Continuous fiber ceramic matrix composites require fiber/matrix interfaces which allow load transfer from the matrix to the fibers when the composite materials are stressed. Crack deflection and fiber pullout are also necessary components of the mechanical behavior of composites. Screening interface materials and determining their optimum characteristics is a lengthy and expensive procedure if standard chemical vapor infiltration composite processing is used. A procedure for fabricating minicomposites was developed to address this problem. Minicomposites require very little material and much less labor than is necessary to produce a standard composite. Also, the mechanical property measurements made on minicomposites target the behavior of the interface coatings and their effect on the properties of the composite. Tensile testing of minicomposites was used to optimize the matrix infiltration process and will be utilized in the future to study the mechanical behavior of new materials systems, and specifically, new interface coating materials.

INTRODUCTION

The characteristics of the fiber-matrix interfaces in ceramic matrix composites control the mechanical behavior of these composites. These interfaces are currently one of the weak links in continuous fiber ceramic matrix composite materials for applications in oxidative environments. At room temperature, pyrolytic carbon (PyC) films provide excellent interfacial layers for SiC/SiC composites. These composites exhibit high strength and graceful failures. At elevated temperatures, PyC continues to function well as long as the SiC matrix remains intact and protects the interface layers from exposure to oxygen. If stressed above the point where the matrix cracks, air can penetrate into the composites and oxidize the fiber/matrix interfaces. After very short times the composites become brittle.1

Alternate interface coatings need to be developed that are chemically stable with respect to the fiber and matrix materials, and thermally stable and oxidation resistant at use temperatures. Unfortunately, processing and characterization of composites to test alternate coatings is labor-intensive and expensive. A procedure for fabricating minicomposites was developed to address this problem. Dupel et al2 introduced the concept of minicomposites. Minicomposites are single fiber tows which have been coated with an interface and infiltrated with matrix material. One advantage of minicomposites is that sample preparation requires very little material and much less labor than is necessary to produce a standard composite. Another advantage is that the mechanical property measurements made on minicomposites target the behavior of the interface coatings and its effect on the properties of the composite. Also, substantial development effort is required to produce uniform interface coatings and matrix infiltration when processing composite parts, so the use of minicomposites should result in less scatter and better interpretation of property data. The use of minicomposites enables a quick assessment of materials for interface coatings or refinement of the characteristics (thickness, morphology, etc.) of a particular interface coating.
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SAMPLE PREPARATION

Minicomposites were produced by depositing an interface coating on the fibers in single tows of ceramic grade Nicalon™ fiber (Nippon Carbon, Yokohama, Japan) via either a sol-gel or a chemical vapor deposition (CVD) route. Each fiber tow contains 500 filaments. The coated fiber tows were subsequently infiltrated with SiC to form the matrix using isothermal chemical vapor infiltration (ICVI). While this work utilized Nicalon™ fibers in a SiC matrix, it should be noted that the technique can generally be applied to any fiber/matrix combination. It may be especially useful for evaluating oxide systems while the processing technology for producing CVI oxide matrices is under development.

To illustrate the processing of minicomposites, the system Nicalon™/C/SiC will be used. As previously noted, this is not a practical materials system for use in high temperature oxidative environments, but it is a system for which the mechanical behavior is well known.

Interface Deposition
The carbon interface coatings were deposited by CVD using the following set of conditions:

- Temperature: 900°C
- Pressure: 1.3 kPa
- Gas flows: \( \text{Ar} - 500 \, \text{cm}^3/\text{min} \)
- \( \text{C}_3\text{H}_6 - 25 \, \text{cm}^3/\text{min} \).

The furnace in which these coatings were produced is a resistively heated vertical tube furnace. The reactant gases are fed in at the bottom and exhausted at the top. Temperature was measured on the top of the graphite fixture in which the fiber tows were hung. Figure 1 is a schematic diagram of this fixture. The standard deposition time for carbon interfaces is 2 hours. This deposition time results in a coating thickness of about 0.25 \( \mu \text{m} \).

The fibers are mounted for coating by feeding the ends of a fiber through two holes in the lid of the fixture so that the lid supports the fiber. Generally, five tows are mounted for each coating run. Graphite stubs with holes drilled through them are used as weights to keep the fibers straight and to prevent them from interfering with each other. If the fibers hang too close together they can become cemented to one another during the deposition process. The graphite pieces weigh ~0.5 g, which is enough of a load to straighten the fibers without subjecting them to a damaging stress. The stubs are hung on the fibers using either graphite adhesive or by simply running the fiber end through the hole in the graphite and tying a knot in the fiber below the weight.

