ISSUES TO ADDRESS

- Ceramic Matrix Composites
  - Fabrication
  - Applications
Processing methods can be broken down into two broad groups: powder consolidation and chemically based methods. The latter class consists of:

- melt processing
- hot pressing
- slip casting and low-pressure sintering
- reaction sintering
- pressureless sintering
- slurry
- chemical vapour infiltration
- directed melt oxidation
- sol–gel processing
- self-propagated high temperature synthesis or combustion synthesis.

### Main processing routes for CMCs

<table>
<thead>
<tr>
<th>Processing route</th>
<th>Matrices</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical vapour infiltration</td>
<td>Carbides, nitride carbon, oxides, borides</td>
</tr>
<tr>
<td>Viscous phase hot pressing (2D performs)</td>
<td>Glasses, ceramic-glasses</td>
</tr>
<tr>
<td>Sol–gel route (2D, 3D preforms)</td>
<td>Oxides</td>
</tr>
<tr>
<td>Polymer precursor route (3D preforms)</td>
<td>SiC, Si$_x$N$_y$, Si$_x$C$_y$N$_z$</td>
</tr>
<tr>
<td>Liquid metal infiltration</td>
<td>Si $\rightarrow$ SiC</td>
</tr>
<tr>
<td>Gas–metal reaction</td>
<td>Oxide (Al, nitrides [Al, Zn, Ti])</td>
</tr>
<tr>
<td>Solid-state hot pressing</td>
<td>SiC, Si$_3$N$_4$</td>
</tr>
<tr>
<td>Prepreg curing and pyrolysis</td>
<td>SiC, Si$_3$N$_4$</td>
</tr>
<tr>
<td>Hot pressing (2D preforms)</td>
<td>Oxides</td>
</tr>
</tbody>
</table>

The choice of method is determined by the geometry, the complexity of shape and the production volume of the component.

Processing of whisker and short fiber reinforced composites:

Whisker and short fiber composites are difficult to produce using conventional cold forming techniques followed by pressureless sintering. The main source of difficulty is the poor packing characteristics of particles with high aspect ratio.

However, these composites can be prepared using conventional processing with relatively straightforward modifications provided pressure assisted sintering methods such as hot pressing.

Processing of these composites includes following stages: whisker cleaning to remove impurities, wet mixing of matrix powder and whiskers, sintering (hot pressing); i.e. uniaxial hot pressing is the most common method in the commercial production of cutting tools.
There are also alternative methods in research such as injection molding and slip casting in association with hot isostatic pressing.

Some reported examples are:

cold isostatic + sintering to closed porosity + post HIP
cold isostatic pressing

or

slip casting + HIP
injection molding + HIP
slip casting + HIP slip casting + reaction bonding
Wetting between ceramic and metal is very critical for the infiltration process.
A contact angle can be measured by producing a drop of pure liquid on a solid. The angle formed between the solid/liquid interface and the liquid/vapor interface and which has a vertex where the three interfaces meet is referred to as the contact angle.

Young's equation as shown below is used to describe the interactions between the forces of cohesion and adhesion and measure what is referred to as surface energy.

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta$$

- $\theta$ is the contact angle
- $\gamma_{sl}$ is the solid/liquid interfacial free energy
- $\gamma_{sv}$ is the solid surface free energy
- $\gamma_{lv}$ is the liquid surface free energy

http://www.ramehart.com/glossary.htm
**Wettability** defines the degree to which a solid will wet. If a drop spreads out indefinitely and the contact angle approaches 0°, then total wetting is occurring. In most cases, however, the drop will bead up and only partial wetting (or non-wetting) will occur. The extent to which a solid will wet can be quantified by measuring the contact angle. Wettability determined by the cohesive forces of the liquid molecules among themselves and the adhesive forces that result from the molecular interactions between the liquid and the solid as illustrated in the diagram below. (In real life, the molecules are not so neatly organized.)

![Diagram of wetting](http://www.ramehart.com/glossary.htm)
Wettability can be explained by the relative strength of the cohesive (Liquid/Liquid) and adhesive (Solid/Liquid) forces as shown above and below. Strong adhesion with weak cohesion produces very low contact angles with nearly complete wetting. As the solid/liquid interactions weaken and the liquid/liquid interactions strengthen, wetting diminishes and contact angle increases.

