could extend this temperature capability has been stimulated by the results of several research programs dealing with glass matrix composites reinforced with either graphite (Refs. 1-4) or alumina fibers (Ref. 5). In all of these programs it was found that the use of fibers exhibiting high strength and stiffness was successful in reinforcing lower modulus glass matrices. The graphite fiber reinforced glass system demonstrated exceptionally high levels of strength, fatigue resistance and fracture toughness while also being susceptible to fiber oxidation during elevated temperature exposure. In contrast, the alumina fiber reinforced silica matrix composite was unaffected by exposure to temperature above 1000°C in air, however, the overall levels of strength and toughness attained were far less than those of the graphite reinforced glass system.

There have recently become available on the commercial market two new types of high temperature fibers based on silicon carbide. A SiC monofilament of 140μ (5.6 mil) diameter, that is fabricated by a chemical vapor deposition process on a carbon filament core, is now being produced in pilot plant quantities by the AVCO Systems Div., Lowell, MA. This fiber exhibits a UTS of up to 3450 MPa (500 ksi), has a temperature capability of over 1300°C, and is stable in oxidizing environments. It has a density of 3.2 gm/cc and an elastic modulus of 415 GPa (60×10^6 psi).

The second type of SiC fiber, recently synthesized by Yajima, et al (Ref. 6) in Japan, consists of continuous length SiC yarn that is produced from an organometallic polymer. The tows of yarn contain ~2000 fibers/tow with average fiber diameters of 10μ. The SiC fiber is highly flexible with an extremely smooth surface. The average strength of this fiber, as measured at UTRC, is 2060 MPa (300 ksi) with the fracture surfaces of the highest strength fibers indicating a dependence on surface flaws. Tensile strengths of up to 3450 MPa (500 ksi) have been reported for this fiber by the manufacturer with a use temperature of up to 1300°C. With its similarity to graphite yarn, this fiber can be incorporated into glass matrices by using the processes already developed for the graphite-glass composites. The SiC yarn density is approximately 2.7 gms/cc and the elastic modulus is 221 GPa (31×10^6 psi).

From the results of a study at UTRC (Ref. 7) on the SiC fiber reinforced glass matrix composite system, it was demonstrated that a material with excellent mechanical properties up to 600°C could be achieved. The flexure strength, elastic modulus, and fracture toughness values achieved for both SiC monofilament and SiC yarn reinforced Corning 7740 (Pyrex) borosilicate glass are summarized in Table I. The SiC reinforced glass system can provide flexural strengths equivalent to those obtainable with graphite fiber reinforced glass and at the same time be unaffected by exposure to air at elevated temperatures. However, to fully utilize the high temperature potential of the SiC fiber reinforcement, a matrix material must be found that will allow a composite use temperature of 1000°C or greater. It is towards this goal that the current program is aimed, with the first year of effort as reported herein concentrating on the development of fabrication parameters that will result in complete densification of a high temperature glass or glass-ceramic matrix around SiC monofilament and/or SiC yarn reinforcement.

II. TECHNICAL DISCUSSION

A. SiC Yarn/Glass-Ceramic Matrix Composites

1. Materials

The types of glass matrices available for use above 1000°C are rather limited. The choice is essentially between high silica glasses such as Corning 7930 (Vycor), fused silica, titanium silicate glasses (Corning 7971), and glass-ceramics based either on the lithium aluminosilicate (LAS) system, or on the magnesium aluminosilicate (MAS) system. Due to the high viscosity of the high silica and the titanium silicate glasses at reasonable hot pressing temperatures (<1400°C) and their very low thermal expansion coefficients, it was decided to concentrate efforts on the glass-ceramic materials.

Glass-ceramic materials could offer advantages as a matrix for SiC composites over the high silica and titanium silicate glasses in that they have thermal expansion coefficients more closely matching that of SiC than do the high temperature glasses. They also offer the possibility of being fabricated in the glassy state where the viscosity may be low enough to permit complete densification after which they can be "ceramed" or transformed into the crystalline state. Once transformed into the crystalline state, glass-ceramics when reinforced with SiC fibers could exhibit a use temperature of up to 1200°C.

Five different glass-ceramic matrices are being investigated in combination with the SiC yarn. Four of these are Corning Glass Works products; 9608, with either TiO_2 or ZrO_2 as the nucleating agent, and 9617 which are based on the lithium aluminosilicate (LAS) type of material, and 9606 which is primarily a magnesium aluminosilicate (MAS). An essentially phase-pure LAS material of composition $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ (β-spodumene) was obtained from Research Organic/Inorganic Chemical Corp. in crystalline powder form (Cat. #A1-95) and has been used to fabricate a few composites.

These matrix materials have been characterized at UTRC by chemical analysis, X-ray diffraction, and, in the case of three of the Corning materials which were received in sheet form in the crystalline or "ceramed" state, for thermal expansion coefficient. The results of these analyses are presented in Table II. It is apparent that the Corning materials are rather complex combinations of Li, Mg, Al, Ti (or Zr), Zn, Si, and oxygen and, although the phase compositions and thermal expansion coefficients are those common to the as-received materials, depending on the thermal history of the material, many different phases with varying thermal and mechanical properties could be formed. The TiO_2 or ZrO_2 in these materials is present as a nucleating agent for crystallization. The normal nucleating agent in Corning glass-ceramics is TiO_2. The batch of 9608 with ZrO_2 as the nucleating agent was obtained on special order. A detailed discussion of glass-ceramic materials is not appropriate here, but can be found in "Glass-Ceramics" by P. W. McMillan (Ref. 8).

Since all but one of the glass-ceramic materials investigated were received in the crystalline state, it was necessary to melt them into a glassy form and subsequently crush the glasses into fine -325 mesh powder. Melting of broken pieces of the Corning materials was carried out in Pt crucibles in air at temperatures of 1275 to 1425°C. X-ray diffraction analysis of melted material was utilized in order to insure that the materials were completely glassy. It was found that the volatile constituents such as Li and Na were usually slightly reduced in amount after the melting procedure. The melting points of the various glass-ceramics were determined to be approximately 1250°C for the 9617 and 9608 with TiO_2 additive LAS materials, 1350°C for the LAS 9608 plus ZrO_2 additive and the MAS 9606, and 1425°C for the pure β-spodumene (Al-95).

The silicon carbide (SiC) fiber, produced by Sumitomo Shoji, Inc., was obtained for use under this program in the form of tows of yarn with ~2000 fibers/tow with average fiber diameters of 10μ. Initially, the SiC tows were approximately one meter in length and it was not until March 1979 that tows of continuous length were received. The continuous length (~500 m) fiber tows contain only 250 fibers/tow.

2. Composite Fabrication

The SiC yarn/glass-ceramic composites were fabricated by passing the SiC yarn through an agitated slurry of the glass powder and isopropyl alcohol, drying the tape and then cutting the tapes into the appropriate length to fit the hot-pressing die. With the receipt of the continuous length SiC yarn in March 1979, this step became much easier than with the one meter length tows previously used. After the tapes were cut to length, sufficient tape was stacked in the die to obtain the desired thickness composite and then the assembly was hot-pressed in vacuum at temperatures of 1100°C to 1550°C, times of 10 min to 1 hr, and pressures of 6.9 MPa (1000 psi) to 13.8 MPa (2000 psi). The resulting composites were 7 cm (2 3/4") long by 1.5 cm (5/8") wide with thicknesses ranging from 1.9 mm (.075") to 5.1 mm (.200"). The pressed composites were then weighed and measured for density determinations, cut lengthwise into three strips, and tested in 3-pt bending at temperatures from 20°C (RT) to 1000°C. Pieces of each composite were also examined metallographically and by X-ray diffraction in order to determine the amounts of glassy and crystalline phases present after the hot-pressing step.

3. Composite Properties

a. Corning 9617/SiC Yarn Composites

Corning 9617 type LAS glass-ceramic is used commercially as cook tops on kitchen stoves. As can be seen from Table II, its composition and crystalline phase structure are very similar to the LAS Corning 9608 material, which is used primarily as cooking ware, i.e. Corningware dishes and pans. The 9617 material was received in the form of crystallized flat plates. The plates were broken up, melted in a Pt crucible at 1300°C, and then crushed to -325 mesh both by hand in a mortar and pestle (carefully removing any Fe contaminants with a magnet), and by milling with WC balls in plastic jars for periods to time up to 48 hrs. The plastic pickup was removed by heating the milled powder to 600°C in air for 1 hr. The WC milling was instituted for two reasons. The first was that hand grinding is a very slow process and quite labor intensive. The second was that, from work on graphite/glass composites, it was found that milled powder had a much smaller average particle size and thus resulted in a better distribution of powder around the fibers when pulled through the glass powder slurry. Figure 1 shows a glass-ceramic powder (9606) in the glassy state that has been ground by hand and then passed through a -325 mesh screen (Fig. 1a) and the same powder after milling rather coarse -100 mesh material for 48 hrs (Fig. 1b). The largest particle size for the hand ground powder is ~40μ while the milled powder is ~10μ or less.

Approximately twenty hot-pressings were done with the 9617/SiC yarn in the temperature range 1200 to 1350°C. These samples were then tested in 3-pt bending at RT, 700, 800, 900 and 1000°C. The results of these tests, along with the results for as-received Corning 9617, are shown in Fig. 2. It can be seen that the strength of 9617/SiC yarn composites varies considerably, apparently due to the amount of matrix crystallization that occurs during the hot-pressing step. It was found that some of the 9617/SiC yarn composites that were hot-pressed at 1250°C, contained a completely glassy matrix after pressing. In the as-pressed condition, this material exhibited a RT strength of 790 MPa (~115 ksi), an 800°C strength of 890 MPa (129 ksi), and a 1000°C strength of 55 MPa (8 ksi), as represented by the top curve in Fig. 2.

