Ceramic Matrix and Resin Matrix Composites: A Comparison

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Abstract

The underlying theory of continuous
fiber reinforcement of ceramic
matrix and resin matrix composites,
their fabrication, microstructure,
physical and mechanical properties
are contrasted. The growing use of
organometallic polymers as pre-
cursors to ceramic matrices is
discussed as a means of providing
low temperature processing capabil-
ity without the fiber degradation
encountered with more conventional
ceramic processing techniques.
Examples of ceramic matrix com-
posites derived from particulate-
filled, high char yield polymers
and silsesquioxane precursors are
provided.

1. INTRODUCTION

The increasing acceptance of resin
matrix composites as structural
materials for aerospace applica-
tions has led to a heightened
interest in extending the use of
composites to higher temperatures,
particularly in engine environ-
ments. Ceramics, because of their
stability at elevated temperatures,
offer significant potential in
engine applications; however, their
use has been limited by their
brittle fracture behavior and high
degree of flaw sensitivity. The
incorporation of particulates,
whiskers or continuous fibers into
a ceramic matrix could provide
mechanisms for "toughening" the
ceramic, increasing reliability by
decreasing flaw sensitivity, and,
in the case of continuous fibers,
ameliorating the tendency toward
catastropic failure.

The base of knowledge gained
with resin matrix composites can in
part, serve as a base for the
development of structural ceramic
composites. However, there are
important differences between
ceramic matrix and resin matrix
composites in fabrication, micro-
structure, physical properties and
mechanical behavior. This paper
offers a comparison of the two, as
well as a discussion of opportuni-
ties for the utilization of

organometallic polymers as precursors to ceramic composites. The focus will be on continuous fiber reinforced materials.

2. THEORY

In resin matrix composites typically the fiber modulus and strength are much greater than those of the matrix. The fiber, therefore, provides stiffness and load bearing capability, while the matrix serves to distribute the load among the fibers. Often, especially in the case of epoxy matrix materials, a coupling agent is introduced to enhance the strength of the interface, increasing load transfer capability from matrix to fiber. The strain capability of the matrix typically exceeds that of the fiber; hence, initiation of fracture is from the failure of a fiber or group of fibers. The load is then redistributed to the remaining fibers until additional fiber breakage occurs.

In contrast, in a ceramic matrix composite the moduli of the fiber and matrix typically are very similar. The fiber therefore is not the source of stiffness or necessarily of strength for these materials (1). Monolithic ceramics offer sufficient strength for structural applications, so incorporation of fibers is not necessary to achieve load bearing capability. Rather, the fiber is relied upon to bridge cracks or flaws in the matrix. Because of differences in processing between resin and ceramic matrices, the ceramic matrix is anticipated to have a higher population of processing introduced flaws and microcracks than its resin counterpart. The strain capability of the fiber is expected to exceed that of the matrix. Hence, matrix failure precedes fiber fracture. Microcracking of the matrix may provide some toughening as well as some pseudoplasticity (2-4). The desired mode of failure is debonding at the interface. Because ultimate matrix strain, ε_m, is less than ultimate fiber strain, ε_f, fiber fracture would result in brittle failure of the material. By bridging microcracks or flaws, the fiber can increase the strain to failure of the composite over that of the monolithic (see Figure 1), imparting non-catastrophic failure. If the fiber/matrix interface is not strong, cracks can propogate around the fibers rather than through them. Therefore, the primary role of the fibers in a ceramic matrix composite is crack bridging and toughening by matrix crack blunting and debonding at the interface, as opposed to providing stiffness and strength in the resin matrix composite.

3. FABRICATION

Resin matrix composites typically are processed at relatively low temperature (<350°C). The polymer resin may be either a thermoplastic or thermoset, but typically will undergo viscoelastic

flow, providing a means of fiber impregnation and matrix consolidation.

Glasses do become molten, and offer the advantage of forming glass matrix composites by hot pressing or transfer molding. A number of glass matrix composites have been studied (5-7). However, the melting points of many glasses are sufficiently high so that reaction with the fiber can become a problem. As with resin matrix composites, the use temperature of glass matrix composites will be well below their softening point. Carbon reinforced glass composites have been reported which offer zero coefficients of thermal expansion (7).

Ceramics, by contrast, do not melt flow at temperatures low enough for composite fabrication. Conventional sintering and hot pressing temperatures usually exceed those at which available fiber reinforcements degrade in strength.