<table>
<thead>
<tr>
<th>Contact Angle</th>
<th>Wettability</th>
<th>S/L</th>
<th>L/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>Complete</td>
<td>Strong</td>
<td>Weak</td>
</tr>
<tr>
<td>60°</td>
<td>High</td>
<td>Strong</td>
<td>Weak</td>
</tr>
<tr>
<td>90°</td>
<td>Moderate</td>
<td>Weak</td>
<td>Weak</td>
</tr>
<tr>
<td>120°</td>
<td>Low</td>
<td>Weak</td>
<td>Strong</td>
</tr>
<tr>
<td>180°</td>
<td>None</td>
<td>Weak</td>
<td>Strong</td>
</tr>
</tbody>
</table>

http://www.ramehart.com/glossary.htm
Liquid Silicon Infiltration (LSI) process is a type of Reactive Melt Infiltration (RMI) technique, in which the ceramic matrix forms as a result of chemical interaction between the liquid metal infiltrated into a porous reinforcing preform and the substance (either solid or gaseous) surrounding the melt.

Liquid Silicon Infiltration (LSI) is used for fabrication of silicon carbide (SiC) matrix composites. The process involves infiltration of carbon (C) microporous preform with molten silicon (Si) at a temperature exceeding its melting point 1414°C.

The liquid silicon wets the surface of the carbon preform. The melt soaks into the porous structure driven by the capillary forces. The melt reacts with carbon forming silicon carbide according to the reaction:

\[
\text{Si(liquid)} + \text{C(solid)} \rightarrow \text{SiC(solid)}
\]
Liquid Silicon Infiltration (LSI)

SiC produced in the reaction fills the preform pores and forms the ceramic matrix. Since the molar volume of SiC is less than the sum of the molar volumes of silicon and carbon by 23%, the soaking of liquid silicon continues in course of the formation of silicon carbide. The initial pore volume fraction providing complete conversion of carbon into silicon carbide is 0.562. If the initial pore volume fraction is lower than 0.562 the infiltration results in entrapping residual free silicon. Commonly at least 5% of residual free silicon is left in silicon carbide matrix.

The porous preform may be fabricated by either pyrolysis of a polymerized resin or by Chemical Vapor Infiltration (CVI). The preform microstructure is important for complete infiltration. Large pores helps to obtain a complete infiltration but may result in non-complete chemical interaction and formation of a structure with high residual free silicon and unreacted carbon. Small preform pores results in more complete chemical reaction but in non-complete infiltration due to the blockage (chock-off) of the infiltration channels.
Liquid Metal Infiltration

Liquid Silicon Infiltration (LSI)

Polymer impregnated fibers → Carbon matrix composite → SiC matrix composite

Pyrolysis at 800-1200 °C

polymer → C

Si (liquid) + C → SiC

www.substech.com
Liquid Metal Infiltration

In contrast to the composites fabricated by Polymer Infiltration and Pyrolysis (PIP) and Chemical Vapor Infiltration (CVI) ceramic matrices formed by Liquid Silicon Infiltration are fully dense (have zero or low residual porosity).

The infiltrated at high temperature molten silicon is chemically active and may not only react with the carbon porous preform but also attack the reinforcing phase (SiC or C fibers, whiskers, or particles). A protective barrier coating (interphase) of SiC, C or Si₃N₄ prevents the damage of the fibers by the melt. The barrier coatings are applied over debonding coatings (pyrolytic carbon (C) and hexagonal boron nitride (BN)). The interphases may be deposited by Chemical Vapor Infiltration (CVI). The protective barrier from pyrolytic carbon is formed by Polymer Infiltration and Pyrolysis (PIP).
Advantages and disadvantages of Liquid Silicon Infiltration (LSI) process

Advantages of fabrication of Ceramic Matrix Composites by Liquid Silicon Infiltration (LSI):

- Low cost;
- Short production time;
- Very low residual porosity;
- High thermal conductivity;
- High electrical conductivity;
- Complex and near-net shapes may be fabricated.

Disadvantages of fabrication of ceramic matrix composites by Liquid Silicon Infiltration (LSI):

- High temperature of molten silicon may cause a damage of the fibers;
- Residual silicon is present in the carbide matrix;
- Lower mechanical properties of the resulting composite: strength, modulus of elasticity.
**Liquid Metal Infiltration**

**Liquid Silicon Infiltration (LSI) process**

**Application of Interphases.** A thin (commonly 0.1-1 µm) layer of a debonding phase (pyrolytic carbon (C) or hexagonal boron nitride (BN)) is deposited on the fiber surface by Chemical Vapor Infiltration (CVI) method. In addition to this the fibers are protected from the highly reactive liquid silicon by a barrier coating (commonly SiC). The interphases are deposited by Chemical Vapor Infiltration (CVI). Fabrication of the prepreg. The reinforcing fibers (tow, tape, weave) are impregnated with a resin and then dried or cured to B-stage (partial curing). The resin contains carbon, which further will react with molten silicon.