A cross-section of the 9617/SiC yarn composite hot-pressed at 1250°C is shown in Fig. 3. A high fiber volume fraction is evident along with very good penetration of the glass between fibers. Small white flecks are evident in the matrix and appear to be emanating in most instances from the fiber-matrix interface. From electron microprobe examination, these white particles were shown to be very high in Ti. X-ray diffraction analysis of the 1250°C hot-pressed composite crushed to a fine powder revealed that the matrix was completely glassy. Incidentally, the SiC showed only a very broad, rounded peak at a d spacing of ~2.50, which corresponds to the highest intensity peak for α-SiC, indicating that the SiC yarn is not entirely crystalline but contains a substantial amount of amorphous SiC.

It was found to be very difficult to repeat the results of the 1250°C pressing. A great many samples hot-pressed from 1250 to 1350°C resulted in a partially crystalline matrix (β-spodumene) after pressing and exhibited strengths in the 400-480 MPa (60-70 ksi) range from RT to 800°C, falling to 138 MPa (20 ksi) at 1000°C.

When the 9617 matrix powder was subjected to the WC milling procedure, and then consolidated with SiC yarn at either 1250, 1275, or 1300°C, the resulting composite matrix was very high in crystalline β-spodumene, with bend strengths in the 200-280 MPa (30-40 ksi) range at RT and at 1000°C. Figure 4 shows a cross section of a WC milled 9617/SiC yarn composite hot-pressed at 1250°C that exhibited a RT bend strength of only 29 ksi (193 MPa). The matrix appears somewhat crystalline, confirming X-ray observations, and it appears there may be a slight reaction between the fibers and matrix. Fracture surfaces of WC milled 9617/SiC yarn composites show very little evidence of fiber pullout. It appears that the fine particle size, i.e. greater surface area, of the WC milled 9617 powder leads to greater nucleation of crystalline phases during the hot-pressing procedure and/or the small amount of WC pickup during milling (~1 wt %) is acting as a nucleating agent.

Electron microprobe examination of a WC milled composite of low strength and of the sample hot-pressed at 1250°C that exhibited very high strength showed that in both samples there was a high concentration of Ti around the SiC fibers, as shown in Figs. 5 and 6. It appears, in fact, that the Ti concentration is even higher around the fibers of the higher strength composite. The difference in fiber diameter between the two specimens is due to the slightly larger size of the continuous SiC yarn used in the WC milled 9617 composite over the short length tows of SiC used previously for the sample in Fig. 5. This slight difference in fiber diameter is not responsible for the observed property differences since the 1 meter tows were also used with WC milled 9617 powder with the same results. No concentration of any other element in the 9617 powder around the SiC fibers was observed.

Although crystallization during the hot-pressing step apparently leads to poor composite properties, a sample of completely glassy 9617/SiC yarn composite, cut from the previously discussed specimen with high strength (790 MPa), that was "ceramed" according to a procedure obtained from Corning, exhibited a RT strength of 820 MPa (119 ksi). The "ceraming" or nucleation and crystal growth schedule followed was a 780°C hold for 2 hrs, followed by a 250°C/hr uprate to 1140°C with a hold at 1140°C of 1 hr. This schedule conducted on a piece of glassy 9617 resulted in essentially complete conversion to β-spodumene, however, the 9617/SiC yarn composite was only about 50% converted. It is apparent that the "ceraming" schedule for 9617/SiC composites may not be the same as for monolithic 9617 material.

b. Corning 9608/SiC Yarn Composites

Corning 9608 in ceramic form was obtained from Corning Glass Works, melted at temperatures of 1300-1400°C, ground into -325 mesh powder by hand in an iron mortar and pestle and by milling in WC, and made into tapes with the SiC yarn, as described in a previous section. Approximately 25 composites were hot-pressed at temperatures of 1150°C to 1350°C, pressures of 3.5 - 13.8 MPa (500-2000 psi), and times of 10-60 min. Composites hot-pressed below 1300 C did not consolidate and exhibited very poor properties. Composites hot-pressed above 1300°C could be pressed to full density but in all cases the matrix was primarily crystalline (β-spodumene) after hot-pressing. In addition, as shown in Fig. 7, a white reaction product around the SiC fibers was present in areas throughout each composite. All 9608/SiC composite samples exhibited bend strengths of between 172 MPa (25 ksi) and 275 MPa (40 ksi) from RT to ~1000°C with very little fiber pullout during fracture.

Figure 8 shows the fracture surfaces of a 9617/SiC composite that exhibited high strength and a large amount of fiber pullout and a 9608/SiC composite hot-pressed at 1325°C that shows little or no fiber pullout and exhibited a very poor RT bend strength of 214 MPa (31 ksi). It appears that either the fibers in the 9608 composite are very weak or that the fiber-matrix bond is very strong, or both.

During melting of the 9608 material into a glassy form, it was noticed that while both the 9608 and 9617 materials became glassy at ~1250-1275°C, the 9608 glass was much more viscous than the 9617 glass at the same temperature. SiC yarn composites fabricated with the 9608 powder did not exhibit any "flash" or exudation of matrix material up the die walls until temperatures of 1300°C or greater, while the 9617/SiC yarn composites exhibited flashing at 1250°C. The flashing or high fluidity of the matrix material appears to be necessary for complete matrix penetration around the small SiC filaments. This has been observed in previous work on SiC or graphite yarn/borosilicate glass composites, as well.

It is evident that at the hot-pressing temperature of 1300°C or greater that is necessary to consolidate the 9608/SiC yarn composites, crystallization of the matrix occurs as well as a reaction between the matrix and fibers. The matrix crystallization occurs whether hand ground, i.e. large particle size, or milled 9608 glass powder is used. The reaction product has been identified as being very high in Ti and is most likely a titanium silicide, probably Ti_3Si_5.

Although the Ti content of 9608 and 9617 glass-ceramics is very similar (~2.6 wt %), the higher hot-pressing temperature necessary to consolidate the 9608/SiC yarn composites may be responsible for the greater fiber/matrix reaction observed in this system. Crystallization of the matrix during the hot-pressing step may occur due to nucleation of β-spodumene crystals at the high Ti concentration at the fiber/matrix interface. As has been shown for the 9617/SiC composite that had a glassy matrix and high strength, Ti concentration at the interface also occurred, so that the cause of nucleation may be more subtle than just concentration of Ti. However, completely glassy matrices after hot-pressing of the 9617 material are infrequently obtained. Although not completely understood, it is apparent that glass-ceramics containing Ti as a nucleating agent cannot be used with SiC yarn to form a useful composite if the hot-pressing temperataure for consolidation is greater than 1250-1275°C. The normal 9608 matrix material is then not a viable candidate; nor is the 9606 MAS material as will be shown in a later section. The 9617 LAS glass-ceramic is a viable candidate but, as has been previously shown, is difficult to fabricate in the glassy state. It would be preferable to investigate glass-ceramic materials that contain less reactive nucleating agents (ZrO_2, P_2O_5, TaO_2, etc) but still exhibit compatible thermal expansion coefficients with the SiC yarn.

c. Corning 9608 + ZrO_2/SiC Yarn Composites

An experimental batch of Corning 9608 material was obtained from Corning Glass Works that contained ZrO_2 as a nucleating agent rather than the usual TiO_2. This material was received in powder form in the glassy state so no processing needed to be done prior to composite fabrication. To date, seven composite samples have been hot-pressed at temperatures of 1250°C to 1550°C for 15 min under an applied pressure of 6.9 MPa (1000 psi).

The results of RT 3-pt bend tests on these samples are presented in Fig. 9. Samples pressed below 1350°C did not consolidate completely but still exhibited bend strengths greater than the 9608 (TiO_2)/SiC yarn composites that were completely consolidated. Samples pressed at temperatures between 1350 and 1500°C exhibited average strengths of ~550 MPa (80 ksi) and a large amount of fiber pullout on the fracture surface, similar to that observed previously for the few 9617/SiC yarn composites that did not crystallize during hot pressing.

X-ray diffraction analysis indicated that the composites pressed at temperatures from 1350-1500°C contained completely glassy matrices. Some crystallization was noted for the sample pressed at 1550°C, but it could not be identified. A typical cross section is shown in Fig. 10 for a sample pressed at 1450°C. No fiber-matrix interaction can be seen.

It is apparent that the TiO_2 nucleating agent present in the normal 9608 and 9617 LAS glass-ceramics can lead to fiber-matrix interaction under most circumstances, and while high strength 9617/SiC yarn composites have been fabricated, the control of fiber-matrix reactivity is extremely difficult if not impossible. The 9608 glass-ceramic with ZrO_2 nucleating agent, on the other hand, appears to allow the reproducible fabrication of SiC yarn composites. While the RT strength of these composites is not quite as high as obtained previously for a very limited number of 9617/SiC composites, the fracture mode and microstructure obtained are extremely promising. Future plans call for the fabrication of larger (7.5 x 7.5 cm) composite plates so that a large number of samples from the same pressing can be evaluated for flexural strength from RT to 1200°C, both in the as-pressed condition and after crystallization of β-spodumene in the LAS matrix.

d. Corning 9606/SiC Yarn Composites

Corning 9606 MAS glass-ceramic is used commercially as radomes and nose cones for missiles and is being considered for use as a ceramic heat exchanger material. Although the measured thermal expansion coefficient of this material is somewhat higher ($43 \times 10^{-7}/^{\circ}C$, RT→800°C) than the measured coefficient for the SiC yarn [($\sim 31 \times 10^{-7}/^{\circ}C$, RT→600°C), as determined from SiC/borosilicate glass composite measurements], and thus the matrix would be expected to be in a state of residual tension after pressing, it was decided to fabricate and evaluate composites in the 9606/SiC yarn system.

