COMPOSITE MATERIALS

Asst. Prof. Dr. Ayşe KALEMTAŞ

Office Hours: Tuesday, 16:30-17:30
akalemtas@mu.edu.tr, akalemtas@gmail.com
Phone: +90 – 252 211 19 17
Metallurgical and Materials Engineering Department

ISSUES TO ADDRESS

Ceramic Matrix Composites

- Properties
- Applications
- Fabrication

Ceramic Matrix Composites

Ceramic materials are in general brittle, and, according to the fracture mechanics, **the strength is governed by the flaw size and the fracture toughness.**

General approaches for producing strong ceramics are to reduce the maximum size of processing flaws or to enhance the fracture toughness.

The former approach, however, is limited by the nature of the microstructure of ceramics, since a grain boundary itself can be a flaw responsible for brittle fracture, and surface flaws generated in use may also reduce the strength of ceramics.

Considerable effort has been made to develop toughened ceramics with high fracture toughness.

Ceramic Matrix Composites

The fracture toughness of ceramics is improved by introduction of secondary phases into matrix materials when the secondary phases are chosen to act as barriers to crack propagation.

Whiskers introduced into a ceramic matrix, for example, can retard the crack propagation because the stresses in a whisker spanning the crack plane will tend to pull the crack shut. This phenomenon, known as **"crack bridging"**, leads to higher fracture toughness due to the additional stress required for further propagation of the crack.

Moreover, continuous fiber composites exhibit quasi-ductile fracture behavior resulting from extensive **fiber bridging**.

Ceramic Matrix Composites

Ceramic matrix composites may be classified into two categories.

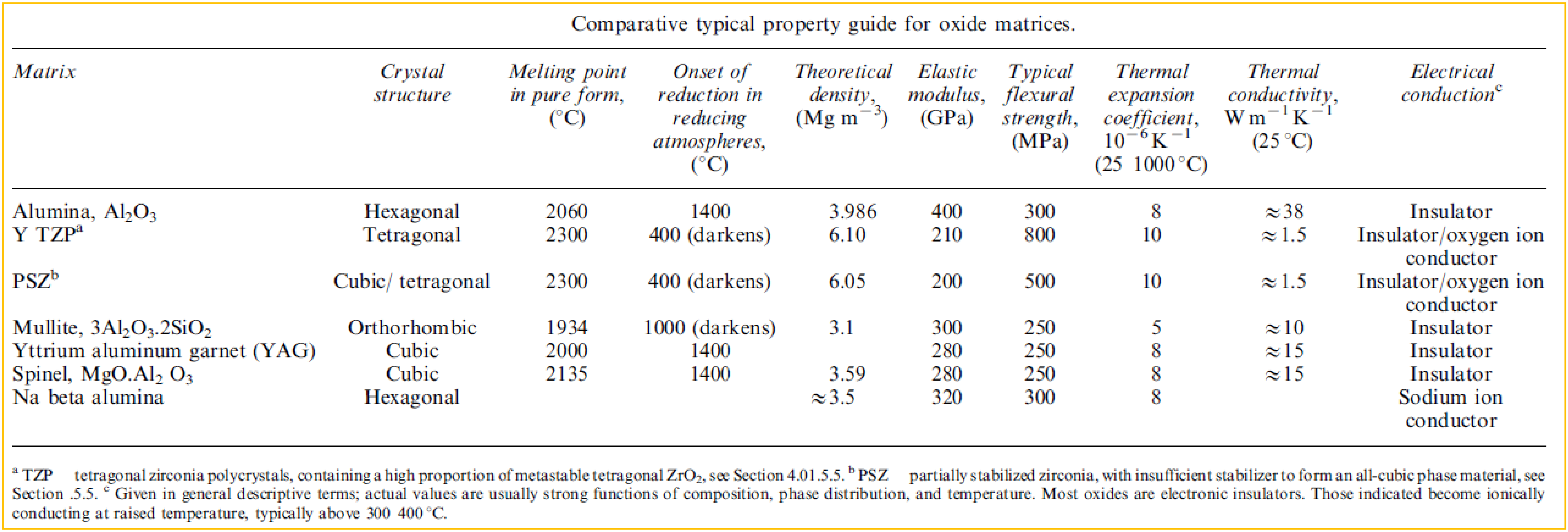
One is a group of **toughened ceramics reinforced with particulates and whiskers**, and these materials exhibit brittle behavior in spite of considerable improvements in fracture toughness and strength. The maximum in fracture toughness is around 10 MPam$^{1/2}$ or more.

The second consists of **continuous-fiber composites** exhibiting quasi-ductile fracture behavior accompanied by extensive fiber pull out. The fracture toughness of this class of materials can be higher than 20 MPam$^{1/2}$ when produced with weak interfaces between the fibers and matrix.

Ceramic Matrix Composites

- The matrix is relatively hard and brittle
- The reinforcement must have high tensile strength to arrest crack growth
- The reinforcement must be free to pull out as a crack extends, so the reinforcement-matrix bond must be relatively weak

Ceramic Matrix Composites



Comparative typical property guide for oxide matrices.

Matrix	*Crystal structure*	*Melting point in pure form,* (°C)	*Onset of reduction in reducing atmospheres,* (°C)	*Theoretical density,* (Mg m^{-3})	*Elastic modulus,* (GPa)	*Typical flexural strength,* (MPa)	*Thermal expansion coefficient,* 10^{-6} K^{-1} (25 1000 °C)	*Thermal conductivity,* W m^{-1} K^{-1} (25 °C)	*Electrical conduction*[c]
Alumina, Al_2O_3	Hexagonal	2060	1400	3.986	400	300	8	≈38	Insulator
Y TZP[a]	Tetragonal	2300	400 (darkens)	6.10	210	800	10	≈1.5	Insulator/oxygen ion conductor
PSZ[b]	Cubic/ tetragonal	2300	400 (darkens)	6.05	200	500	10	≈1.5	Insulator/oxygen ion conductor
Mullite, $3Al_2O_3.2SiO_2$	Orthorhombic	1934	1000 (darkens)	3.1	300	250	5	≈10	Insulator
Yttrium aluminum garnet (YAG)	Cubic	2000	1400		280	250	8	≈15	Insulator
Spinel, $MgO.Al_2O_3$	Cubic	2135	1400	3.59	280	250	8	≈15	Insulator
Na beta alumina	Hexagonal			≈3.5	320	300	8		Sodium ion conductor

[a] TZP tetragonal zirconia polycrystals, containing a high proportion of metastable tetragonal ZrO_2, see Section 4.01.5.5. [b] PSZ partially stabilized zirconia, with insufficient stabilizer to form an all-cubic phase material, see Section .5.5. [c] Given in general descriptive terms; actual values are usually strong functions of composition, phase distribution, and temperature. Most oxides are electronic insulators. Those indicated become ionically conducting at raised temperature, typically above 300 400 °C.

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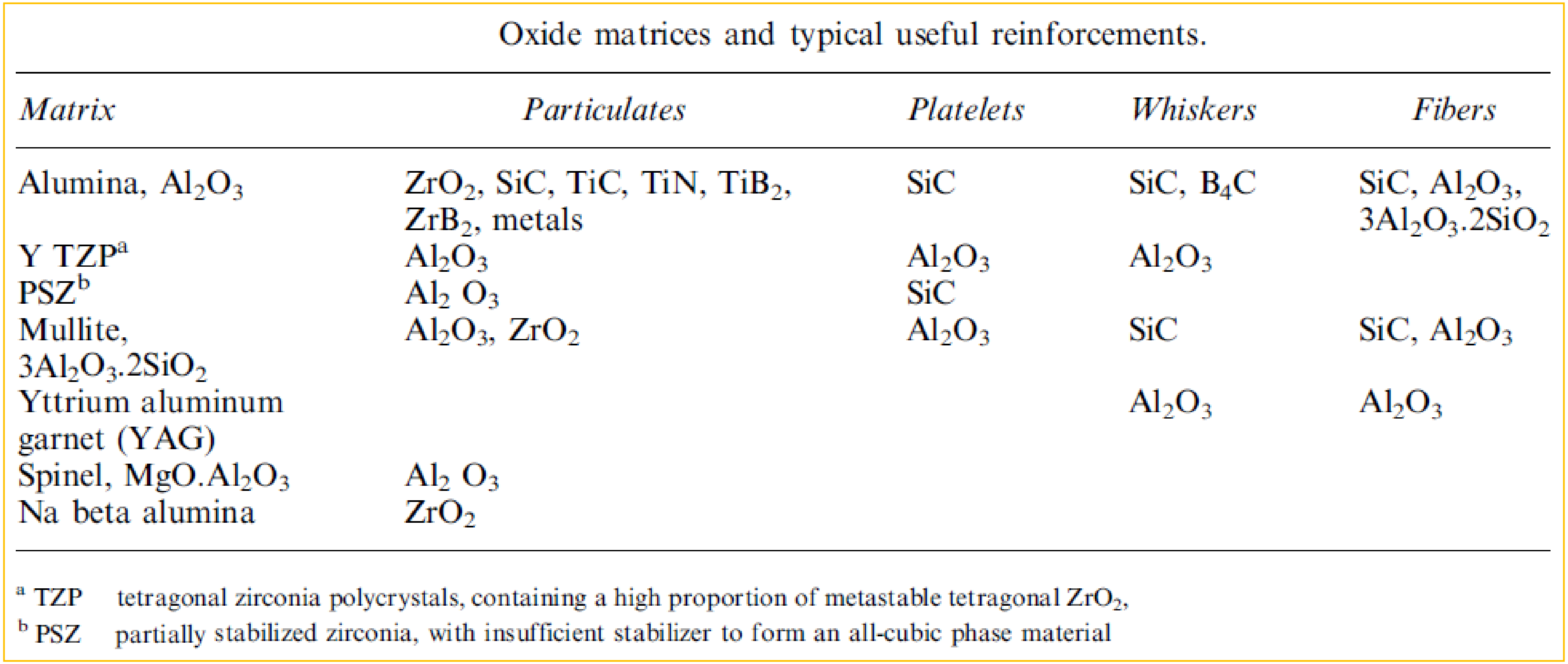
Ceramic Matrix Composites