Oxide interface coatings were deposited via sol-gel as described by Shanmugham et al.³ and also by CVD as described by Lee et al.⁴.

Matrix Infiltration
The coated fiber tows were infiltrated in the same furnace in which the interface coatings were deposited without removing them from the graphite fixture. Tows with interface coatings deposited using a sol-gel method were mounted in a similar fixture. Since the coated tows were no longer as flexible as the as-received fibers, they could not be
doubled over and hung in the fixture. They were instead held by graphite wedges in the holes in the fixture's lid. The SiC matrix was deposited from a mixture of methyltrichlorosilane (MTS, CH₂SiCl₃) and hydrogen gases.

Initial attempts at infiltration resulted in a heavy overcoating of the tows and low intra-bundle densities. Figure 2 is a scanning electron micrograph of the center of the cross-section of a poorly infiltrated fiber tow. There are areas within the tow where the fibers are barely coated, yet the tow itself is completely surrounded by a thick layer of SiC. The lack of matrix around each fiber and the resultant large voids in the material do not allow samples with this structure to behave as fiber-reinforced composites because the load transfer capability from the matrix to the fibers is limited.

Refinements in the infiltration process led to more uniformly infiltrated minicomposites, as illustrated in Figure 3. This micrograph shows a minicomposite made using improved processing conditions. The infiltration conditions which resulted in the most uniform and dense materials are:

- Temperature: 900°C
- Pressure: 3.9 kPa
- Gas flows: H₂ - 500 cm³/min
  CH₂SiCl₃ - 0.3 g/min
- Time: 8 h.

The major refinement in the infiltration process was to lower the temperature of infiltration. This had the effect of slowing the deposition kinetics to the point where diffusion of the reaction gases into the fiber tow was faster than the deposition reaction. Thus the gases could reach the intra-bundle spaces before reacting and the tow did not overcoat prematurely. It is clear that the material shown in Figure 3, made using the improved infiltration process, is more dense than the material shown in Figure 2.

**TESTING**

Once the minicomposites were infiltrated they were mounted for tensile testing. Mounting involves affixing the samples to some type of grip which can subsequently be mounted in the tensile test equipment. In this case, the ends of the minicomposites are imbedded in metal tube sections using epoxy. The metal tubing is then held in grips in the testing machine. Load vs. displacement data are collected as the sample is exposed to a constant displacement rate exerted in a tensile direction. As with composite processing, specimen preparation for tensile testing is easier, less expensive and less time consuming than preparing standard composites. Standard composites require precision machining, but no machining is required with minicomposites.

To date these tests have been used simply to provide feedback on the quality of matrix infiltration into the minicomposites. Figure 4 contains plots of the tensile tests performed on an early sample (a) and one infiltrated at the refined processing conditions (b). The early sample exhibited brittle fracture, which indicated that the material had not been processed properly since carbon is known to be an excellent interlayer material for SiC/SiC composites. After optimizing the CVI process, the minicomposites exhibited composite behavior in tensile tests. Multiple matrix cracks and extensive fiber pullout were observed and graceful failure occurred [Figure 4(b)].
Promising results were obtained in initial tests of SiC/SiC minicomposites with CVD ZrO₂ interface coatings. The fracture surfaces revealed crack deflection at the fiber/interface coating interfaces and composite-type failure. In the future, tensile and push-out testing of minicomposites will be used as a method to screen candidate interface coatings in SiC/SiC composites as well as in oxide systems and to gauge improvements in the characteristics of promising candidates. In addition, models are being developed to extract information about the stress state in the interfacial region. This information will further the understanding of the specific characteristics of an interface material which are beneficial to the mechanical properties of composite materials.

CONCLUSIONS

Development of a process for making minicomposite specimens from single fiber tows was undertaken. The advantages of utilizing minicomposite samples include ease of preparation, and time and cost savings involved in their processing and characterization relative to producing standard composites.