From melting experiments to form the glass from the crystalline as-received 9606 plate, it was found that a temperature of 1375°C was necessary to form a glass. The glassy material, however, was very fluid compared to glassy 9617 and 9608 at the same temperature. Thus, hot-pressings of 9606/SiC yarn composites were conducted from 1300 to 1450°C, 6.9 MPa (1 ksi) to 13.8 MPa (2 ksi), 20 min, in vacuum. Composites hot-pressed at 1300-1350°C did not consolidate and therefore were not evaluated further. AT 1375°C, good consolidation was achieved with extensive "flash" of matrix material up the die walls. However, the strength of the composite was very low, being 109 MPa (15.8 ksi) at RT and 119 MPa (17.3 ksi) at 1000°C, with very little or no fiber pullout occurring. Metallographic examination of the composite showed that there was extensive reaction between the fibers and matrix, as shown in Fig. 11a. Figure 11b shows a reacted fiber on the fracture surface of the sample broken at RT. The extensive reaction product visible is a titanium silicide. In addition to the fiber/matrix reaction, the 9606 matrix was essentially completely crystallized into cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) plus cristobalite ($SiO_2$). It is apparent that the 9606 MAS glass-ceramic with its relatively large amount of Ti and high melting point is not a compatible matrix for SiC yarn composites.

e. β-Spodumene ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$)/SiC Yarn Composites

A sample of β-spodumene -325 mesh crystalline powder was purchased from Research Organic/Inorganic, Inc. Part of the powder was melted into glass and then reground by hand to -325 mesh. During melting of the crystalline powder, it was noticed that a temperature of 1425-1450°C was necessary in order to form a completely glassy material, in agreement with current phase diagrams. Composites were fabricated with SiC yarn using both the crystalline and glassy powders.

None of the composites fabricated would densify until a temperature of 1425°C was reached. At this temperature, no gross reaction between fibers and matrix was observed; however, the fibers were bonded very strongly to the matrix and there was an extensive network of cracks throughout the matrix. These cracks, when viewed perpendicular to the fiber direction, were not deflected by the fibers but passed right through them. Consequently, the RT bend strength of the composite was quite low at 130 MPa (19 ksi).

The crack network in the β-spodumene/SiC yarn composite is very similar to that noticed previously for SiC yarn composites with a high silica (96%) glass matrix. Both the β-spodumene and the high silica matrices exhibit very low thermal expansion coefficients ($\sim 10 \times 10^{-7}/^{\circ}C$) compared to the SiC yarn ($\sim 31 \times 10^{-7}/^{\circ}C$) and, on cooling from the fabrication temperature, can put the fibers in considerable residual tension and the matrix in compression. It appears that, in the case of the pure β-spodumene matrix, the SiC fibers are fracturing in tension during cooling and, being very well bonded to the matrix, propagating the crack through the matrix as well. Pure β-spodumene, thus, does not appear to be a viable candidate matrix for SiC yarn composites.

B. SiC Monofilament/Glass-Ceramic Matrix Composites

1. Materials

The SiC monofilament used in this study was obtained in continuous length (~10,000 m) from the AVCO Systems Div., Lowell, MA. This fiber is 140μ (5.6 mils) in diameter and is fabricated by chemical vapor deposition onto a carbon filament core. The tensile strength of the fiber, as measured at UTRC, averages 2420 MPa (350 ksi) at RT. This is considerably less than the 3450 MPa (500 ksi) claimed by the manufacturer.

The matrix materials investigated in combination with the SiC monofilament consisted of the two Corning LAS materials, 9608 and 9617, and the MAS 9606. The properties of these materials have been described previously.

2. Composite Fabrication

The steps in fabricating a SiC monofilament/glass-ceramic composite consisted of winding the SiC fiber with the desired spacing on a drum, bonding it together at periodic intervals with polystyrene, and then cutting the fiber arrays into individual tapes. The tapes are then stacked in the hot-press die to form the composite by alternating a SiC tape with a layer of glass-ceramic powder. The relative number of tapes and amount of powder was set so that a composite of ~50 vol % fiber would result after pressing to a composite thickness of 2.0 mm (0.080"). The thickness was controlled by using 2 mm moly stops at each end of the die cavity. After pressing the composites were examined visually, weighed and measured for density determinations, and cut into two strips for bend testing.

3. Composite Properties

a. Corning 9617 and 9608/SiC Monofilament Composites

Both of these LAS materials were used to fabricate composites with SiC monofilament. At hot-pressing temperatures of ~1200°C or lower the LAS materials apparently crystallized during heat-up and would not consolidate upon application of pressure. At ~1250°C, the LAS materials became glassy and, upon application of pressure, flowed up the die walls. The LAS matrix that was left in the composite did not wet the SiC fibers with the result being a rather porous composite with many bare SiC fibers. Since the thermal expansion coefficient of the SiC fibers was measured from SiC/borosilicate glass composites as being $\sim 47 \times 10^{-7}/^{\circ}C$ from RT→800°C, it was felt that the MAS 9606 glass-ceramic would be a better matrix candidate, since its thermal expansion coefficient was measured as $43 \times 10^{-7}/^{\circ}C$. Thus, no further work was performed on LAS/SiC monofilament composites.

b. Corning 9606/SiC Monofilament Composites

Approximately 20 9606/SiC monofilament composites have been fabricated at temperatures of 1150-1450°C. Below ~1325°C, the 9606 matrix material would not consolidate as it had crystallized during heat-up in the hot-press. At ~1350°C, the 9606 material melts to become a very fluid glass, as described in a previous section. While the 9606 wets the SiC fibers better than the 9608 and 9617 materials, loss of the matrix from the composite can sometimes be a problem. A well consolidated 9606/SiC monofilament composite hot-pressed at 1350°C is shown in Fig. 12. On cooling, the 9606 material always becomes highly crystalline (cordierite + cristobalite), as can be seen in Fig. 12.

The 3-pt bend strength vs temperature of the best 9606/SiC composites fabricated to date is shown in Fig. 13, along with the strength of monolithic Corning 9606. The composite strength remains essentially constant from RT to 1000°C. An attempt was made to completely crystallize the matrix by subjecting the composite to the "ceraming" treatment recommended by Corning for the 9606 material. This heat-treatment in air consists of a 2 hr hold at 820°C, a heat-up to 1260°C at 60°C/hr, and then a 3 hr hold at 1260°C. The resultant 9606 matrix was essentially identical to that before the heat treatment, as shown in Fig. 14. However, the carbon core of the SiC fibers had disappeared due to oxidation. The RT bend strength of this composite was only 48 ksi (350 MPa), so that the oxidation of the SiC fiber core apparently was detrimental to the strength of the fibers.

As in the case of the 9617/SiC yarn composites, the 9606/SiC monofilament composite results were extremely variable from run to run. While reaction between the SiC yarn and the 9617 matrix is a problem in that system, the lack of wetting and bonding between the 9606 matrix and SiC monofilament is the major problem in this system. Since the SiC monofilament is supplied from AVCO with a carbon rich surface layer, various heat treatments of the fiber were conducted in order to remove this layer and possibly form a thin oxide coating in an attempt to improve the wetting behavior.

The SiC fibers were slowly pulled through a tube furnace such that the fiber was heated to temperatures of 800, 900, 1200 and 1300°C for a period of ~1 min. The color of the fibers heated to 800 and 900°C changed from black to blue and the surface became nonconducting. The fibers heated to 1200 and 1300°C became greenish in appearance. No change in strength of the fibers was observed except at 1300°C, where the average fiber strength decreased to 1900 MPa (275 ksi) from the as-received strength of 2400 MPa (350 ksi).

Composites fabricated from the 800°C and 900°C heat-treated fibers did not exhibit any change in wetting characteristics from as-received fibers. Bare SiC fibers on the edge of the composite were still in evidence with fracture of the composite due to matrix cracking and interfacial splitting between fibers and matrix. Composites fabricated from both the 1200 and 1300°C heat-treated fibers exhibited good wetting characteristics with no bare fibers evident in the as-pressed condition. However, the RT bend strength of these composites was a very low 138-207 MPa (20-30 ksi) with very little fiber pullout evident on the fracture surface. The fibers appear to have become degraded during pressing.

4. Conclusions

From the work done during the first year of this program, it has been demonstrated that SiC/glass-ceramic composites can be fabricated that exhibit good strength properties from RT to 900-1000°C. The system of 9617 LAS matrix with SiC yarn reinforcement has been shown to possess bend strengths of over 690 MPa (100 ksi) from RT to 800°C, with the potential of increasing this temperature capability to ~1000°C. However, due to the tendency of the 9617 glass-ceramic matrix to crystallize during the hot-pressing cycle, and the reactivity of the SiC yarn with titanium additives in the matrix, the fabrication of consistently high strength composites is extremely difficult. The LAS 9608 material with ZrO_2 nucleating agent, on the other hand, shows excellent promise for producing a high strength composite with SiC yarn without reactivity or crystallization problems during fabrication. This system will be evaluated further during the second year of the program.

Composites fabricated from SiC monofilament have, on occasion, exhibited relatively high strengths of greater than 550 MPa (80 ksi) from RT to 1000°C when fabricated with the MAS 9606 matrix material. Fabrication difficulties in this system center on the lack of wetting and bonding between the fiber and matrix. To date, surface treatments of the SiC fiber have not been particularly successful in producing a well-bonded yet strong composite. While further fabrication studies and/or fiber surface treatments may improve this situation, it is felt that the large size of the SiC monofilament does not lend itself well to the reinforcement of a brittle matrix. The large SiC fibers can act as stress-concentrating flaws, especially if they intersect the surface under stress, thus limiting the usable strength of the composite to the stress at which the matrix strain-to-failure occurs. Future work in glass-ceramic/SiC monofilament composites shall be rather limited, with effort concentrated at improving the bond formation at the SiC/matrix interface.