**Lay-up.** The prepreg is shaped by a tooling (mold).

Molding. The laid-up prepreg is molded. Various molding methods may be used. In the bag molding a rigid lower mold is combined with a flexible upper mold (bag), which is pressed against the prepreg by either atmospheric pressure (vacuum bag mold) or increased air pressure (gas pressure bag mold). The pressurized preform is cured in an autoclave. A combination of a pressure with an increased temperature may also be achieved in compression molding.

**Pyrolysis.** Pyrolytic decomposition of the preceramic polymer is performed in the atmosphere of Argon at a temperature in the range 800-1200°C. Volatile products are released as a result of pyrolysis forming a porous carbon structure.

**Primary machining.** This operation may be performed after the steps of molding and/or pyrolysis. Infiltration of the porous prepreg with Liquid Silicon. The prepreg is immersed into a furnace with molten silicon where its porous carbon structure is infiltrated with the melt. The infiltration process is driven by the capillary forces. Liquid silicon reacts with carbon forming in situ silicon carbide matrix.

**Final machining.**
These composites can be divided into two as follows:

Composites prepared by impregnation of a continuous, multifilament yarn of fibers with matrix (most commonly in the form of a powder slurry). The impregnated yarn can be laid up into various geometries prior to consolidation.

Composites prepared by infiltration of a fiber preform of predetermined shape and usually with a multiaxial fiber geometry.

An underlying principle of techniques developed for long-fiber composites is that a preform of fibers with the required geometry is infiltrated with the matrix or a matrix precursor. The infiltrating matrix can for example take the form of a powder slurry (slurry infiltration), a liquid solution (liquid infiltration), or a mixture of gases or vapors that react to form the matrix.
Liquid Infiltration:

This technique is very similar to liquid polymer or liquid metal infiltration. Proper control of the fluidity of liquid matrix is very important.

It yields a high density matrix, i.e. no pores in the matrix.

Almost any reinforcement geometry can be used to produce a virtually flaw-free composite in a single processing step, with small dimensional change from preform to final product.

However the process is limited by fiber-damaging chemical interactions between the fibre and the matrix at the high temperatures required and by the high viscosities of molten ceramics and glasses.
A variety of materials are produced by infiltration processes. In these techniques a fluid phase (i.e., a gas or a liquid) is transported into a porous structure, where it then reacts to form a solid product.

These methods are particularly important for producing composite materials, where the initial porous perform is composed of the reinforcement phase (i.e., fibers, whiskers, or particles) and infiltration produces the matrix.

**Chemical Vapor Infiltration (CVI)**

In this process a vapor phase precursor is transported into the porous preform, and a combination of gas and surface reactions leads to the deposition of the solid matrix phase. During infiltration the formation of the solid product phase eventually closes off porosity at the external surface of the body, blocking the flow of reactants and effectively ending the process. This is a key feature of most infiltration processes. Isothermal, isobaric CVI often requires extremely long times, so it is generally important to minimize the total processing times.
Chemical Vapor Infiltration method of Ceramic Matrix Composites fabrication is a process, in which reactant gases diffuse into an isothermal porous preform made of long continuous fibers and form a deposition. Deposited material is a result of chemical reaction occurring on the fibers surface.

The infiltration of the gaseous precursor into the reinforcing ceramic continuous fiber structure (preform) is driven by either diffusion process or an imposed external pressure. The deposition fills the space between the fibers, forming composite material in which matrix is the deposited material and dispersed phase is the fibers of the preform. Chemical Vapor Infiltration (CVI) is similar to Chemical Vapor Deposition (CVD), in which deposition the forms when the reactant gases react on the outer substrate surface. Chemical Vapor Infiltration is widely used for fabrication of silicon carbide matrix composites reinforced by silicon carbide long (continuous) fibers.