Oxide ceramic matrices can be formed by sol-gel processing (8-9). Ceramic composites can also be fabricated by chemical vapor infiltration (CVI) or by chemical vapor deposition (CVD) (10-11). Silicon nitride matrix composites have been fabricated successfully by reaction bonding of silicon powder in a nitrogen atmosphere (12-13). Organometallic polymers also might serve as precursors which can be pyrolyzed to a ceramic char (14-24); these are discussed in greater detail below. In addition, porous carbon chars can be formed by polymerization around a pore former, and the resulting porous carbon reacted with silicon to form silicon carbide (25). All of these techniques can be expected to produce matrices with rather high levels of porosity (up to 35 - 40 percent), as opposed to perhaps <3 - 5 percent porosity typically found in resin matrix composites. How well this porosity can be tolerated will depend on the uniformity of pore size and distribution and the diameter of bridging fibers.

4. FIBERS

Resin matrix composites can be fabricated from a wide variety of fibers, offering a broad choice of modulus and strength for tailoring to particular applications. The selection of fibers available for ceramic composites is much more limited, however, due to the higher temperatures required for composite processing and in use.

Carbon fibers have been used with glass matrices to temperatures of about 600°C (7). However, at higher temperatures carbon will react to form carbides and will be extremely susceptible to oxidation when used in a porous matrix.

SiC fibers would offer good modulus and high temperature properties. Large diameter (140 µm) SiC fibers produced by CVD are available with temperature capabilities to 1400°C (26), but their diameter precludes their use in woven structures

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or in the formation of complex shapes. For strengthening a ceramic matrix, interfiber spacing less than the critical flaw size is needed; this requires fiber diameters to be smaller than the interfiber spacing. The ultimate matrix tensile strain also is influenced by fiber diameter and the strength of the fiber-matrix interface (2).

Available small diameter fibers include polymer-derived Nicalon SiC and oxide fibers such as Nextel 312, 440 and 480 (27), comprised of boria, alumina and silica, and FP-alumina (28). However, all of these become thermally unstable at temperatures from 1000 to 1200°C.

5. PHYSICAL AND MECHANICAL PROPERTIES

In any composite system where there is a difference in coefficient of thermal expansion (CTE) between fiber and matrix, residual thermal stresses will be expected to develop during both composite fabrication and on thermal cycling. For most fibers, expansion is anisotropic, differing along the fiber axis and the radial direction. A pure β-SiC fiber might prove to be the exception.

When graphite fiber is used as the reinforcement, the CTE along the fiber axis is slightly negative. Residual stresses developed during fabrication place the fiber in compression and the matrix in tension. In any ceramic composite fabrication approach in which matrix shrinkage takes place, and especially in polymer derived materials, the matrix will likely be in tension as well. However, since ceramic matrix composites can be expected to see high temperatures both in fabrication and in service, the residual stresses are expected to be much greater than in their resin matrix counterparts, and may give rise to microcracking on fabrication. In terms of designing with composites this leads to a significant difference between resin and ceramic matrix materials. Whereas resin, glass and probably RBSN matrix composites can be designed as a crossply layup of unidirectional lamina, ceramic matrix composites in which matrix shrinkage occurs in processing likely will have to be fabricated from 2D cloth or as 3D woven structures to minimize shrinkage cracking.

Some ceramic matrix composites might alleviate the problem of residual stresses by choice of fibers with high axial CTE's relative to the matrix, which would place the matrix in compression. However, if the CTE of the fiber is much greater than that of the matrix, debonding of the interface will result (3).

Decreased matrix strain capability relative to the fiber may decrease tensile strength, as the matrix cannot plasticly deform to accommodate stress concentrations. Behavior under flexural loading might become more complex. Prewo

(6) has studied Nicalon/epoxy and Nicalon/lithium aluminosilicate (LAS) composites in both tension and flexure, and notes that while the Nicalon/epoxy composites had the higher tensile strength, in flexure the LAS matrix material appeared stronger as it "yielded" due to microcracking, shifting the neutral axis of the beam toward the compressive side of the test specimen. Thus, ceramic composites may appear to have greater strength in flexure than their resin matrix counterparts as a result of both their higher matrix compressive strength and the pseudoductility imparted by microcracking.

Microcracking also can become a problem to the environmental stability of the fibers in air, leading to fiber degradation and fracture during use at elevated temperature.