Oxide matrices and typical useful reinforcements.

Matrix	*Particulates*	*Platelets*	*Whiskers*	*Fibers*
Alumina, Al_2O_3	ZrO_2, SiC, TiC, TiN, TiB_2, ZrB_2, metals	SiC	SiC, B_4C	SiC, Al_2O_3, $3Al_2O_3.2SiO_2$
Y TZP[a]	Al_2O_3	Al_2O_3	Al_2O_3	
PSZ[b]	$Al_2 O_3$	SiC		
Mullite, $3Al_2O_3.2SiO_2$	Al_2O_3, ZrO_2	Al_2O_3	SiC	SiC, Al_2O_3
Yttrium aluminum garnet (YAG)			Al_2O_3	Al_2O_3
Spinel, $MgO.Al_2O_3$	$Al_2 O_3$			
Na beta alumina	ZrO_2			

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[a] TZP tetragonal zirconia polycrystals, containing a high proportion of metastable tetragonal ZrO_2,

[b] PSZ partially stabilized zirconia, with insufficient stabilizer to form an all-cubic phase material

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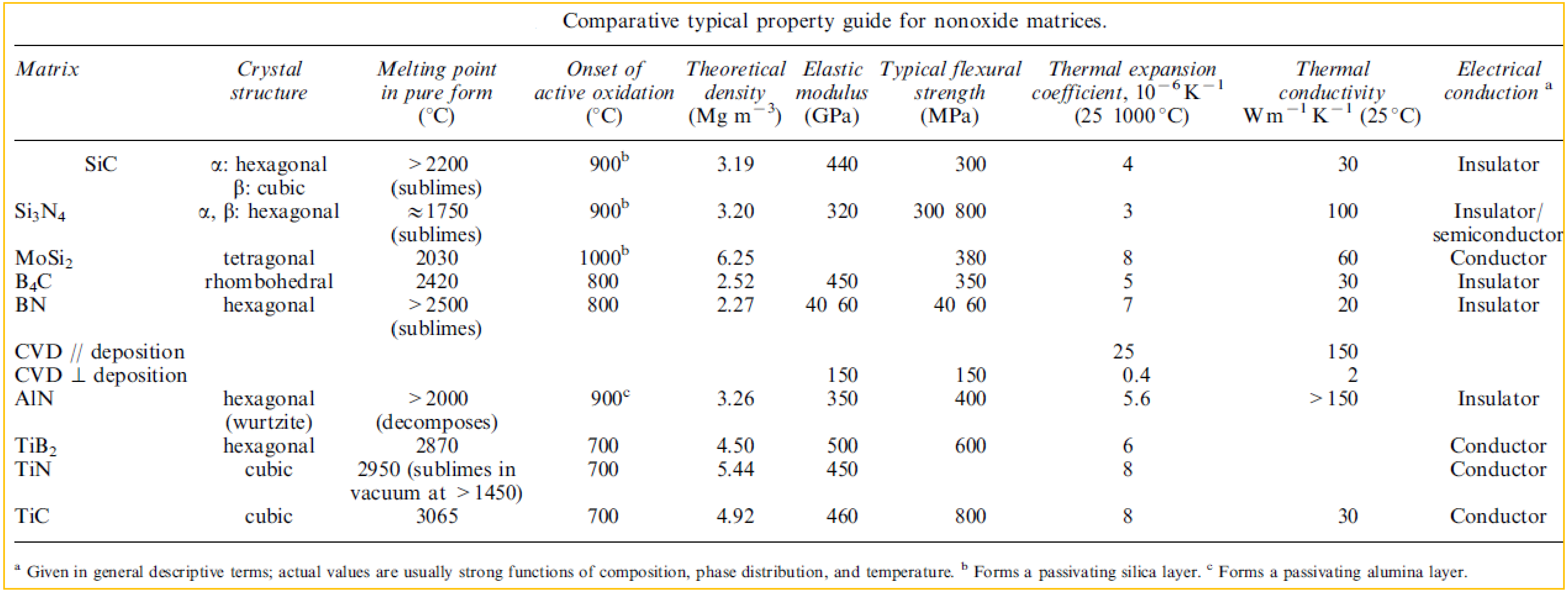
Ceramic Matrix Composites



Comparative typical property guide for nonoxide matrices.

Matrix	*Crystal structure*	*Melting point in pure form* (°C)	*Onset of active oxidation* (°C)	*Theoretical density* (Mg m^{-3})	*Elastic modulus* (GPa)	*Typical flexural strength* (MPa)	*Thermal expansion coefficient*, 10^{-6} K^{-1} (25 1000 °C)	*Thermal conductivity* W m^{-1} K^{-1} (25 °C)	*Electrical conduction* [a]
SiC	α: hexagonal β: cubic	> 2200 (sublimes)	900[b]	3.19	440	300	4	30	Insulator
Si_3N_4	α, β: hexagonal	≈ 1750 (sublimes)	900[b]	3.20	320	300 800	3	100	Insulator/ semiconductor
$MoSi_2$	tetragonal	2030	1000[b]	6.25		380	8	60	Conductor
B_4C	rhombohedral	2420	800	2.52	450	350	5	30	Insulator
BN	hexagonal	> 2500 (sublimes)	800	2.27	40 60	40 60	7	20	Insulator
CVD // deposition							25	150	
CVD ⊥ deposition					150	150	0.4	2	
AlN	hexagonal (wurtzite)	> 2000 (decomposes)	900[c]	3.26	350	400	5.6	> 150	Insulator
TiB_2	hexagonal	2870	700	4.50	500	600	6		Conductor
TiN	cubic	2950 (sublimes in vacuum at > 1450)	700	5.44	450		8		Conductor
TiC	cubic	3065	700	4.92	460	800	8	30	Conductor

[a] Given in general descriptive terms; actual values are usually strong functions of composition, phase distribution, and temperature. [b] Forms a passivating silica layer. [c] Forms a passivating alumina layer.

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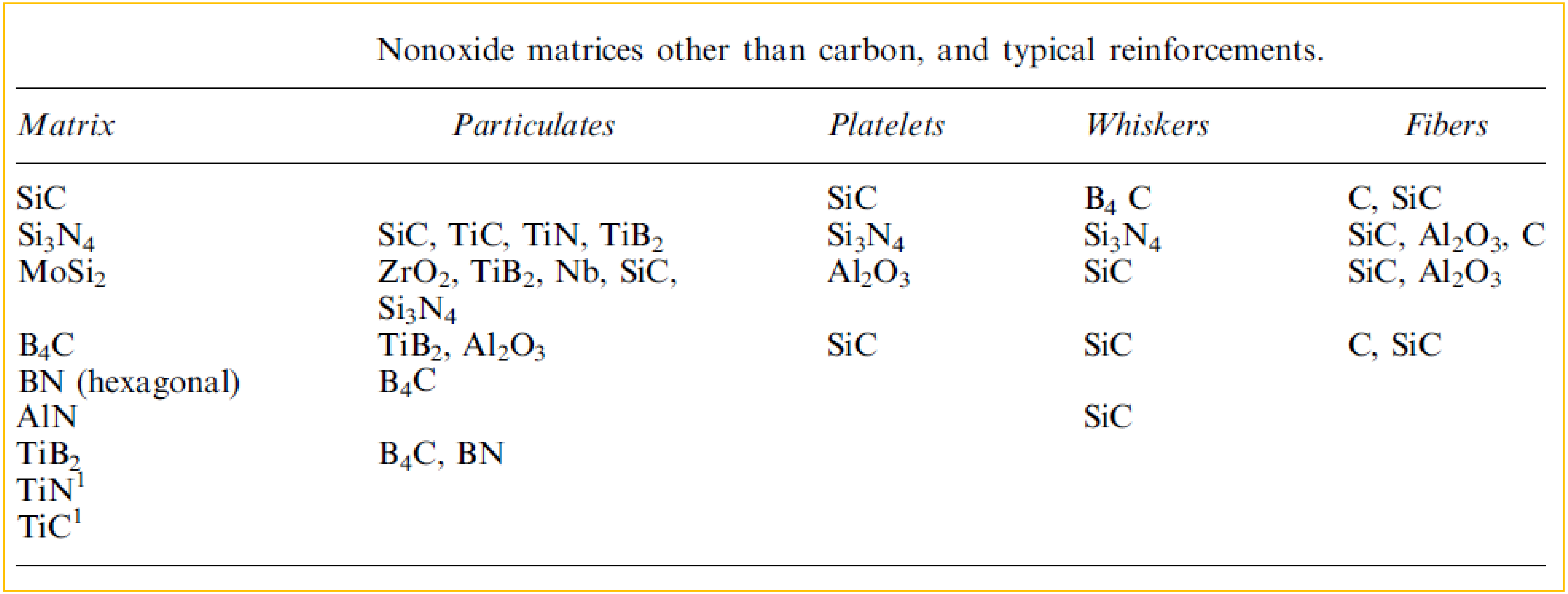
Ceramic Matrix Composites