Commonly the vapor reagent is supplied to the preform in a stream of a carrier gas (H2, Ar, He). Silicon carbide (SiC) matrix is formed from a mixture of methyltrichlorosilane (MTS) as the precursor and Hydrogen as the carrier gas. Methyltrichlorosilane is decomposed according to the reaction:

\[
\text{CH}_3\text{Cl}_3\text{Si} \rightarrow \text{SiC} + 3\text{HCl}
\]
The gaseous hydrogen chloride (HCl) is removed from the preform by the diffusion or forced out by the carrier stream. Carbon matrix is formed from a methane precursor (CH₄). The ceramic deposition is continuously growing as long as the diffusing vapor is reaching the reaction surface. The porosity of the material is decreasing being filled with the formed solid ceramic. However in the course of the CVI process the accessibility of the inner spaces of the preform is getting more difficult due to filling the vapor paths with the forming ceramic matrix. The precursor transportation is slowing down. The growing solid phase separates the spaces in the material from the percolating network of the vapor precursor. Such inaccessible pores do not decrease any longer forming the residual porosity of the composite. The matrix densification stops when the preform surface pores are closed. The final residual porosity of the ceramic composites fabricated by CVI method may reach 10-15%.
Chemical Vapor Infiltration

Types of Chemical Vapor Infiltration process

*Isothermal/isobaric (I-CVI)* is the most commonly used type of CVI process. The fiber preform infiltrated in I-CVI process has no temperature gradient (kept at a uniform temperature). The reactant gas is supplied to the preform at a uniform pressure (no pressure gradient). I-CVI is a very slow process because of the low diffusion rate.

*Temperature gradient (TG-CVI).* In this process the preform is kept at a temperature gradient. The vapor precursor diffuses through the preform from the cooler surface to the hotter inside regions. The temperature gradient enhances the gas diffusion. The precursor decomposes mostly in the hot inner regions since the rate of the chemical reaction is greater at higher temperatures. TG-CVI method allows better densification of the ceramic matrix due to prevention of early closing the surface pores.
Types of Chemical Vapor Infiltration process

**Isothermal-forced flow (IF-CVI)** utilizes forced flow (pressure gradient) of the gas precursor penetrating into the uniformly heated preform. The rate of the ceramic matrix deposition is increased by the enhanced infiltration of the forced reactant gas.

**Thermal gradient-forced flow (F-CVI)** combines the effects of both temperature gradient and forced flow (pressure gradient) enhancing the infiltration of the vapor precursor. A scheme of Chemical Vapor Infiltration process is shown in the picture below. The presented process combines both temperature gradient and pressure gradient for reduction of densification time. Temperature gradient in preform is achieved by heating the top region of it when the bottom region is cooled. Pressure gradient is determined by the difference in the pressures of the entering and exhausting gases.

**Pulsed flow (P-CVI).** In P-CVI process the surrounding precursor gas pressure changes rapidly. The pressure changes in each cycle are repeated many times. A cycle of the pressure change consists of the evacuation of the reactor vessel followed by its filling with the reactant gas.
Chemical Vapor Infiltration (CVI) process

- Fabrication of the fiber preform.

- Application of a debonding interphase. A thin (commonly 0.1-1 µm) layer of pyrolytic carbon (C) or hexagonal boron nitride (BN) is deposited on the fiber surface by Chemical Vapor Infiltration (CVI) method.

- Infiltration of the preform with a preceramic gaseous precursor. The preform is heated and placed into a reactor with a gaseous precursor. The preform is infiltrated with the gas, which decomposes and forms a ceramic deposit (matrix) on the fiber surface. The process continues until the open porosity on the preform surface is closed.

- Abrading/machining the preform surface in order to open the paths of the percolating network, which allow further densification of the matrix.

- Multiple re-infiltration-abrading cycles until maximum densification is achieved.

- Protection surface coating. The open porosity is sealed in order to prevent a penetration of the environmental gases into the composite during the service. Additional layer protecting the composite surface from the oxidation may be applied over the sealcoat. The coatings are deposited by Chemical Vapor Infiltration (CVI).
Advantages and disadvantages of CVI

Advantages of fabrication of Ceramic Matrix Composites by Chemical Vapor Infiltration

- Low fiber damage due to relatively low infiltration temperatures;
- Matrices of high purity may be fabricated;
- Low infiltration temperatures produce low residual mechanical stresses;
- Enhanced mechanical properties (strength, elongation, toughness);
- Good thermal shock resistance;
- Increased Creep and oxidation resistance;
- Matrices of various compositions may be fabricated (SiC, C, Si₃N₄, BN, B₄C, ZrC, etc.);
- Interphases may be deposited in-situ.
Advantages and disadvantages of CVI

Disadvantages of fabrication of ceramic matrix composites by Chemical Vapor Infiltration

- Slow process rate (may continue up to several weeks);
- High residual porosity (10-15%);
- High capital and production costs.
Direct metal oxidation process (DIMOX) of Ceramic Matrix Composites fabrication is a type of reactive melt infiltration (RMI) technique, involving a formation of the matrix in the reaction of a molten metal with an oxidizing gas.