ACKNOWLEDGEMENTS

I would like to thank Dr. Kenneth Chyung and Mr. Richard Mace of Corning Glass Works for helpful suggestions and samples.

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Table I

Properties of SiC Fiber Reinforced 7740 Glass

	Monofilament		Yarn
Fiber Content (Vol %)	35	65	40
Density (gm/cm^3)	2.6	2.9	2.4
Axial Flexural Strength (MPa)			
22°C	650	830	290
350°C	-	930	360
600°C	825	1240	520
22°C Axial Elastic Modulus (GPa)	185	290	120
Axial Fracture Toughness (MN/m$^{3/2}$)			
22°C	18.8	-	11.5
600°C	14.3	-	7.0

Table II

Properties of Glass-Ceramic Materials

Material	Thermal Expan. Coefficient (RT→800°C)	Phase Composition	Chemical Analysis (wt %)										
			Li	Al	Mg	Ti	Zn	Zr	Fe	Ca	Na	Ba	Si
$Li_2O \cdot Al_2O_3 \cdot 4SiO_2$	$10 \times 10^{-7}/^{o}C$*	β-spodumene	3.0	13.8	-	-	-	-	1	1	.3	-	Major
Corning 9608	$19.4 \times 10^{-7}/^{o}C$	β-spodumene/silica sol. soln. ($Li_2O \cdot Al_2O_3 \cdot 8SiO_2$) + rutile ($TiO_2$) (minor)	1.2	8.9	1.8	2.6	1.4	-	.1	.3	.3	-	"
Corning 9608 (special order)	-	received in glassy state	1.3	10.7	1.0	0.1	0.8	2.2	.2	.3	.5	.8	"
Corning 9617	$32.5 \times 10^{-7}/^{o}C$	β-spodumene/silica sol. soln. ($Li_2O \cdot Al_2O_3 \cdot 8SiO_2$)	1.6	11.3	1.4	2.4	1.5	.1	.2	.1	.2	-	"
Corning 9606	$43 \times 10^{-7}/^{o}C$	Cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) + cristobalite ($SiO_2$) + rutile ($TiO_2$)	-	11.3	24.0	4.9	-	-	.2	.2	.2	-	"

*From Ref. 9

FIG. 1

9606 GLASS MILLED BY
(A) GRINDING IN MORTAR AND PESTLE AND SIEVING THROUGH – 325 SCREEN AND
(B) BALL MILLING WITH WC BALLS FOR 48 HRS.

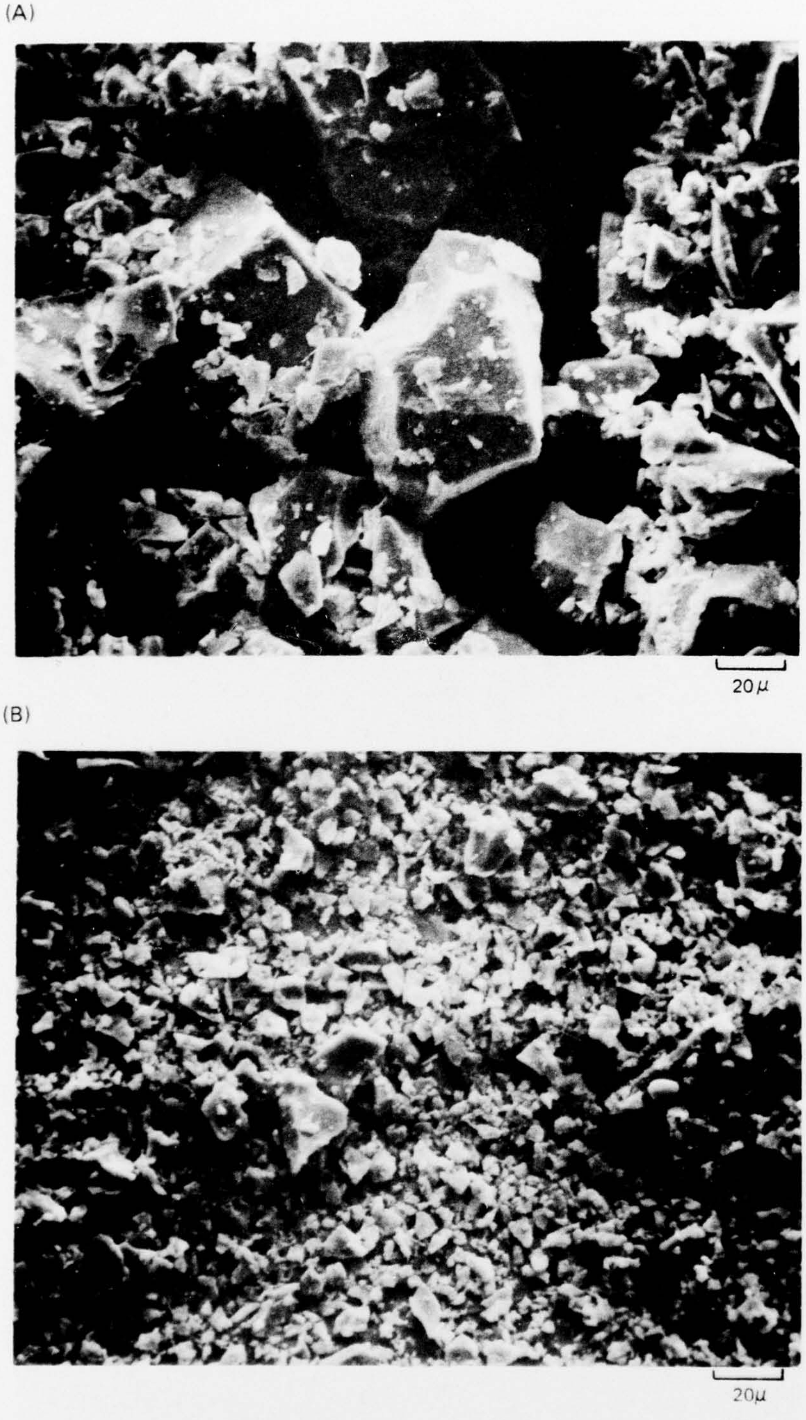
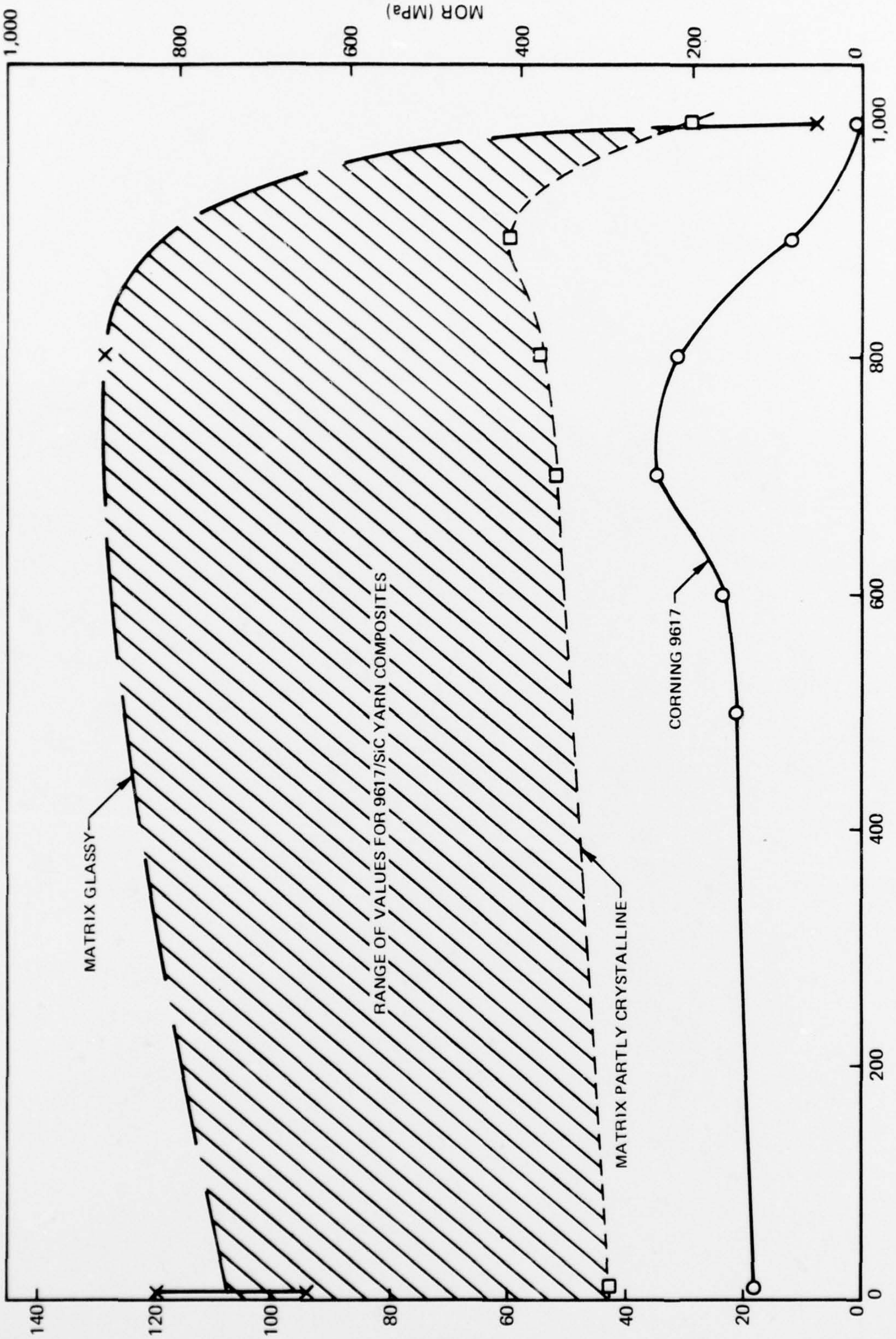