6. POLYMERIC PRECURSORS TO CERAMIC MATRICES

The use of organometallic precursors which can be pyrolyzed to a ceramic char provides a means for forming ceramic matrices utilizing the advantages of ease of fiber infiltration, control of rheology and low temperature processing typical of resin matrix composites. Choice of polymer is influenced by stoichiometry of the resulting char and shrinkage on pyrolysis. Ideally, the closer to stoichiometric SiC or Si_3N_4 the final product, the more thermally stable it may be expected to be. Also,

the smaller the weight loss and volumetric shrinkage on pyrolysis, the less the need for multiple re-impregnation cycles and the less the likelihood of large cracks.

A number of organometallic polymers have been studied; some of these are shown in Table I. The polycarbosilane work of Yajima (14-16) serves as the basis for Nicalon fibers. The char is rich in excess carbon. It also contains oxygen intentionally introduced as a cross-linking agent to stabilize the fiber structure prior to pyrolysis. The deviation from stoichiometry results in thermal instability above 1200°C.

Most of the polysilanes and polycarbosilanes listed undergo weight losses of 40-60 percent on pyrolysis. Higher char yields have been demonstrated for the polysilazanes; 80-85 percent char yields have been reported by Seyferth (23). The polysilazanes are, however, moisture sensitive, and require composite processing to be carried out in inert atmospheres.

Recent work in our laboratory (29) has examined a group of silsesquioxanes (Figure 2) having the general structure $RSiO_{1.5}$, where R = methyl, phenyl, propyl, or vinyl, as SiC precursors. The silsesquioxanes melt flow, thermally crosslink, and then can be pyrolyzed at nominally 500°C. At higher temperatures they can be expected to undergo a carbothermal reduction to SiC with loss of CO (Figure 3). By controlling the starting ratio of

Si/C we hope to control the stoich-
iometry of the end product.

Microstructure of Nicalon/
silsesquioxane composites is shown
in Figures 4 and 5. Initial impreg-
nation shows few voids. After
pyrolysis followed by heating to
1000°C in argon, matrix shrinkage
and pore formation are evident.
(Figure 4). The darkest phase seen
in the optical micrograph (Figure
4b) is epoxy which was vacuum in-
filtrated into the composite after
pyrolysis for polishing, and shows
the extent of matrix cracking. The
composite might be reimpregnated
with silsesquioxane and again pyro-
lyzed to increase matrix density.

Matrix surface cracks both
parallel and perpendicular to the
fibers also are observed (Figure 5),
with the more matrix rich surfaces
showing the higher extent of crack-
ing. These cracks likely arise
from a combination of shrinkage on
pyrolysis, mismatch in CTE between
fiber and matrix and anisotropic
fiber expansion.

We also have studied a SiC
particulate filled, high char yield
carbon resin (30) which introduced
the particulate third phase as a
means of minimizing matrix shrink-
age and cracking. We were able to
fabricate unidirectional composites
with very low pore volumes and few
cracks on a single impregnation and
pyrolysis cycle, provided that we
used small fiber tow sizes and
fibers which were not uniformly
cylindrical (compare Figures 6 and

7). However, strain capability of
the matrix was low ($\sim$.3%), and ten-
sile specimens failed in shear in
the tab region. Stress-strain
behavior was linear to fracture.
Cross-ply layups showed extensive
matrix cracking and delamination,
the result of residual thermal
stresses.

Jamet et al. (31) have shown
that additives of a BN particulate
to a polyvinylsilane minimizes
linear shrinkage and weight loss on
pyrolysis. Thus, the concept of
particulate filled precursors would
seem to warrant further study.

New polymers which yield more
stoichiometric ceramic products, as
well as small diameter, thermally
stable fibers are needed, as is a
greater understanding of the pyro-
lysis process and resulting stresses
at the fiber-matrix interface, for
major advances in new ceramic com-
posite materials to be achieved.