Preform of dispersed phase (fibers, particles) is placed on the surface of parent molten metal in an atmosphere of oxidizing agent (oxygen).

Two conditions are necessary for conducting direct oxidation process: dispersed phase is wetted by the melt; dispersed phase does not oxidize in an atmosphere of oxygen.

Liquid metal oxidizes when it is in contact with oxygen, forming a thin layer of ceramic with some dispersed phase incorporated in it.

Capillary effect forces the melt to penetrate through the porous ceramic layer to the reaction front where the metal reacts with the gas resulting in growing the ceramic matrix layer.
The melt advances to the reaction front continuously at a rate limited by the oxidation reaction rate.

Some residual metal (about 5-15% of the material volume) remains in the inter-granular spaces of the ceramic matrix.

The resulting materials have no pores and impurities, which are usually present in ceramics fabricated by sintering (binders, plasticizers, lubricants, deflocculants, water etc.).

Commonly Direct Melt Oxidation (DIMOX) technique is used for fabrication composites with the matrix from aluminum oxide ($\text{Al}_2\text{O}_3$). A reinforcing preform (SiC or $\text{Al}_2\text{O}_3$ in either particulate or fibrous form) is infiltrated with a molten aluminum alloy heated in a furnace to a temperature 900-1150°C.

The aluminum alloy is doped with additives (e.g. magnesium, silicon) improving the wettability of the reinforcing phase with the melt and enhancing the oxidation process.

The typical rate of DIMOX process is 1-1.5 mm/h.

In principle the direct oxidation process and the oxide growth may continue even after the reaction front has reached the outer surface of the preform. In this case the aluminum oxide will be deposited over the preform changing its dimensions. In order to prevent an advance of the reaction front beyond the preform surface it is coated with a gas permeable barrier. The ceramic matrix growth stops when the reaction front reaches the barrier.
Lay-up. At the lay-up stage the fibrous preform is shaped.

Application of Interphases. A thin (commonly 0.1-1 μm) layer of a debonding phase (pyrolytic carbon (C) or hexagonal boron nitride (BN)) is deposited on the fiber surface by Chemical Vapor Infiltration (CVI) method.

Deposition of a gas permeable barrier on the preform surface. The surface through which the melt should wick into the preform is not coated.

Direct Metal Oxidation. The preform is put in contact with liquid aluminum alloy. The melt wicks into the reinforcing structure through the non-coated surface. The oxidant (air) penetrates into the preform in the opposite direction through the gas permeable barrier. Aluminum and oxygen meet at the reaction front and form the growing layer of the oxide matrix. The process terminates when the reaction front reaches the barrier coating.

Removal of excessive aluminum. The residual aluminum is removed from the part surface.

CMC Fabrication by Direct Oxidation

Advantages of DIMOX process:
- Low shrinkage. Near-net shape parts may be fabricated.
- Inexpensive and simple equipment;
- Inexpensive raw materials;
- Good mechanical properties at high temperatures (e.g. creep strength) due to the absence of impurities or sintering aids;
- Low residual porosity.

The disadvantages of DIMOX process:
- Low productivity – growth rate is about 1mm/hour. The fabrication time is too long: 2-3 days.
- Residual (non-reacted) aluminum may be present in the oxide matrix.
Compare to the conventional methods, the most attractive features and advantages of sol-gel process include:

(a) molecular-level homogeneity can be easily achieved through the mixing of two liquids;
(b) the homogeneous mixture containing all the components in the correct stoichiometry ensures a much higher purity; and,
(c) much lower heat treatment temperature to form glass or polycrystalline ceramics is usually achieved without resorting to a high temperature.
(d) More recently, the sol-gel method has been extensively developed and used in biotechnology applications.
Sol-gel process usually consists of 4 steps:

- The desired colloidal particles once dispersed in a liquid to form a sol.

- The deposition of sol solution produces the coatings on the substrates by spraying, dipping or spinning.

- The particles in sol are polymerized through the removal of the stabilizing components and produce a gel in a state of a continuous network.