FIG. 2

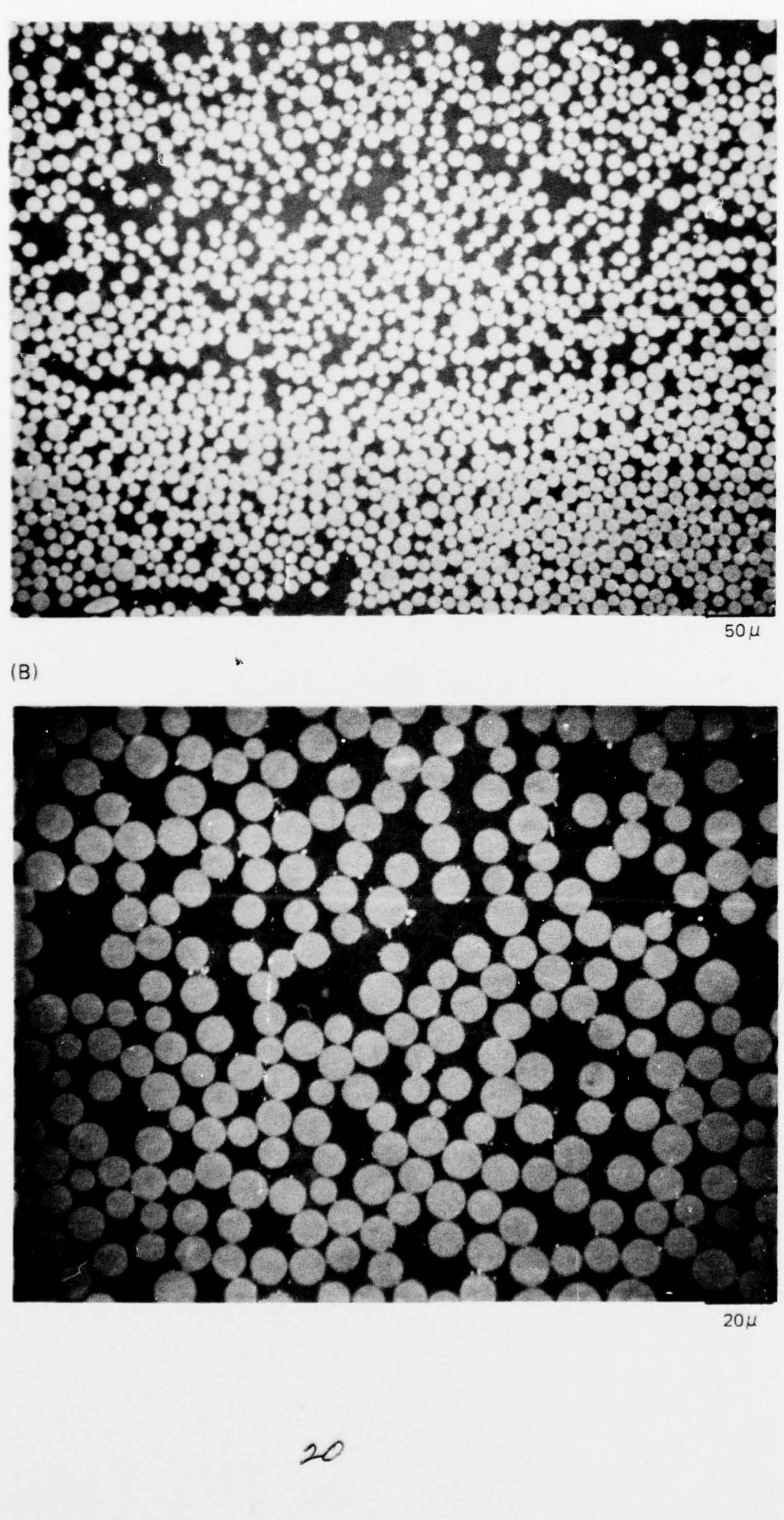


BEND STRENGTH VS TEMPERATURE FOR CORNING 9617 AND 9617/SiC YARN COMPOSITES (AS – PRESSED)

79–04–174–10

FIG. 3

CROSS – SECTION OF A 9617 – SiC YARN COMPOSITE, AS – PRESSED, 1250° C, 1 KSI, 20MIN., VACUUM



79–04–174–6

FIG. 4

CROSS – SECTION OF A WC MILLED 9617 – SiC YARN COMPOSITE, AS – PRESSED, 1250 °C, 1 KSI, 20 MIN., VACUUM (MATRIX CRYSTALLIZED), σ = 29 KSI (193 MPa)

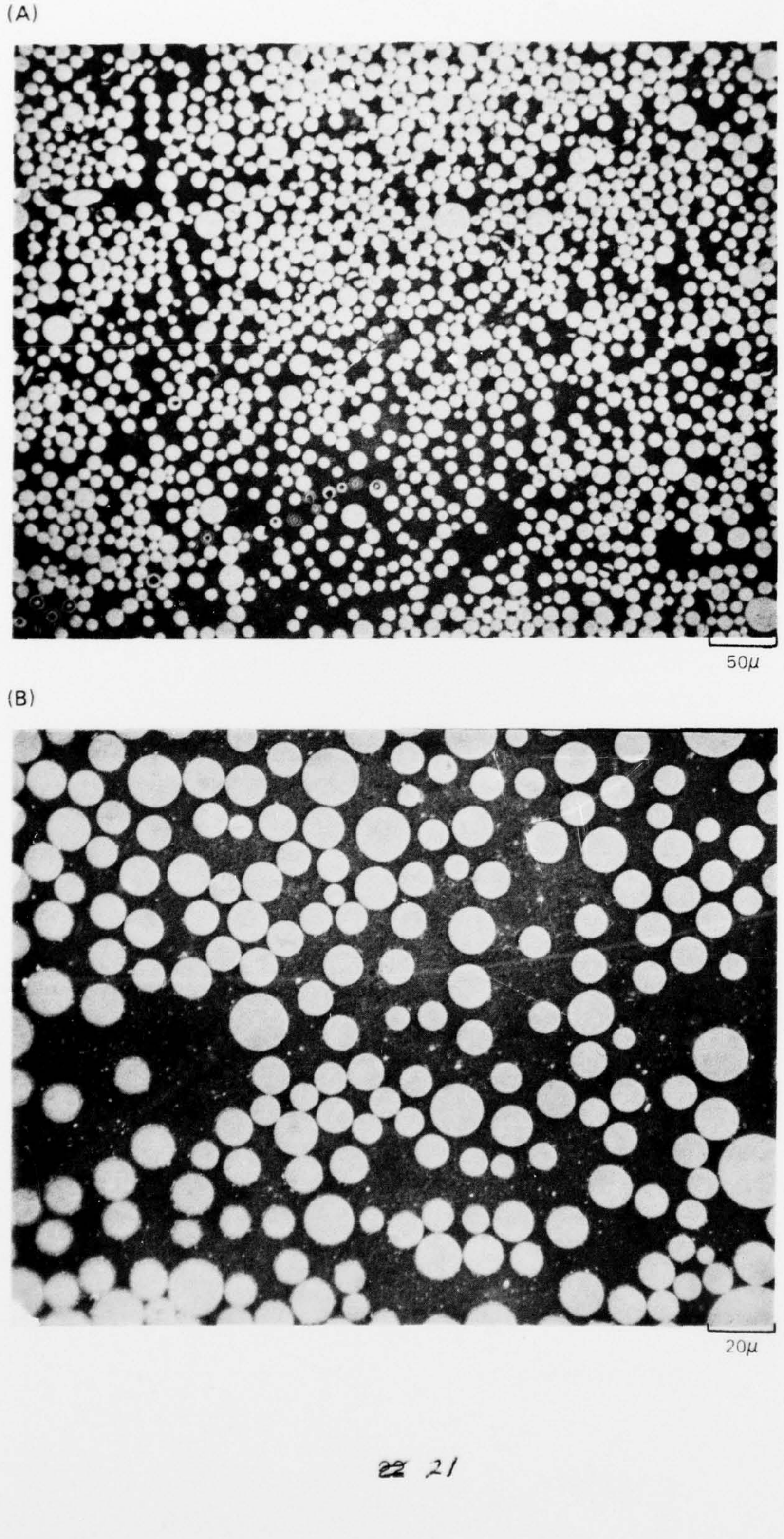
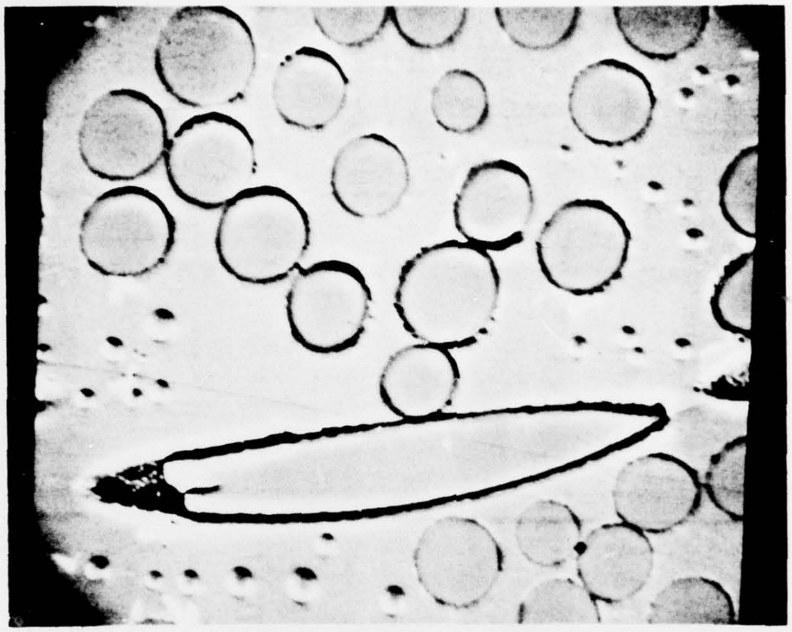
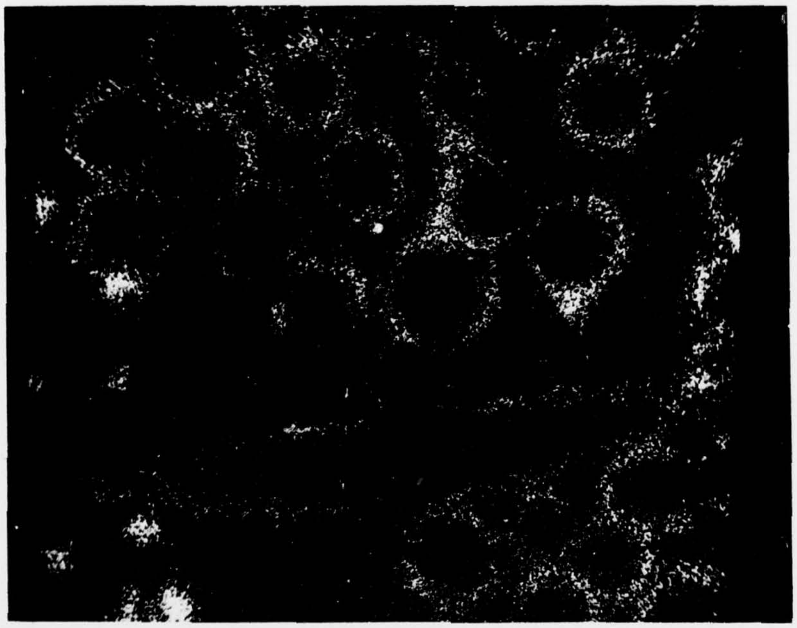