Nonoxide matrices other than carbon, and typical reinforcements.

Matrix	*Particulates*	*Platelets*	*Whiskers*	*Fibers*
SiC		SiC	B_4 C	C, SiC
Si_3N_4	SiC, TiC, TiN, TiB_2	Si_3N_4	Si_3N_4	SiC, Al_2O_3, C
$MoSi_2$	ZrO_2, TiB_2, Nb, SiC, Si_3N_4	Al_2O_3	SiC	SiC, Al_2O_3
B_4C	TiB_2, Al_2O_3	SiC	SiC	C, SiC
BN (hexagonal)	B_4C			
AlN			SiC	
TiB_2	B_4C, BN			
TiN[1]				
TiC[1]				

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Ceramic Matrix Composites

Fibers and whiskers for reinforcement

(typical diameters – fibers 10 µm, whiskers 1-5 µm)

- Carbon fibers
- SiC fibers
- Oxide fibers (glass fibers, mullite fibers, zirconia fibers, alumina fibers)
- SiC whiskers

Ceramic Matrix Composites

Types of ceramic-matrix composites

- Al_2O_3-ZrO_2 composites
- SiC particulate / Si_3N_4 matrix composites
- SiC whisker / Al_2O_3 matrix composites
- SiC whisker / Si_3N_4 matrix composites
- Continuous fiber / glass matrix composites
- Carbon / carbon composites
- SiC / SiC composites
- Oxide / oxide composites.

Processing of CMCs

To put a rigidized or densified matrix in place, the precursor of the matrix has to be positioned within the mass of reinforcement. This can be done by a number of methods:

(i) Powder dispersion
(ii) Liquid precursors
(iii) Gaseous infiltration

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Processing of CMCs

Powder Dispersion

Impregnating the reinforcement with a suspension of matrix precursor in powder form, either by passing the reinforcement through a slurry or by pressure impregnation of a preform, or by electrophoretic infiltration.

The powder dispersion method is the most widely used where a simple approach using substances of known composition or characteristics is required. Most types of matrix can be positioned using this method. Normally it requires that the fiber or whisker architecture is opened up so that powder particles can completely surround each reinforcing element, and that there is sufficient powder entrained for the densified matrix to fill the space around the reinforcement to an adequate degree, usually completely. Matrix precursors entrained in this way, even if sinter-active, tend to be reluctant to sinter to full density because of the restraint posed by the nonshrinking reinforcement structure, and hot-pressing, usually uniaxial, is required to close voids between reinforcing elements. This process does not readily lend itself to complex shapesĐgenerally plate shapes with planar reinforcement are easiest to produce because the reinforcement is not greatly distorted and thus it is not particularly versatile for producing components with complex architecture.

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Processing of CMCs

Liquid precursors

Impregnating the reinforcement preform with a liquid organic or organometallic or inorganic substance, typically a polymer or a sol, which on heating rigidizes by curing or gelling, and then decomposes to leave a ceramic matrix.

A more reliable way of penetrating the reinforcement architecture is to use a liquid precursor. This can be in the form of an aqueous sol (e.g., boehmite, AlOOH, later to form alumina), or an organic or organometallic polymer which decomposes on heating to form a ceramic.

The disadvantage of this method is that it is not very efficient because the volume occupied by the resulting solid is much less than that of the impregnating liquid. Several stages of repeated impregnation and decomposition may be needed to obtain an impervious final product, which even so still contains interreinforcement closed porosity.

The advantage of the method is that complex shapes can be made based on the reinforcement preform shape, but the disadvantage is the cost in terms of the number of processing steps involved.

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Processing of CMCs

In the *liquid phase routes*, *the fibres first coated with an* interphase (e.g. by I-CVI) are embedded in a liquid precursor of the matrix.

In the ***reactive melt infiltration (RMI) processes***, a fibre preform is impregnated by capillary forces with a liquid which reacts either with a solid phase used to consolidate the fibre preform (SiC-Si matrices formed through liquid silicon infiltration of a carbon-consolidated preform) or with the atmosphere (Al_2O_3-Al matrices formed through liquid aluminium infiltration and chemical reaction with an oxidizing atmosphere).

Among other **advantages**, the RMI-processes are ***fast*** and ***can be applied to thick preforms***. They also yield materials of ***low residual porosities*** and ***high thermal conductivities.***

Processing of CMCs

In the ***polymer impregnation and pyrolysis (PIP) processes***, the fibres are embedded in a polymeric precursor of the matrix, such as a thermosetting resin or a pitch for carbon or a polycarbosilane for SiC, and the green composite is then pyrolyzed.

Such processes are ***relatively flexible*** since the composition of the precursor can be tailored.

Conversely, a shrinking of the matrix occurs during the pyrolysis step owing to the evolution of gaseous species. As a result, several PIP-sequences have to be applied in order to achieve a low enough residual porosity, which is time and labour consuming. Shrinkage can be limited by loading the liquid precursor with suitable fine powder, i.e. by using a slurry. Finally, the residual porosity can also significantly be reduced through a hot pressing step, an alternative that supposes that the matrix displays enough plasticity not to damage the fibres. This liquid impregnation/hot pressing technique is well suited to the fabrication of glass-ceramic matrix composites.

Processing of CMCs

Gaseous infiltration

Using a reactive gas mixture which deposits a ceramic material within a preform of the reinforcement, commonly known as chemical vapor deposition (CVD) or chemical vapor infiltration (CVI), and typically performed at high temperature; all of which have particular advantages or disadvantages for different types of matrix material.

For those matrix materials which can be produced by reaction between gases, such as carbon and silicon carbide, a gas phase route can substitute for the liquid impregnation route. This tends to be a slow process, because if deposition is allowed to occur too quickly, it mostly occurs at the external surface, blocking penetration.

Developments in the technique have concentrated on ensuring that deposition occurs internally to the component, by forcing reactive gas flow through the walls of the component (CVI), using temperature gradients, and on speeding the process up, e.g., by using microwave heating which also has the advantage of improving deposition internally to the preform. However, as with liquid infiltration, full densification of the matrix never occurs as access to remaining pores becomes blocked, but the method can be used for complex shapes.

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Processing of CMCs

In *gas phase routes*, *i.e. the so-called* ***chemical vapor infiltration*** **(CVI) processes**, the reinforcements (usually as a multidirectional preform) is densified by the matrix deposited from a gaseous precursor, e.g. an hydrocarbon for carbon or a mixture of methyltrichlorosilane and hydrogen for silicon carbide.

There are several versions of the CVI-process.

It is now well established that a fibre coating, referred to as the interphase, has to be deposited on the fibre prior to the infiltration of the matrix in order to control the fibre-matrix (FM) bonding and the mechanical behavior of the composite.

The main role of the interphase is to deflect the microcracks which form in the matrix under loading and hence to protect the fibre form notch effect (mechanical fuse function).

Processing of CMCs

Particulate-, platelet-, whisker- and short-fiber-reinforced ceramic-matrix composites can be fabricated via the usual ceramic processes used for multiphase ceramics.

Whisker and short fiber reinforced composites can be processed by hot pressing. For continuous-fiber reinforced composites the first step is building up a 3D architecture from the fibers by textile production techniques (weaving, stitching, knitting and braiding).

For fiber- and whisker-reinforced composites, the reaction between the reinforcement and the matrix must be minimized, i.e. The processing temperature should not be too high.

→ Chemical vapor impregnation (CVI) or liquid impregnation (ceramic precursor infiltration) with thermal decomposition (pyrolysis).