- The final heat treatments pyrolyze the remaining organic or inorganic components and form an amorphous or crystalline coating.
**Sol**: a stable suspension of colloidal solid particles or polymers in a liquid

**Gel**: porous, three-dimensional, continuous solid network surrounding a continuous liquid phase

**Colloidal (particulate) gels**: agglomeration of dense colloidal particles

**Polymeric gels**: agglomeration of polymeric particles made from subcolloidal units
SOL-GEL PROCESSING OPTIONS

Sol Fibers → Sol → Gel → Solvent Evaporation → Supercritical Extraction

Powders → Gelation Evaporation → Xerogel

Xerogel Film → Heat → Dense ceramic

Dry Heat → Dense glass or ceramic

Aerogel
Schematic diagram illustrating the enormous shrinkages accompanying the drying by liquid evaporation and sintering of a polymeric gel.

\[ \Delta L / L_0 = 50\% \]  
\[ \Delta V / V_0 = 90\% \]  
\[ \Delta L / L_0 = 20\% \]  
\[ \Delta V / V_0 = 50\% \]

Gelled material  \rightarrow  Drying  \rightarrow  Dried Gel  \rightarrow  Sintering  \rightarrow  Dense Product

\[ \Delta L / L_0 = \text{linear shrinkage} \]  
\[ \Delta V / V_0 = \text{volumetric shrinkage} \]
Processing of CMCs

Some processes for continuous fibre-reinforced CMCs

<table>
<thead>
<tr>
<th>Processing method</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Fibre</th>
<th>Matrix</th>
<th>Temperature range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Slurry infiltration</td>
<td>Commercially developed</td>
<td>Limited max. temperature due to matrix</td>
<td>Graphite</td>
<td>Glass-ceramic</td>
<td>800–1000</td>
</tr>
<tr>
<td>(a) Glass ceramic matrix</td>
<td>Good mechanical properties</td>
<td>Needs to be hot pressed, expensive</td>
<td>Nicalon</td>
<td>Glass-ceramic</td>
<td>800–1000</td>
</tr>
<tr>
<td>(b) Ceramic matrix</td>
<td>Potentially inexpensive</td>
<td>Shrinkage during sintering cracks matrix</td>
<td>Alumina</td>
<td></td>
<td>800–1400</td>
</tr>
<tr>
<td>1. Sintered matrix</td>
<td>Could produce complex shapes</td>
<td>Temperature limit due to glassy phase</td>
<td>SiC</td>
<td></td>
<td>800–1600</td>
</tr>
<tr>
<td>2. “Cement bonded matrix”</td>
<td>Inexpensive</td>
<td>Relatively poor properties to date</td>
<td>Graphite</td>
<td></td>
<td>800–1500</td>
</tr>
<tr>
<td></td>
<td>Ability to produce large complex shapes</td>
<td></td>
<td>Nicalon</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low temperature processing</td>
<td></td>
<td>“New” fibres</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Temperature limit depends on fibre. Currently all systems are limited to ~1200°C available fibres.

## Processing of CMCs

### Some processes for continuous fibre-reinforced CMCs

<table>
<thead>
<tr>
<th>Processing method</th>
<th>Advantages</th>
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<th>Fibre</th>
<th>Matrix</th>
<th>Temperature range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3. Reaction bonded matrix</td>
<td>Good mechanical properties</td>
<td>Has required hotpressing of Si powder in silicon nitride system prior to reaction bonding</td>
<td>Nicalon</td>
<td>Si₃N₄</td>
<td>800–1500</td>
</tr>
<tr>
<td></td>
<td>Pressureless densification</td>
<td>Simple shapes only</td>
<td>“New” fibres</td>
<td>SiC</td>
<td>800–1600</td>
</tr>
</tbody>
</table>

**II. Sol–gel and polymer processing**

<table>
<thead>
<tr>
<th>Processing method</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Fibre</th>
<th>Matrix</th>
<th>Temperature range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Good matrix composition control</td>
<td>Low yields</td>
<td></td>
<td>Nicalon</td>
<td>Nonoxide</td>
<td>800–1200</td>
</tr>
<tr>
<td>Easy to infiltrate fibres</td>
<td>Very large shrinkage</td>
<td></td>
<td>–</td>
<td>Alumina</td>
<td>800–1400</td>
</tr>
<tr>
<td>Lower densification temperature</td>
<td>Woud require multiple infiltration/densification steps</td>
<td>No promising results reported</td>
<td>–</td>
<td>Silicates</td>
<td></td>
</tr>
</tbody>
</table>