FIG. 5

ELECTRON MICROPROBE ANALYSIS OF Ti DISTRIBUTION IN SAMPLE OF FIG. 3
(HIGH STRENGTH)



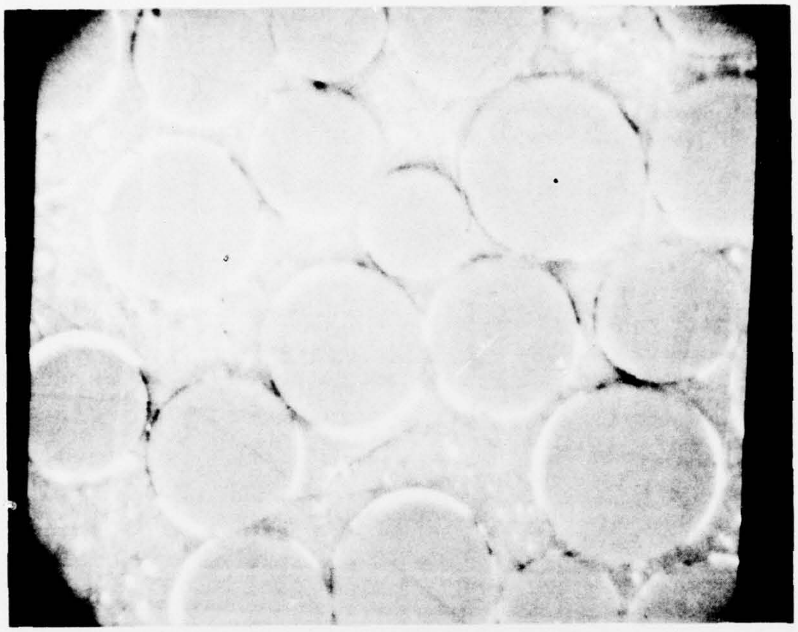
MAG: 10μ



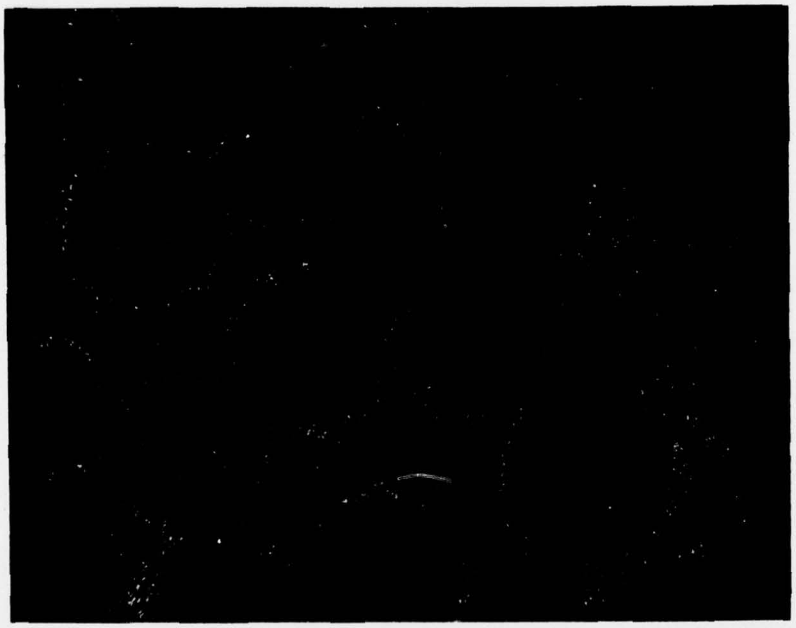
Ti–X–RAYS

MAG: 10μ

ELECTRON MICROPROBE ANALYSIS OF Ti DISTRIBUTION IN SAMPLE OF FIG. 4 (LOW STRENGTH



MAG: 10μ



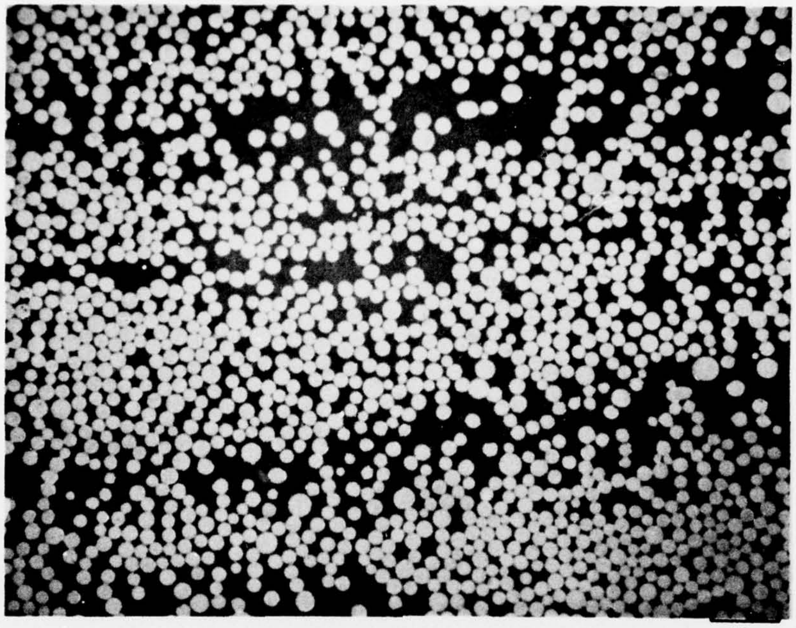
Ti–X–RAYS

MAG: 10μ

FIG. 7

CROSS – SECTION OF A 9608 – SiC YARN COMPOSITE, AS –PRESSED,
1300° C, 1 KSI, 20 MIN., VACUUM

(A)



(B)

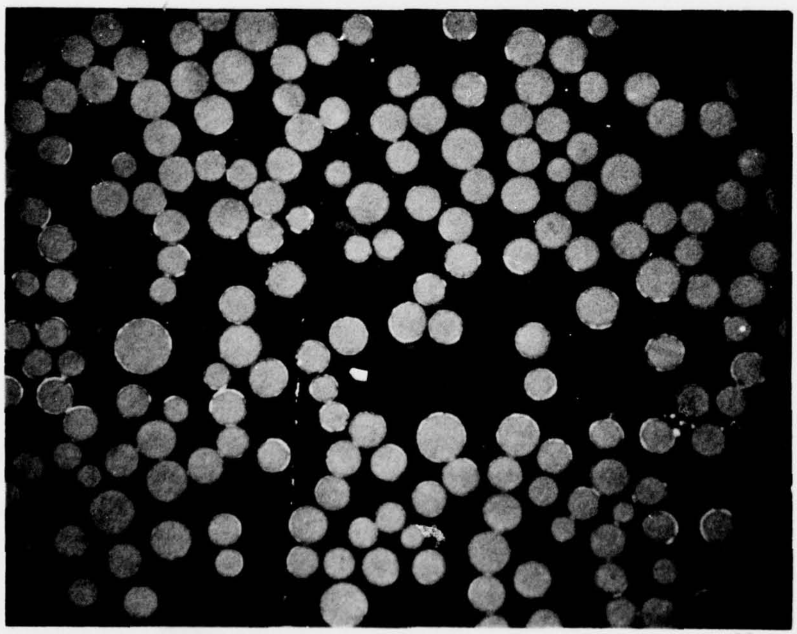


FIG. 8

FRACTURE SURFACES OF
(A) 9617 – SiC YARN COMPOSITE, $\sigma = 119$ KSI 820 (820 MPa) AND
(B) 9608 – SiC YARN COMPOSITE, $\sigma = 31$ KSI (214MPa)