Processing of CMCs

When fabricating ceramic composites, the reaction between the reinforcement and matrix must be minimized. Consequently, a suitable low processing temperature should be selected to minimize degradation of the reinforcing phases.

Use of continuous fibers can modify the mechanical properties if suitable fiber orientations are chosen. A well-designed fiber architecture is first prepared, and the matrix material introduced into the voids of the structure. Infiltration into the fiber architecture is often performed using chemical vapor infiltration or pre-ceramic polymer infiltration-pyrolysis techniques. These techniques have the advantage of requiring low temperatures in comparison with sintering processes.

Textile production techniques, such as weaving, stitching, knitting and braiding are used for producing three-dimensional composite structures, and the stacked sheets of fabrics are used for manufacturing panel structures.

Hot pressing is used for fabricating glass matrix composites due to the relatively low processing temperatures, and this is also used for the fabrication of whisker composites.

Chapter 15.1, Ceramic-Matrix Composites, AKIRA OKADAS, Handbook of Advanced Ceramics, 2003, Elsevier Inc., Somiya et al. (Eds.),

Processing of CMCs

HOT PRESSING

Uniaxial and two-dimensional fiber composites with glass matrices can be produced by hot pressing.

The fibers are immersed in a slurry of matrix particles and then dried.

The fiber/matrix powder preform is then cut into suitable dimensions, and stacked for hot pressing in order to produce dense composites.

The fabricated composites are usually in the shape of flat disks or rectangular plates. Densification of whisker composites is usually performed by hot pressing.

Careful control is required both to avoid damage to the whiskers and to achieve a homogeneous dispersion of whiskers.

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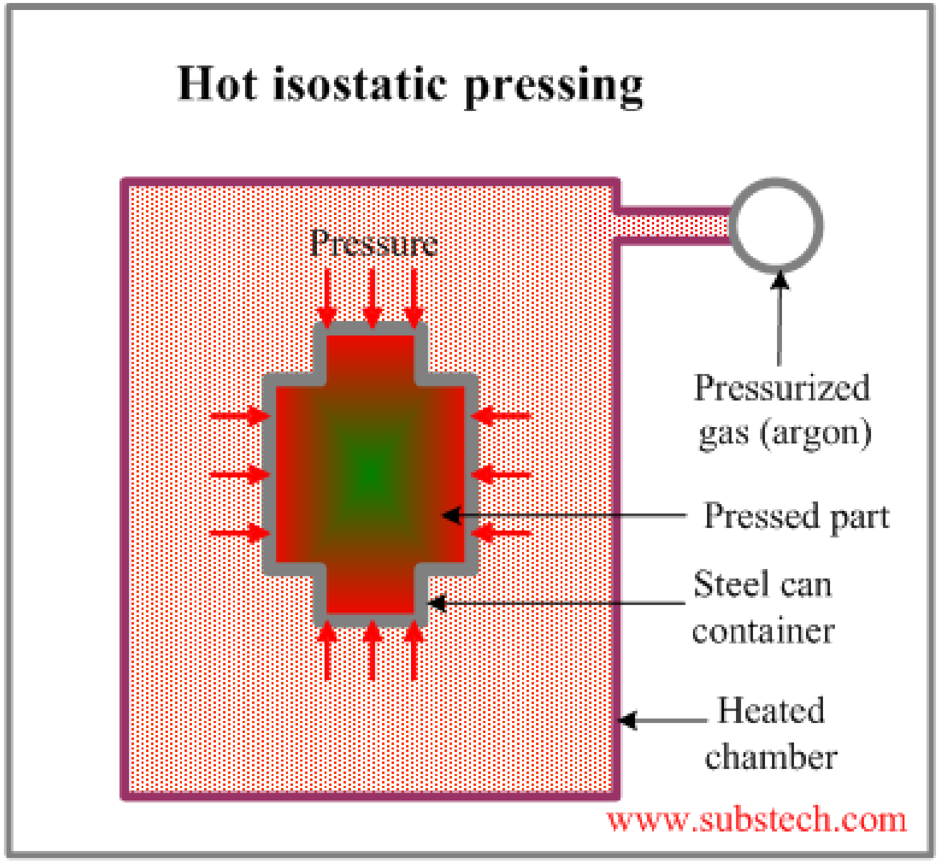
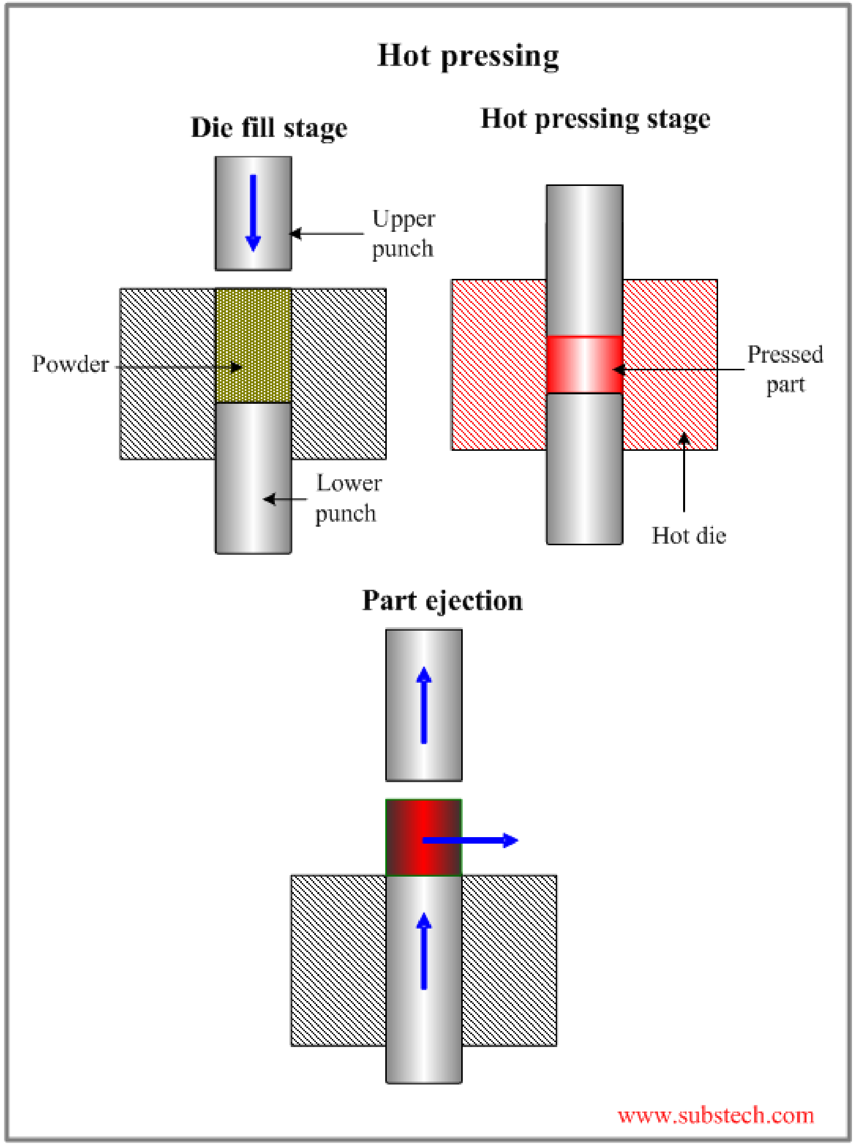
HOT PRESSING





Processing of CMCs

CHEMICAL VAPOR IMPREGNATION

Chemical vapor impregnation (CVI) is a method of infiltrating fiber architectures with matrix particles via the vapor phase.

Although this is a similar process to chemical vapor deposition (CVD) in terms of gas reaction, decomposition conditions in CVI are chosen for in-depth decomposition rather than coating the surface of the substrate.

Several techniques have been developed to introduce the reaction gases into the fiber architecture, such as temperature gradient, pressure gradient and pulse CVI.