**III. Melt infiltration**

<table>
<thead>
<tr>
<th>Processing method</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Fibre</th>
<th>Matrix</th>
<th>Temperature range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Ceramic melt</td>
<td>Potentially inexpensive</td>
<td>High melting temperatures would damage fibres</td>
<td>Graphite</td>
<td>Alumina</td>
<td>800–1100</td>
</tr>
<tr>
<td>Should be easy to infiltrate fibres</td>
<td></td>
<td></td>
<td>Nicalon</td>
<td>Oxides</td>
<td>800–1100</td>
</tr>
<tr>
<td>Lower shrinkage on solidification</td>
<td></td>
<td></td>
<td>–</td>
<td>“New” fibres</td>
<td>800–1100</td>
</tr>
<tr>
<td>(b) Metal melt, followed by oxidation</td>
<td>Potentially inexpensive</td>
<td></td>
<td>Graphite</td>
<td>Alumina</td>
<td>800–1200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Difficult to control chemistry and produce all ceramic system</td>
<td>Nicalon</td>
<td>Alumina</td>
<td>800–1200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Difficult to envision in use for large, complex parts for aerospace applications</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

Temperature limit depends on fibre. Currently all systems are limited to ~1200°C available fibres.

## Processing of CMCs

Some processes for continuous fibre-reinforced CMCs

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<thead>
<tr>
<th>Processing method</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Fibre</th>
<th>Matrix</th>
<th>Temperature range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="#">IV. Chemical vapour infiltration</a></td>
<td></td>
<td>-</td>
<td>“New” fibres</td>
<td>B₄C</td>
<td>800–1200</td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>Slow and expensive</td>
<td>Nicalon</td>
<td>SiC</td>
<td>800–1600</td>
</tr>
<tr>
<td>-</td>
<td>Has been commercially developed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) General approach</td>
<td>Best mechanical properties</td>
<td>Requires iterative process</td>
<td>Nextels</td>
<td>SiC</td>
<td>800–1800</td>
</tr>
<tr>
<td>-</td>
<td>Considerable flexibility in fibres and matrices</td>
<td>Never achieved full density</td>
<td></td>
<td>HfC</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>High quality matrix, very pure</td>
<td>Capital intensive</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>Little fibre damage</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>-</td>
<td>In situ fibre surface treatment</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>-</td>
<td>Ability to fill small pores</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>(b) Lanxide</td>
<td>Ability to produce complex shapes</td>
<td>Slow reaction and growth kinetics</td>
<td>Graphite</td>
<td>Alumina</td>
<td>800–1200</td>
</tr>
<tr>
<td>-</td>
<td>Properties dominated by ceramic</td>
<td>Long processing time &amp; high temp.</td>
<td>Nicalon</td>
<td>AlN</td>
<td>800–1200</td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>limits chemistry</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>Very pore grain boundaries</td>
<td>Wetting and reaction are limitations</td>
<td></td>
<td>TiN</td>
<td>800–1200</td>
</tr>
<tr>
<td>-</td>
<td>Systems include: AlN/Al, TiN/Ti, ZrN/Zr</td>
<td></td>
<td></td>
<td>ZrN</td>
<td>800–1200</td>
</tr>
</tbody>
</table>

[1] Temperature limit depends on fibre. Currently all systems are limited to ≈ 1200 °C available fibres.
Interaction between the matrix and the reinforcing fibers provides higher toughness of a ceramic composite as compared to the matrix material in the monolithic state.

Such effect is a result of cracks deflection at the matrix-fiber interface. When a crack propagating through the matrix reaches a fiber, the relatively weak bonding (debonding) between the matrix and the fiber at their interface allows their relative sliding, which prevents the fiber fracture. The fiber bridges the cracked matrix.

The effect of the crack deflection mechanism is determined by the matrix-fiber bonding strength. If it is too great the fibers are not capable to slide in the matrix therefore the crack passes through the fibers breaking them. The fracture of the composite is brittle like in the monolithic ceramics.

In most infiltration processes of fabrication of ceramic composites strong bonds between the matrix and the fibers form due to chemical interaction between the materials or due to their diffusion into each other. Debonding may be achieved if the fibers and the matrix are separated from each other with a a layer of an interphase preventing their interaction.

Additional interphase layers (for example a film of silicon carbide of the thickness 0.5-5 μm provide protection of the fibers from either environmental attacks (e.g. oxidation) or aggressive action of the infiltrated material (e.g. liquid silicon).

In order to provide weak bonding the interphase material should have a low shear strength. The materials with low shear strength have a layered crystalline structure composed of weak bonded layers allowing easy slippage between them (similar to Graphite): pyrolytic carbon (C) and hexagonal boron nitride (BN).

The structure of pyrolytic carbon is composed of graphene planes bonded to each other by weak Van der Waals forces. The structure of hexagonal boron nitride is also layered. The atoms of boron and nitrogen are strongly bonded within a layer however the bonding between the neighboring layers is weak.