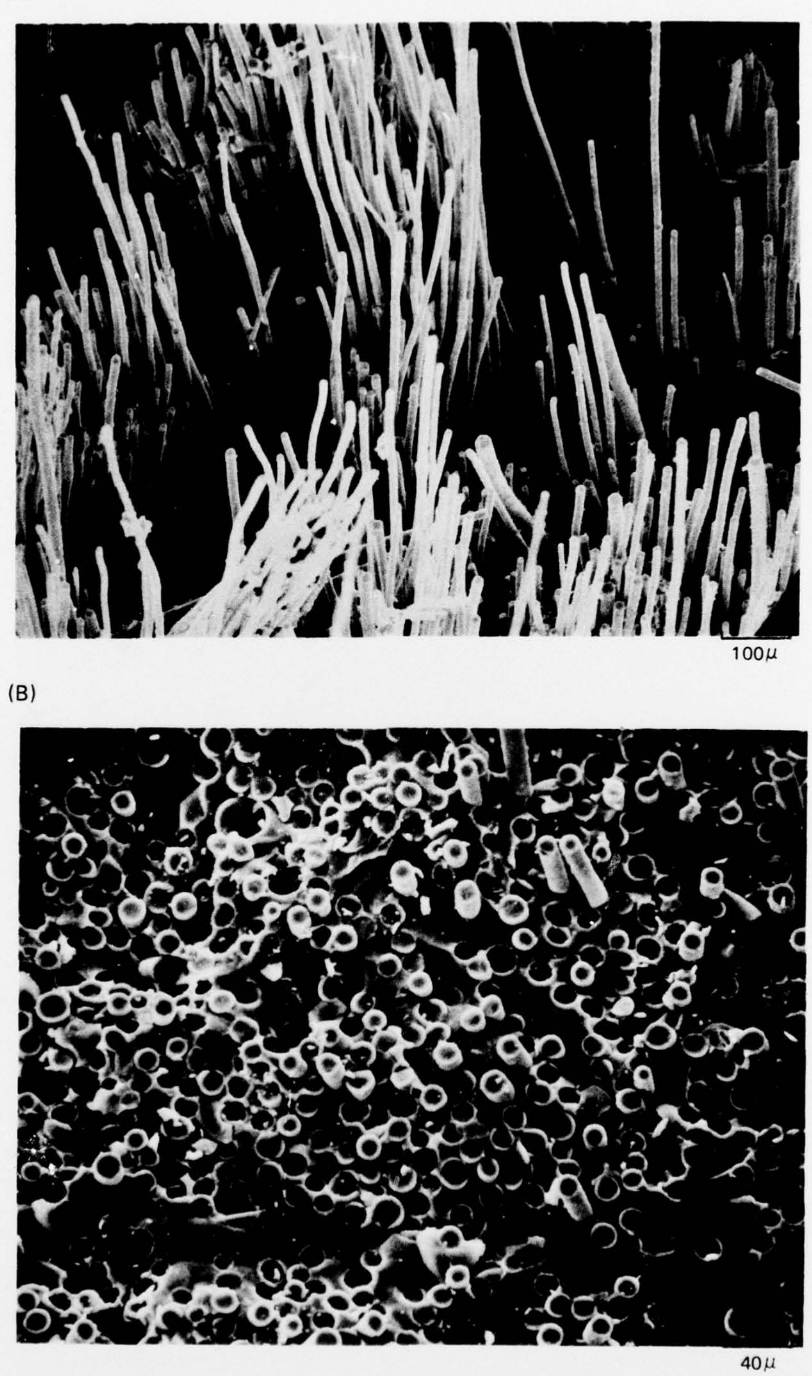
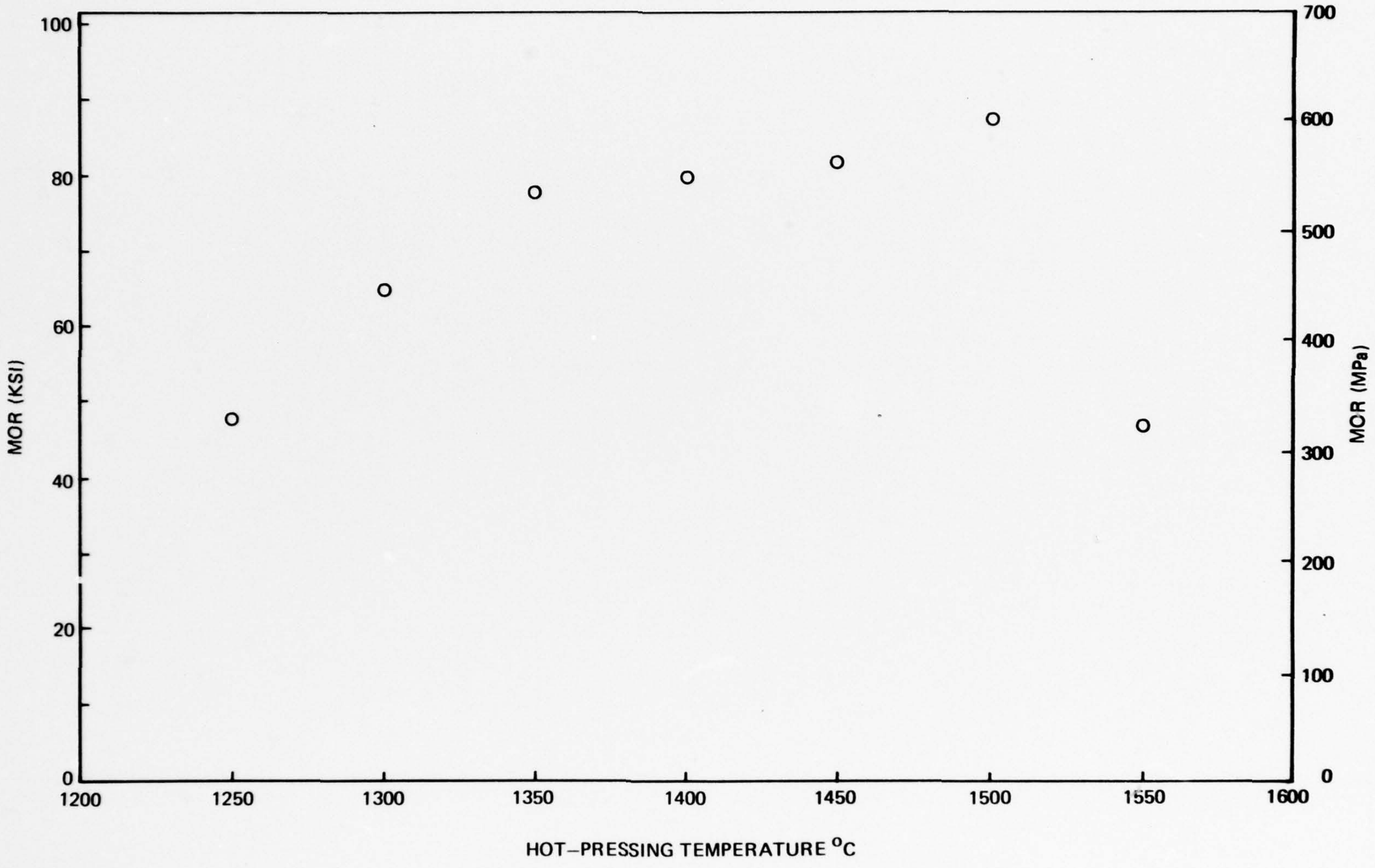


FIG. 9

RT 3–PT BEND STRENGTH VS HOT–PRESSING TEMPERATURE FOR 9608 + ZrO_2/SiC YARN COMPOSITES



79–08–43–3

CROSS–SECTION OF A 9608 + ZrO_2/SiC YARN COMPOSITE HOT–PRESSED AT 1450°C

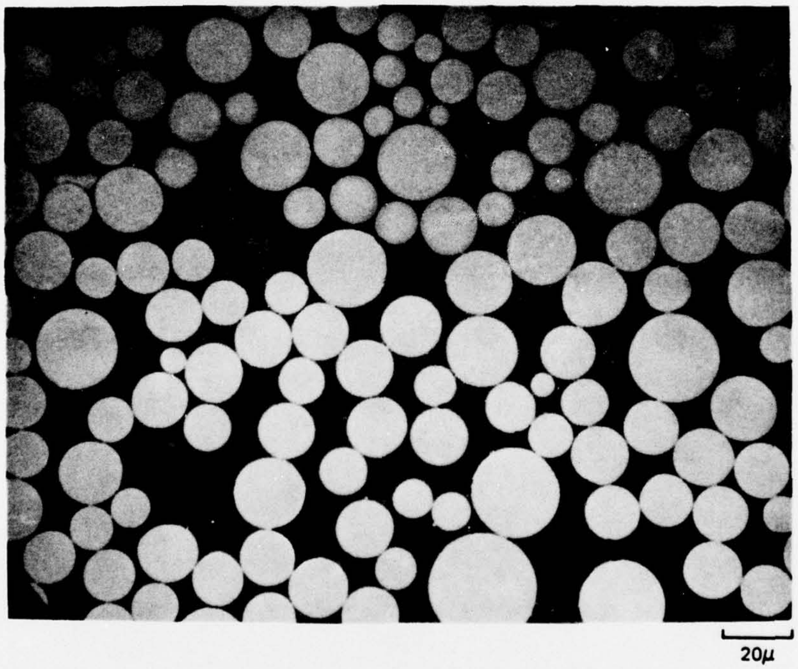
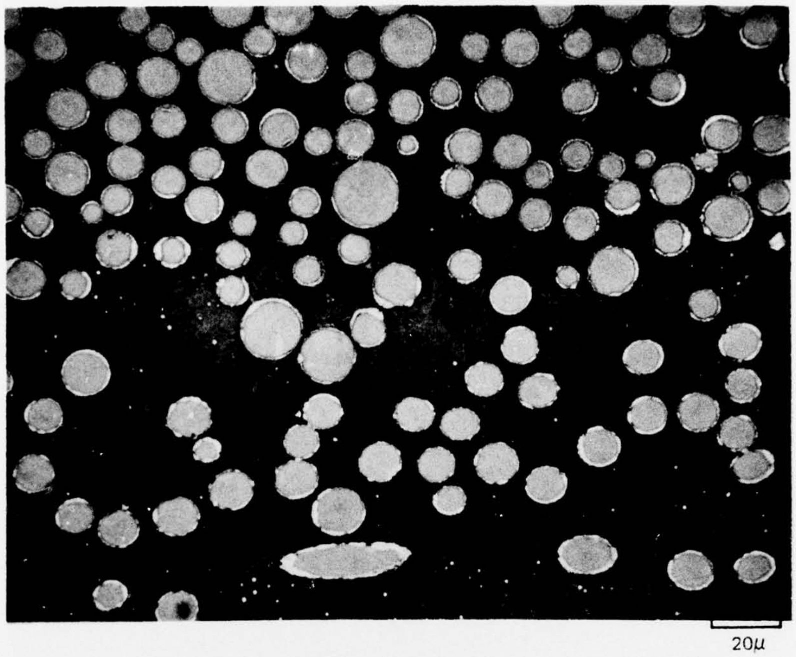