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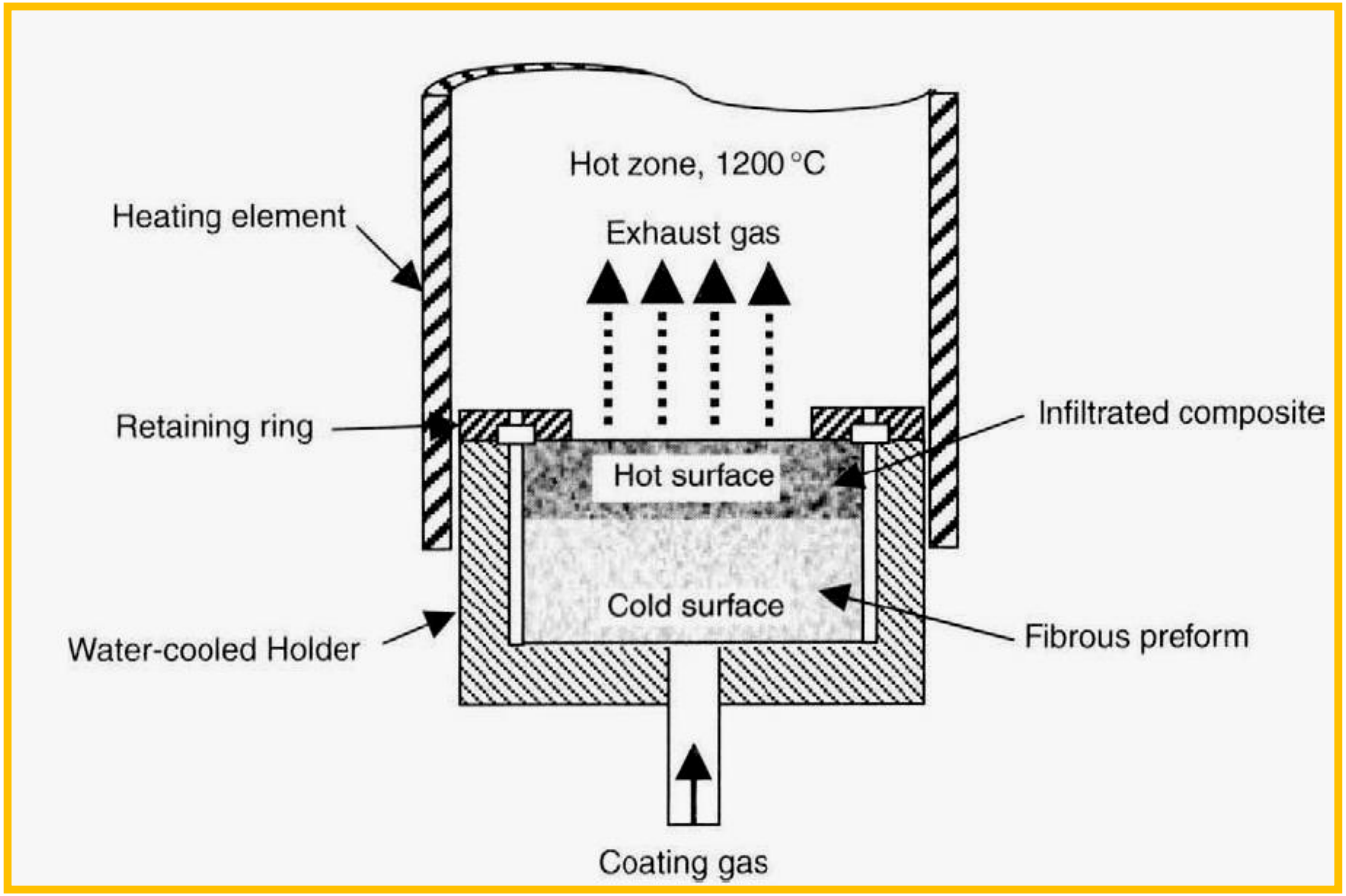
CHEMICAL VAPOR IMPREGNATION



CVI equipment for the temperature gradient technique

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LIQUID IMPREGNATION AND PYROLYSIS

Preceramic polymer can fill a preform with liquid polymers, either molten or in solution, which are then pyrolized to make a ceramic matrix.

Polymer impregnation and thermal decomposition are repeated several times.

Resins, such as phenol and pitch, are used for producing carbon matrix composites, and organosilicon compounds, such as polycarbosilane and polyvinylsilane, are used for the impregnation of silicon carbide.

Sols have also been used for infiltrating preforms to produce oxide matrices, such as alumina, silica, zirconia and mullite.

Following infiltration, they are gelled by drying or by adjusting the temperature, and the matrix is formed after heat treatment.

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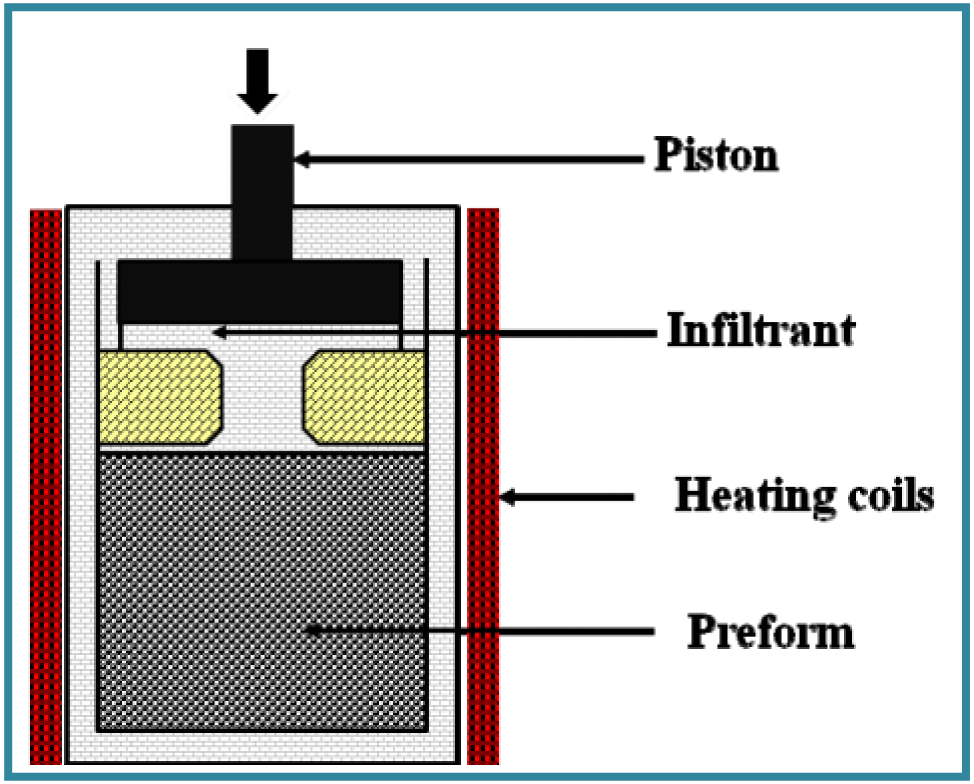

Liquid Infiltration Process

http://nptel.ac.in/courses/112107085/module6/lecture5/lecture5.pdf

Liquid infiltration

It is similar to the resin transfer molding process which is used for the processing of polymer matrix composites. The three major issues to be considered in the liquid infiltration process are:

a) Chemical reactivity: The process is done at an elevated temperature and at high temperatures; the reinforcement and the matrix may react resulting in unnecessary reaction which deteriorates the bonding between the reinforcement phase and the matrix phase.

b) Melt viscosity: The melt viscosity of the ceramics is high compared to that of metals, which can result in the inability of the ceramic infiltrant to infiltrate into the fibrous ceramic preform.

c) Wettability of the reinforcement: The infiltrant may not be able to wet the reinforcement resulting in improper bonding which further leads to the failure of the product at the interface of reinforcement and the matrix.

Processing of CMCs

Liquid Infiltration

The preform is kept in a closed chamber which is surrounded by the heating coils to attain the desired temperature for the infiltration to take place. The infiltrant infiltrates into the preform under pressure with the help of a piston.

Advantages

- Matrix of homogeneous structure can be processed.
- The matrix can be formed in a single processing step.
- Fiber preform in any form (fiber, whisker or particle) can be infiltrated by this process.

Disadvantages

- Infiltration of performs is a complicated task as the ceramics have higher melt viscosities than metals.
- The differential shrinkage between the matrix and reinforcing phase causes crack formation during solidification.
- High melting points of ceramics results in greater possibility of reaction between the liquid matrix and the reinforcement.

http://nptel.ac.in/courses/112107085/module6/lecture5/lecture5.pdf

Processing of CMCs

NOVEL TECHNIQUES

Melt infiltration into fibrous preforms combined with oxidation of the metal matrix can produce ceramic matrix composites.

Since this type of process was developed by Lanxide Corporation, it is called the Lanxide process.

For example, a Nicalon SiC fiber and alumina matrix composite was produced as follows: stacked fibrics of Nicalon fiber were coated by CVD. The major purposes of the coating were to protect the fiber from aluminum alloys during the matrix growth process and to provide a weak fiber-matrix interface. The fiber architectures were then placed on molten aluminum to allow the matrix to grow in the fiber preform by direct oxidation of the aluminum alloy.

Chapter 15.1, Ceramic-Matrix Composites, AKIRA OKADAS, Handbook of Advanced Ceramics, 2003, Elsevier Inc., Somiya et al. (Eds.),

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NOVEL TECHNIQUES

Eutectic consolidation using a single crystal production technique can also be used in the production of two-phase ceramic composites.

Aligned composite structures can be produced by unidirectional solidification of binary eutectics. The $BaFe_{12}O_{19}$-$BaFe_2O_4$ eutectic has been, for example, produced from powder mixtures of Fe_2O_3 and $BaCO_3$. The melt was consolidated by moving the specimen gradually in the furnace, in a similar way to the Bridgman technique.