An interphase film of 0.1-1 µm thickness is deposited prior to the infiltration of the matrix. Thicker interphase provides weaker matrix-fiber bonding. The method of chemical vapor infiltration (CVI) is commonly used for deposition of the interphases.

The interphases from pyrolytic carbon withstand high temperatures in non-oxidizing environments, however in air they oxidize and their maximum operation temperature is 500°C.

High purity hexagonal boron nitride may survive in a dry oxidizing atmosphere up to 1200°C.

Ceramic components can be introduced into automobiles. The most important resultant gain would be a reduction in fuel consumption because of the light weight nature of ceramics and CMCs.

Heat exchangers represent an area of application where ceramics or CMCs can be cost-effective because of their high-temperature capability. One can use the waste heat from the furnace exhaust to preheat the inlet combustion air and thus save fuel consumption. Such heat exchangers can be used in industrial furnaces, gas turbines and fluidized bed combustion units. Ceramics and CMCs can also result in fuel efficiency in heat engines because of higher operating temperatures, and reduction or elimination of cooling systems.
Applications of CMCs

- Because of their light weight with high strength at high temperatures, they are used in aerospace and military applications.
- Because of their corrosion resistance and ability to operate with little lubrication. They are used in bearings in missiles.
- Other applications include wear parts, such as seals, nozzles, pads, liners, grinding wheels, brakes, etc. For instance, carbon fiber reinforced carbon composites are being used in aircraft brakes.
- They are also used in dies and tool bits, medical implants and land-based power and transport engines.
APPLICATIONS OF CMCs

Silicon carbide matrix composites are used for manufacturing combustion liners of gas turbine engines, hot gas re-circulating fans, heat exchangers, rocket propulsion components, filters for hot liquids, gas-fired burner parts, furnace pipe hangers, immersion burner tubes.

CMCs have been used in jet fighters. Industrial uses of CMCs include furnace materials, energy conversion systems, gas turbines and heat engines.

Alumina and alumina-silica (mullite) matrix composites are used for manufacturing heat exchangers, filters for hot liquids, thermo-photovoltaic burners, burner stabilizers, combustion liners of gas turbine engines.
Carbon-carbon composites applications

- aircraft and F1 braking
- rocket motor nozzle throats and exit cones
- nosetips/leading edges
- thermal protection systems
- refractory components
- hot-pressed dies
- heating elements
- turbojet engine components.
APPLICATIONS OF CMCs

C_f/SiC CMC panel, 1" thick, produced by melt infiltration; inset, cross-section

CMC-encased carbon/carbon structures that reduce component weight

http://www.ultramet.com/ceramic_matrix_composites_materialsys.html
CMC SiC/SiC blisk hub fabricated at Ultramet by rapid melt infiltration showing outstanding low porosity and smoothly machined surfaces (outer diameter 8")

http://www.ultramet.com/ceramic_matrix_composites_materialsys.html
APPLICATIONS OF CMCs

Carbon-Ceramic Matrix Rotors

BrakeTech Ceramic Matrix Composite (CMC) Rotor on a BST Carbon Fiber wheel, paired with Brembo Monobloc Calipers, custom anodized spacers & buttons and Ohlins Superbike Forks.

http://www.oppracing.com/category/808-braketechn-brake-rotors/
APPLICATIONS OF CMCs

The Porsche Carrera GT's carbon-ceramic (SiC) composite disc brake

Ceramic Matrix Composite Turbine Blade
APPLICATIONS OF CMCs

An F-16 Fighting Falcon F100 engine exhaust nozzle with five A500 ceramic matrix composite divergent seals, identified by the yellow arrows. (Air Force photo)

CMCs are excellent candidates for replacing the nickel-based superalloys currently used in exhaust nozzle parts, primarily due to their capacity to withstand the high temperatures and severe operational environment for much longer periods of time with minimal changes in structural behavior.

In examining the feasibility of using the A500 seals on the divergent section of the exhaust nozzles, AFRL researchers are addressing a number of key Air Force issues--one of which involves the performance comparison of CMC parts in flight and during engine ground testing. SPS has developed a novel CMC that uses carbon fibers in a sequentially layered carbide matrix produced via chemical vapor infiltration. Because this resultant matrix is self-sealing, it helps protect the carbon fibers from oxidation. The fibers are woven in a multidimensional, ply-to-ply angle interlock pattern to reduce the chance of delamination.

Thanks for your kind attention

THE END
Any Questions