FIG. 11

(A) CROSS – SECTION OF 9606 – SiC YARN COMPOSITE, AS – PRESSED 1375° C, 2 KSI, 30 MIN., VACUUM AND (B) FRACTURE SURFACE OF THIS SAMPLE

(A)



(B)

FIG. 12

CROSS – SECTION OF A 9606 – SiC MONOFILAMENT COMPOSITE, AS – PRESSED, 1350° C, 20 MIN., 1 KSI, VACUUM

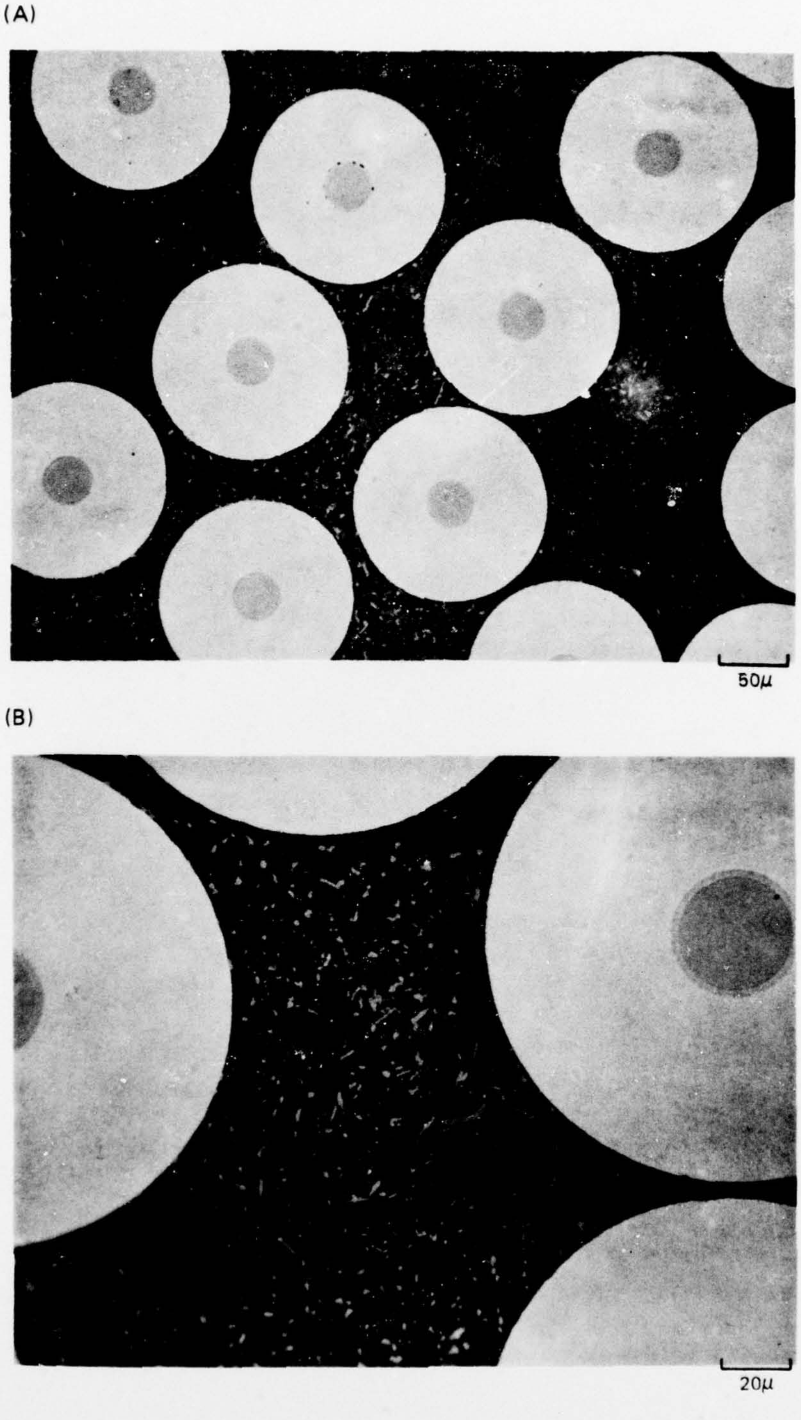


FIG. 13

BEND STRENGTH VS TEMPERATURE FOR
CORNING 9606 AND 9606/SiC MONOFILAMENT COMPOSITES (AS – PRESSED)

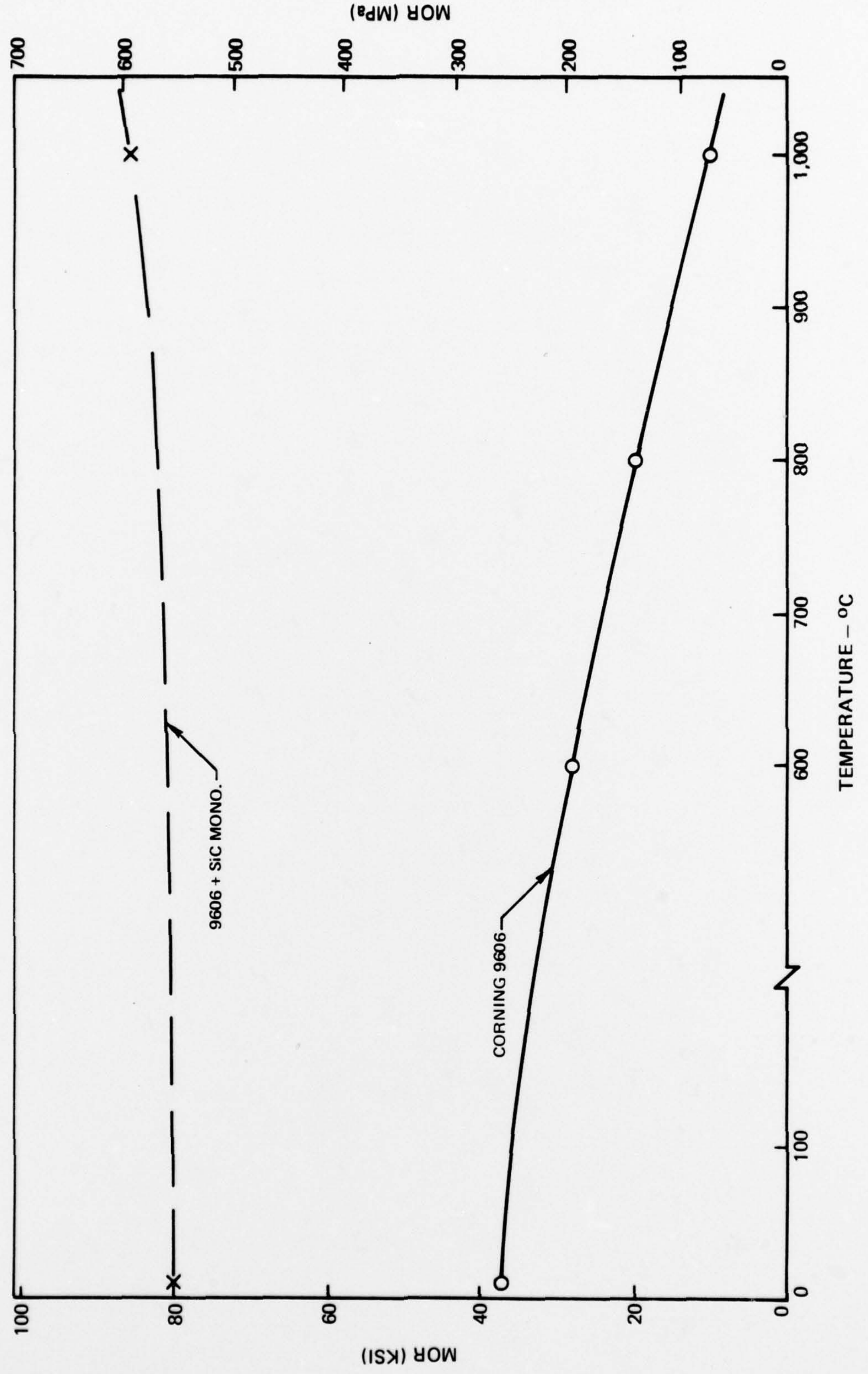


FIG. 14

CROSS – SECTION OF A 9606 – SiC MONOFILAMENT COMPOSITE AFTER HEAT TREATMENT IN AIR TO 1260° C