Using a similar technique, a variety of eutectic systems were investigated. The microstructure revealed that fibrous structures are developed along the longitudinal direction, and the flexural strength is greater when the crack propagates across the fibrous structure.

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PARTICULATE COMPOSITES

Ceramic composites containing particulates are similar to multiphase ceramics, and these materials can be fabricated through traditional ceramic processes.

WHISKER COMPOSITES

The green density of the mixture of whiskers and matrix powders is generally low due to a high aspect ratio of whiskers. Pressure sintering, such as hot pressing, is therefore used for densification. Another problem is due to the agglomeration of whiskers, and careful mixing of whiskers with matrix forming powders is required to avoid inducing serious damage to the whiskers. A typical procedure for this is to disperse the whiskers in liquid followed with successive filtration to remove agglomerated whiskers. The whiskers are then prepared for composite fabrication by blending with powders of the matrix material.

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CONTINUOUS FIBER COMPOSITES

The mechanical behavior of continuous fiber composites is very different to that of other brittle ceramics. In tensile loading, a change in the linear stress-strain relation occurs after matrix cracking, and sliding pullout contributes to the load bearing ability afterward.

Moreover, shear failure and compression failure are often observed in flexural tests, resulting from delamination due to shear stresses and fiber buckling due to compression.

Such a failure mode is obviously derived from the weak interface between the fiber and matrix. Therefore, the presence of lubricant carbon and boron nitride at the interfaces is preferred. Although excess carbon on the surface of SiC fibers acts as a lubricant, the carbon layer may oxidize in air. Boron nitride coating on fibers has been carried out to maintain weak interfaces at high temperatures.

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GLASS MATRIX COMPOSITES

Continuous fibers such as carbon fibers and SiC fibers can be used to reinforce a glass matrix.

The strengthening mechanism is similar to that in resin matrix composites, and the fibers carry most of the load due to their much higher Young's modulus compared to the matrix.

Of all the continuous fiber composites, glass matrix composites are particularly dense as they are produced by impregnation of a glass melt.

The mechanical properties are characterized by high strength and large fracture energy. The large fracture energy is explained in terms of intensive pull out of fibers from the matrix glass. This indicates that the fiber to matrix bond is poor due to the presence of lubricant carbon layers on the surfaces of both graphite and silicon carbide fibers. In contrast glass matrix composites using oxide fibers exhibit low flexural strength due to the high bonding strength between fiber and glass matrix.

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GLASS MATRIX COMPOSITES

Carbon fiber glass matrix composites were intensively studied in the 1970s and SiC fiber composites in the 1980s.

In both cases the fabrication method is essentially the same.

Fiber tows or fabrics are first immersed in a glass powder suspension, and the powder-containing fiber sheets are stacked ready to be hot-pressed into laminates.

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CARBON/CARBON COMPOSITES

The development of carbon/carbon composites began in 1958, and they have been applied to the hot parts of missiles and the Space Shuttle, such as nose caps and leading edges.

Carbon/carbon composites can withstand temperatures higher than 3000°C in a vacuum and in an inert atmosphere, without losing strength as the operating temperature is increased. However, they oxidize and sublime when in an oxygen atmosphere at 600°C.

Silicon carbide coatings are therefore coated with a layer of glass to protect them in high temperature applications. The protection mechanism is as follows. When the part is cooled down from the coating temperature, microcracks develop in the silicon carbide layer, resulting from thermal expansion mismatch between carbon and silicon carbide. These cracks might cause oxidation of the substance if exposed to the air, but are immediately impregnated with the overcoated glass.

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CARBON/CARBON COMPOSITES

Carbon/carbon composites have successfully replaced metallic brake discs in racing cars and aircraft because of their lightweight.

Civilian aircraft, such as the Concorde supersonic jet and Boeing 767 use carbon/carbon composite brakes.

In comparison to steel brakes, a 40% weight saving is achieved using carbon/carbon composites due to their large heat capacity (2.5 times that of steel) and high strength (twice that of steel) at elevated temperatures.

Carbon/carbon composites are produced by pyrolyzing an organic matrix or by CVI. CVI of carbon from hydrocarbon gas is normally accomplished at 1100°C, and pyrolytic carbon is obtained. Carbonized organic composites are typically produced from graphite fabrics pre-impregnated with phenolic resin. The fabrics are laid up as a laminate and cured. They are then pyrolyzed to form a matrix of glassy carbon around the graphite fibers. As a resuk of repeated impregnations of resins and pyrolyzations, densification is achieved.

Chapter 15.1, Ceramic-Matrix Composites, AKIRA OKADAS, Handbook of Advanced Ceramics, 2003, Elsevier Inc., Somiya et al. (Eds.),

Processing of CMCs

SiC/SiC COMPOSITES

Since the oxidation resistance of SiC is much better than that of carbon, SiC/SiC composites have been developed for aerospace application such as propulsion and high velocity systems.

Similar to carbon/carbon composites, the SiC/SiC continuous fiber composites consist of a fiber architecture made of silicon carbide fibers in a matrix of silicon carbide.

The matrix is usually produced by CVI or preceramic polymer impregnation and pyrolysis.

Chapter 15.1, Ceramic-Matrix Composites, AKIRA OKADAS, Handbook of Advanced Ceramics, 2003, Elsevier Inc., Somiya et al. (Eds.),

Processing of CMCs

OXIDE/OXIDE COMPOSITES

In continuous fiber composites, a weak interface between fiber and matrix is preferred because a large fracture energy is generated as a result of frictional slip at the fiber/matrix interface after matrix cracking.

In the case of SiC continuous fibers, the presence of excess carbon on the surface of the SiC fibers contributes to their sliding ability, although the excess carbon may disappear during longterm use due to oxidation and the oxide reaction product formed at the cracked matrix may bond with the interface. As a result, embrittlement occurs. It is therefore important to maintain weak interfaces at high temperatures in oxidative atmospheres, and successful results have been obtained for SiC continuous fiber/Al_2O_3 composites using SiC fibers coated with BN layers.

Since oxide materials have no oxidation problems, development of all-oxide composites has been a major goal of recent research. Such composites have an interface configuration which allows a crack to propagate along the interface after matrix cracking. There are several microstructural design strategies. The first is to use fugitive layers, the second is to use stable oxide interfaces with suitably low fracture toughness, and the third is to use a porous matrix because the porous interlayers act as crack deflection paths

Chapter 15.1, Ceramic-Matrix Composites, AKIRA OKADAS, Handbook of Advanced Ceramics, 2003, Elsevier Inc., Somiya et al. (Eds.),

Processing of CMCs

EUTECTIC COMPOSITES

Recently, Al_2O_3-$Y_3Al_5O_{12}$ eutectic composites have been attracting considerable attention.

Firstly, the creep rates of Al_2O_3-$Y_3Al_5O_{12}$ eutectic composites are considerably lower due to the excellent creep resistance of $Y_3Al_5O_{12}$ single crystals, and meet the design guidelines for use in gas turbines.

Furthermore, these composites have greater fracture toughnesses than single crystals, and maintain their high flexural strengths up to 1700°C.

Chapter 15.1, Ceramic-Matrix Composites, AKIRA OKADAS, Handbook of Advanced Ceramics, 2003, Elsevier Inc., Somiya et al. (Eds.),

Processing of CMCs

The choice of method is determined by the

- *geometry,*
- *the complexity of shape and*
- *the production volume of the component.*

Main Processing Routes for CMCs

Processing Route	Matrices
Chemical vapour infiltration	Carbides, nitride, carbon, oxides, borides
Viscous phase hot pressing (2D preforms)	Glasses, ceramic-glasses
Sol-gel route (2D, 3D preforms)	Oxides
Polymer precursor route (3D preforms)	SiC, Si_xN_y, $Si_xC_yN_z$
Liquid metal infiltration	Si → SiC
Gas-metal reaction	Oxide (Al, nitrides (Al, Zn, Ti))
Solid-state hot pressing	SiC, Si_3N_4
Prepreg curing and pyrolysis	SiC, Si_3N_4
Hot pressing (2D preforms)	Oxides

Processing of CMCs

Some processes for continuous fibre-reinforced CMCs

Processing method	Advantages	Disadvantages	Fibre	Matrix	Temperature range* (°C)
I. Slurry infiltration (a) Glass ceramic matrix	• Commercially developed • Good mechanical properties	• Limited max. Temperature due to matrix • Needs to be hot pressed, expensive • Formations of complex shapes is difficult	• Graphite • Nicalon	• Glass-ceramic • Glass-ceramic	• 800-1000 • 800-1000
(b) Ceramic matrix 1. Sintered matrix	• Potentially inexpensive • Could produce complex shapes	• Shrinkage during sintering cracks matrix • Temperature limit due glassy phase		Alumina SiC Si_3N_4	• 800-1400 • 800-1600 • 800-1500
2. Cement bonded matrix	• Inexpensive • Ability to produce large complex shapes • Low temperature processing	• Relatively poor properties to date	• Graphite • Nicalon • New fibres	• Cements	• 400-1400
3. Reaction bonded	• Good mechanical properties •Pressureless densification	• Has requires hotpressing of Si powder in Si_3N_4 system prior to reaction bonding • Simple shapes only	• Nicalon • “New” fibres	•Si_3N_4 • SiC	• 800-1500 • 800-1600