Minicomposites were produced by depositing interface coatings on single tows of Nicalon™ fiber and then infiltrating the tows with SiC by ICVI. The majority of the development process involved refining the fixture which holds the fiber tows in the reactor and improving the matrix infiltration conditions. The biggest obstacle to optimizing the infiltration procedure was premature overcoating of the fiber tows, resulting in low density materials. Tensile testing of the minicomposites illustrated that proper infiltration resulted in load transfer between the matrix and fiber resulting in classic composite mechanical behavior.

Tensile and push-out testing of minicomposites will be used in the future as an efficient way of studying new composite materials systems. Modeling work based on these tests will also enhance knowledge of composite interfacial region behavior.

ACKNOWLEDGEMENTS


REFERENCES


Figure 1: Schematic diagram of the graphite fixture used to support fibers in CVI reactor during minicomposite fabrication. Note that multiple fiber tows are hung in the fixture.

Figure 2: Scanning electron micrograph of a poorly infiltrated minicomposite.

Figure 3: Scanning electron micrograph of a properly infiltrated minicomposite.
Figure 4: Plots of data from tensile tests conducted on minicomposites exhibiting (a) brittle behavior and (b) classic composite behavior.
CVI Processing of Minicomposites for Evaluation of Interface Coating Materials in Composites
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The characteristics of the fiber-matrix interfaces in ceramic matrix composites control the mechanical behavior of these composites. These interfaces are currently one of the weak links in continuous fiber ceramic matrix composite materials. At room temperature, graphite carbon films provide excellent interfacial layers for SiC/SiC. Composites with C interlayers exhibit high strength and graceful failures. In the high temperature oxidative environments at which these composites are to be put into service, however, the carbon oxidizes and the composites become brittle.¹

Alternate interface coatings need to be developed that are chemically stable with respect to the fiber and matrix materials, and thermally stable and oxidation resistant at use temperatures. Processing and characterization of composites to test alternate coatings is labor-intensive and expensive. A procedure for fabricating minicomposites was developed to address this problem. Minicomposites are single fiber tows which have been coated with an interface and infiltrated with the matrix material. One advantage of minicomposites is that sample preparation requires very little material and much less labor than is necessary to produce a standard composite. Another advantage is that the mechanical property measurements made on minicomposites target the behavior of the interface coatings and their effect on the properties of the composite. This is a good technique for quickly assessing a group of materials for interface coatings or refining the characteristics (thickness, morphology, etc.) of a particular interface coating. When an interface material has been determined to be worthy of further study, standard composites can be made and tested.

Minicomposites were produced by coating the fibers in single tows of Nicalon® fibers with an interface film via either a sol-gel or a CVD route and subsequently infiltrating the tows with SiC to form the matrix using isothermal CVI. The first challenge was to fixture the fiber tows in the CVD reactor so that they would infiltrate as uniformly as possible. The reactor used is a vertical, hot-wall, resistively-heated furnace with the reactant gases flowing in at the bottom and exiting at the top. The temperature in the furnace is measured using an optical pyrometer by sighting on the top of the sample fixture. The fiber tows are generally about 100°C hotter than this reading.

The samples are hung from the holes in a graphite lid which fits on a cylindrical graphite container with a hole in the bottom to allow the flow of the reactant gases into the fixture (see figure 1). The fibers in the tows may have interface coatings deposited on them prior to mounting for CVI or the coatings may be deposited in the CVI reactor by CVD. To keep the fibers straight, small graphite stubs are attached to the bottoms of the tows. The weight of these stubs is enough to straighten the tows without putting undue

The infiltration conditions were developed to produce as dense a composite as possible. It is easy to overcoat the outside of the fiber tow before the center of the tow is completely infiltrated. The result is a porous minicomposite with very little matrix material between the fibers. The optimum conditions for this reactor configuration were determined to be 1000°C (fiber temperature) and low pressure (the runs were made at 30 torr).

As-infiltrated and oxidized minicomposites were tested in tension and by indentation (i.e. push-out). The minicomposites were tested in tension by mounting their ends in Al tubes with epoxy and gripping the tubes in a tensile tester. Fiber push-out was done on thin polished wedges of cross-sections of the composite using a cylindrical indenter. The data generated from these tests was used to calculate the in the interfacial coatings on the fibers and the properties of the composites.

References:

Figure 1: Graphite fixture with lid used to hold fiber tows during infiltration by CVI to make minicomposites.