7. ACKNOWLEDGMENTS

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TABLE I

Some organometallic precursors to ceramics

Polymer	Structure	Reference
polycarbosilane	$(-\overset{\mid}{\underset{\mid}{Si}} - \overset{\mid}{\underset{\mid}{C}}-)_n$	14-16
polyvinylsilane	$CH_3-Si-(\underset{\mid}{\overset{CH_3}{Si}})_n-Si-CH_3$ $CH=CH_2$	21
polyborosiloxane	Φ = phenyl	16
polysilastyrene	$(-\underset{\Phi}{\overset{CH_3}{Si}}-)_n$	17
polysilazane	$R = CH_2$	22-23

FIBER BRIDGING OF MATRIX CRACKS

Figure 1 - Theoretical stress strain behavior for ceramic matrix composite fiber bridging of matrix cracks. (Figure courtesy of Dr. James A. DiCarlo).

$$2\,SiO_{1.5} + 5\,C \longrightarrow 2\,SiC + 3\,CO\uparrow$$

$$SiO_{1.5} + C\,(excess) \longrightarrow SiC + C + CO\uparrow$$

$$SiO_{1.5} + C\,(deficient) \longrightarrow SiC + SiO_2$$
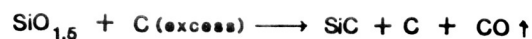$$+ SiO\uparrow + CO\uparrow$$

Figure 3 - Possible carbothermal reduction products of silsesquioxanes based on the Si/C ratio in the starting polymer.

SILSESQUIOXANES

$$RSiO_{1.5}$$

R = methyl, propyl, vinyl, phenyl

T Resin　　　　　　Ladder Polymer

Figure 2 - Silsesquioxanes may exhibit either an extended cross-linked (T resin) or double ladder structure, or a mixture of the two. The extended structure is more prevalent when R = phenyl.
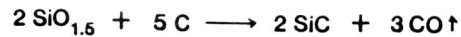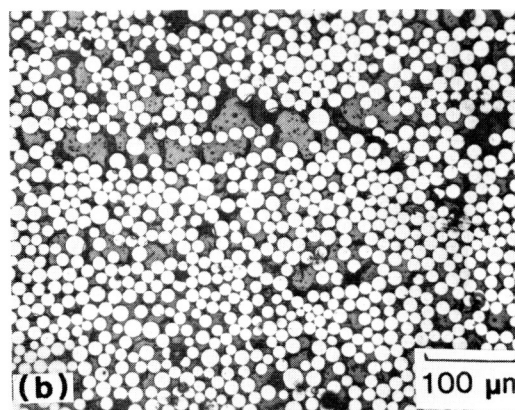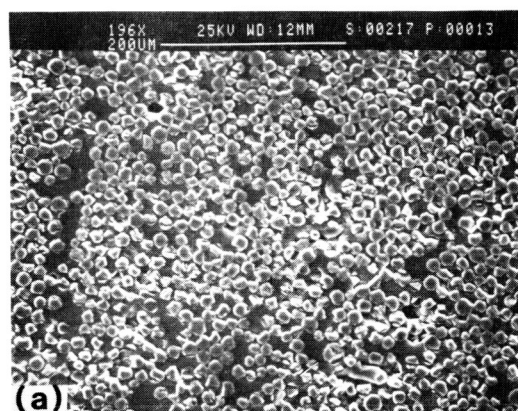

Figure 4 - Nicalon/silsesquioxane composite (a) as fabricated and (b) after pyrolysis followed by heating to 1000°C in argon.
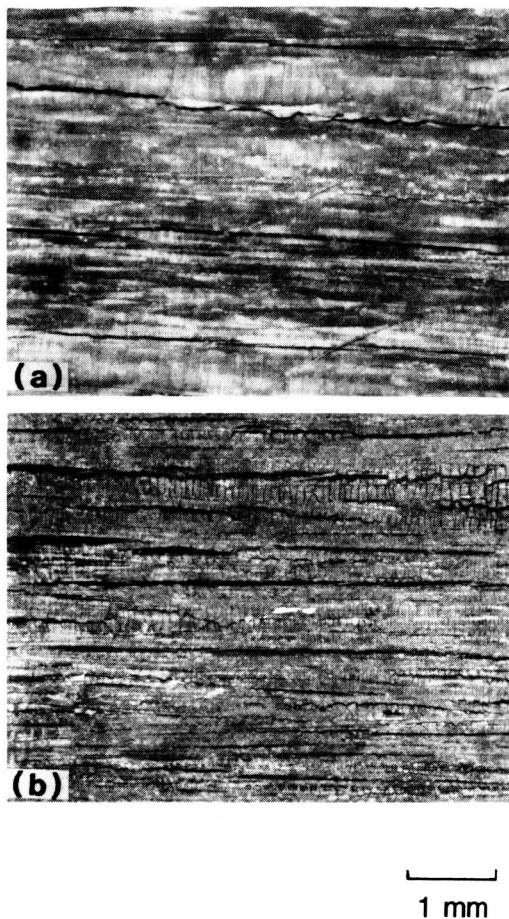
10