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

M. Rosso, Ceramic and metal matrix composites: Routes and properties, Journal of Materials Processing Technology 175 (2006) 364–375

Processing of CMCs

Some processes for continuous fibre-reinforced CMCs

Processing method	Advantages	Disadvantages	Fibre	Matrix	Temperature range* (°C)
II. Sol-gel and polymer processing	• Good matrix composition control • easy to infiltrate fibres •Lower densification temperature	• Low yields • Very high shrinkage • Would require multiple infiltration/densification steps • No promising results reported	• Nicalon • - • -	• Non-oxide • Alumina • Silicates	• 800-1200 •800-1400
III. Melt infiltration a) Ceramic melt	• Potentially inexpensive • Should be easy to infiltrate fibres • Lower shrinkage on solidification	•High melting temperatures would damage fibres	• Graphite • Nicalon • "New" fibres	• Alumina • Oxides	•800-1100 • 800-1100
b) Metal melt, followed by oxidation	• Potentially inexpensive • Cermet type material	• Difficult to control chemistry and produce all ceramic system • Difficult to envision in use for large, complex parts for aerospace applications	• Graphite • Nicalon	• Alumina	•800-1200

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

M. Rosso, Ceramic and metal matrix composites: Routes and properties, Journal of Materials Processing Technology 175 (2006) 364–375

Processing of CMCs

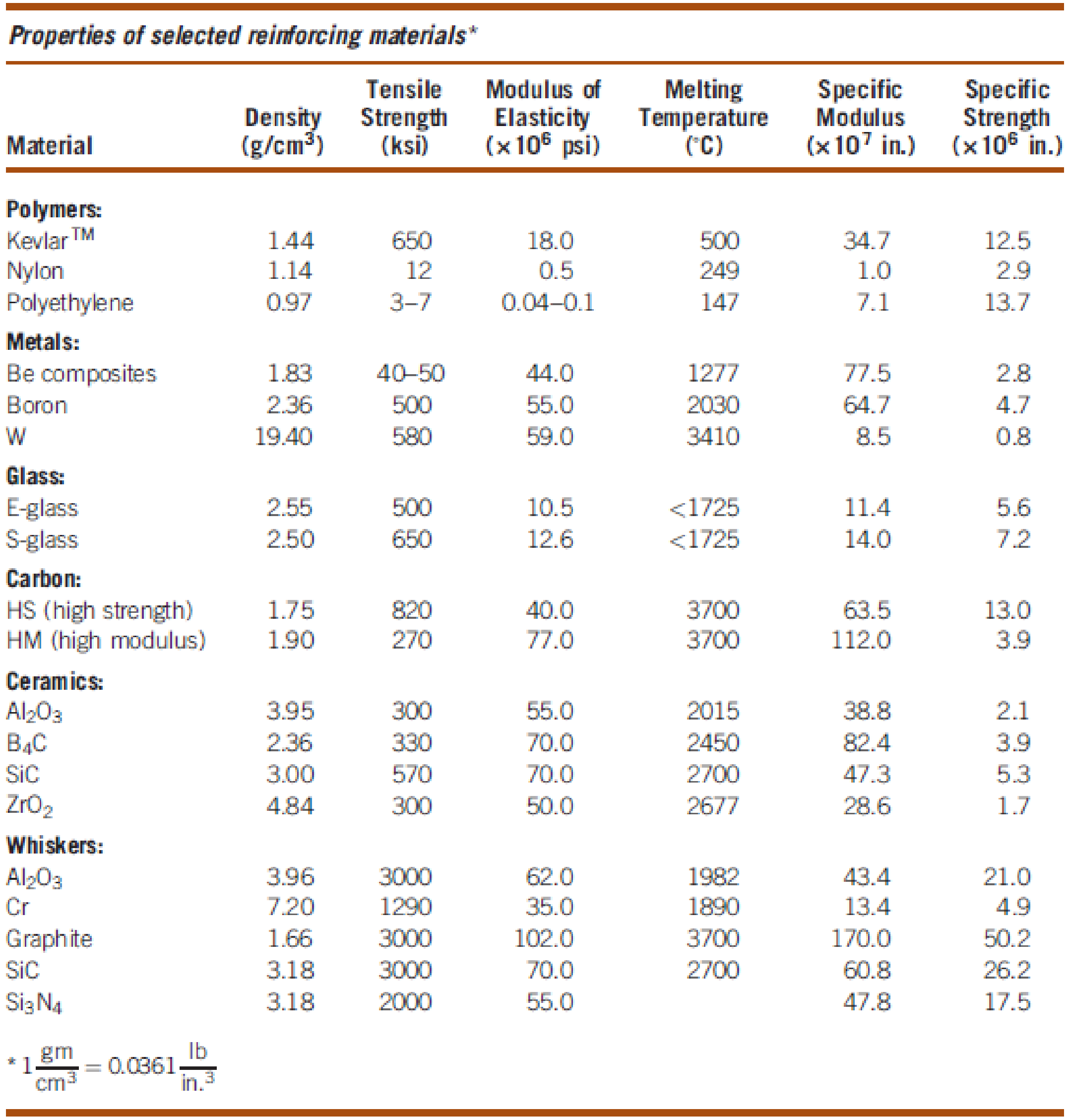
Some processes for continuous fibre-reinforced CMCs

Processing method	Advantages	Disadvantages	Fibre	Matrix	Temperature range* (°C)
IV. Chemical vapour infiltration					
• -	• -	• -	• “New” fibres	• B_4C	• 800-1200
• -	• Has been commercially developed	• Slow and expensive	• Nicalon	• SiC	• 800-1600
• -	• Best mechanical properties	• Requires iterative process	• Nextels	• SiC	• 800-1800
a) General approach	• Considerable flexibility in fibres and matrices	• Never achieved full density	• -	• HfC	• -
	• High quality matrix, very pure	• Capital intensive	• -	• Nitrides	• -
	• Little fibre damage	• -	• -	• Oxides	• -
	• In-situ fibre surface treatment	• -	• -	• Borides	• -
	• Ability to fill small pores	• -	• -	• -	• -
b) Lanxide	• Ability to produce complex shapes	• Slow reaction and growth kinetics	• Graphite	• Alumina	• 800-1200
• -	• Properties dominated by ceramic	• Long processing time and high temperature limits chemistry	• Nicalon	• AlN	• 800-1200
•-	• Very porous grain boundaries	• Wetting and reactions are limitations	• -	• TiN	• 800-1200
• -	• Systems include: AlN/Al, TiN/Ti, ZrN/Zr	• -	• -	• ZrN	• 800-1200

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

M. Rosso, Ceramic and metal matrix composites: Routes and properties, Journal of Materials Processing Technology 175 (2006) 364–375

CMCs



Properties of selected reinforcing materials*

Material	Density (g/cm^3)	Tensile Strength (ksi)	Modulus of Elasticity (× 10^6 psi)	Melting Temperature (°C)	Specific Modulus (× 10^7 in.)	Specific Strength (× 10^6 in.)
Polymers:						
Kevlar™	1.44	650	18.0	500	34.7	12.5
Nylon	1.14	12	0.5	249	1.0	2.9
Polyethylene	0.97	3–7	0.04–0.1	147	7.1	13.7
Metals:						
Be composites	1.83	40–50	44.0	1277	77.5	2.8
Boron	2.36	500	55.0	2030	64.7	4.7
W	19.40	580	59.0	3410	8.5	0.8
Glass:						
E-glass	2.55	500	10.5	<1725	11.4	5.6
S-glass	2.50	650	12.6	<1725	14.0	7.2
Carbon:						
HS (high strength)	1.75	820	40.0	3700	63.5	13.0
HM (high modulus)	1.90	270	77.0	3700	112.0	3.9
Ceramics:						
Al_2O_3	3.95	300	55.0	2015	38.8	2.1
B_4C	2.36	330	70.0	2450	82.4	3.9
SiC	3.00	570	70.0	2700	47.3	5.3
ZrO_2	4.84	300	50.0	2677	28.6	1.7
Whiskers:						
Al_2O_3	3.96	3000	62.0	1982	43.4	21.0
Cr	7.20	1290	35.0	1890	13.4	4.9
Graphite	1.66	3000	102.0	3700	170.0	50.2
SiC	3.18	3000	70.0	2700	60.8	26.2
Si_3N_4	3.18	2000	55.0		47.8	17.5