Figure 5 – Surface cracking of
Nicalon/silsesquioxane composite (a)
on pyrolysis at 525°C for 2 hours
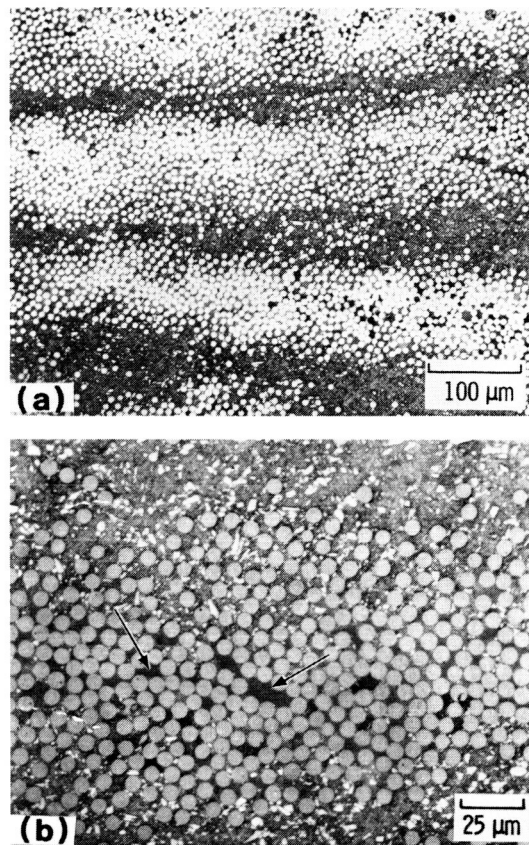and (b) after heating to 1000°C in
argon.

Figure 6 – Celion reinforced high
char yield poly(arylacetylene)
matrix filled with SiC particulate
showing (a) layering of fiber rich
and matrix rich regions and (b)
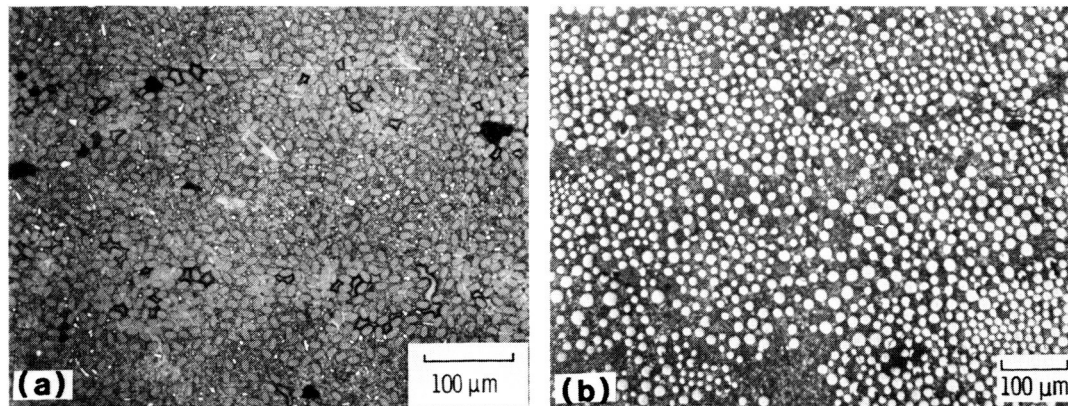matrix areas devoid of particulate
(arrows).

Figure 7 – (a) Nextel and (b) Nicalon reinforced SiC particulate filled
poly(arylacetylene) matrix. Composite homogeneity is enhanced when fibers
cannot close-pack (Compare Figure 6).

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16. Abstract

The underlying theory of continuous fiber reinforcement of ceramic matrix and resin matrix composites, their fabrication, microstructure, physical and mechanical properties are contrasted. The growing use of organometallic polymers as precursors to ceramic matrices is discussed as means of providing low temperature processing capability without the fiber degradation encountered with more conventional ceramic processing techniques. Examples of ceramic matrix composites derived from particulate-filled, high char yield polymers and silsesquioxane precursors are provided.

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