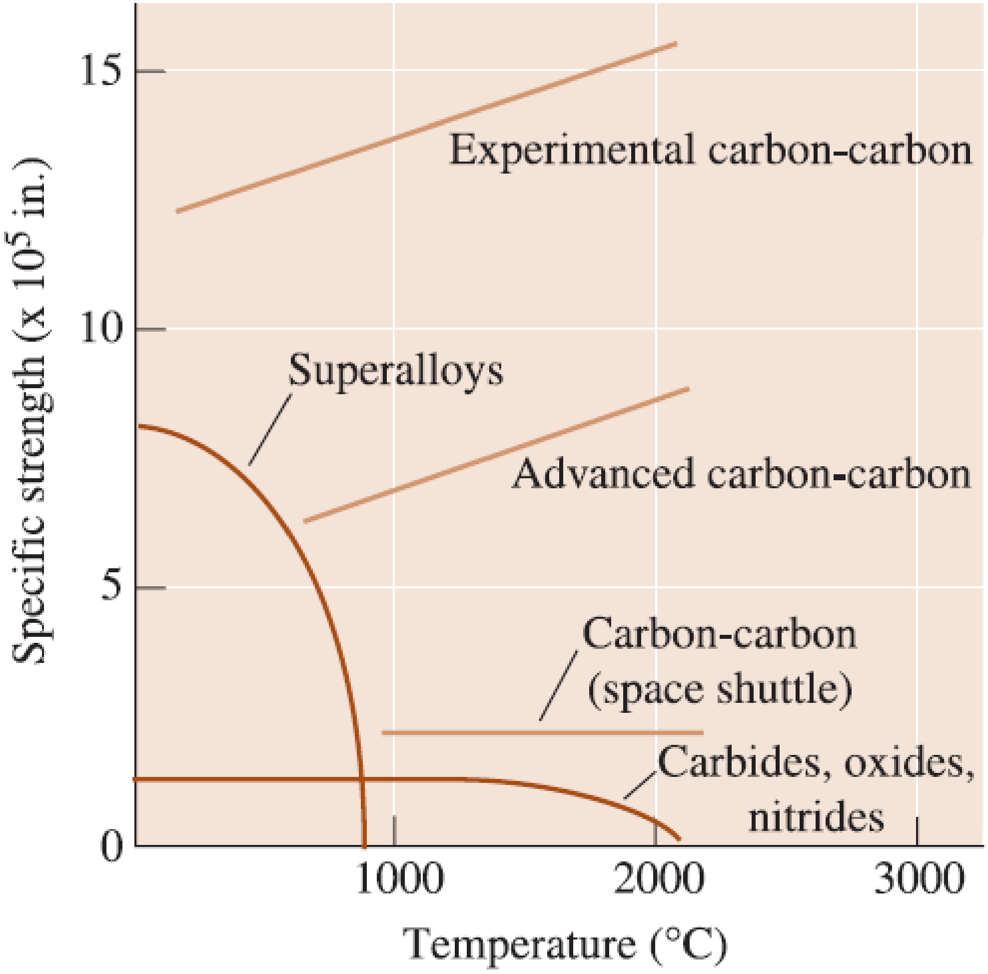
* $1\frac{gm}{cm^3} = 0.0361\frac{lb}{in.^3}$

CMCs

Composites containing ceramic fibers in a ceramic matrix are also finding applications.

Carbon-carbon (C—C) composites are used for extraordinary temperature resistance in aerospace applications.

Carbon-carbon composites can operate at temperatures of up to 3000°C and, in fact, are stronger at high temperatures than at low temperatures.



A comparison of the specific strength of various carbon-carbon compositeswith that of other high-temperature materials relative to temperature.

CMCs

Carbon-carbon composites are made by forming a polyacrylonitrile or carbon fiber fabric into a mold, then impregnating the fabric with an organic resin, such as a phenolic.

The part is pyrolyzed to convert the phenolic resin to carbon. The composite, which is still soft and porous, is impregnated and pyrolyzed several more times, continually increasing the density, strength, and stiffness.

Finally, the part is coated with silicon carbide to protect the carbon-carbon composite from oxidation. Strengths of 300,000 psi and a Young’s modulus (measure of stiffness) of 50 x10^6 psi can be obtained.

Carbon-carbon composites have been used as nose cones and leading edges of high-performance aerospace vehicles such as the space shuttle, and as brake discs on racing cars and commercial jet aircraft.

CMCs

Ceramic-fiber–ceramic-matrix composites provide improved strength and fracture toughness compared with conventional ceramics. Fiber reinforcements improve the toughness of the ceramic matrix in several ways.

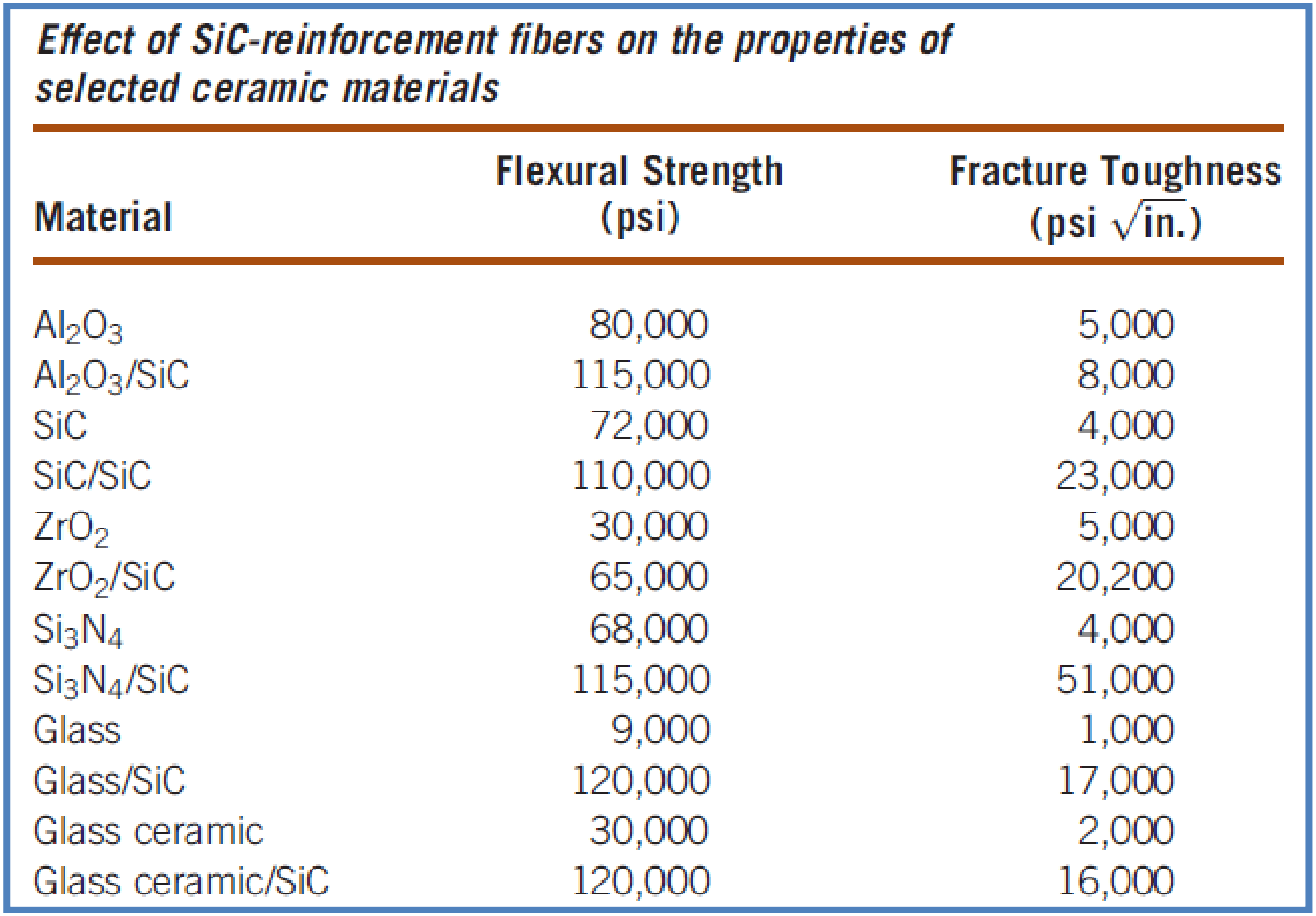
First, a crack moving through the matrix encounters a fiber; if the bonding between the matrix and the fiber is poor, the crack is forced to propagate around the fiber in order to continue the fracture process.

In addition, poor bonding allows the fiber to begin to pull out of the matrix.

Both processes consume energy, thereby increasing fracture toughness.

Finally, as a crack in the matrix begins, unbroken fibers may bridge the crack, providing a compressive stress that helps keep the crack from opening.

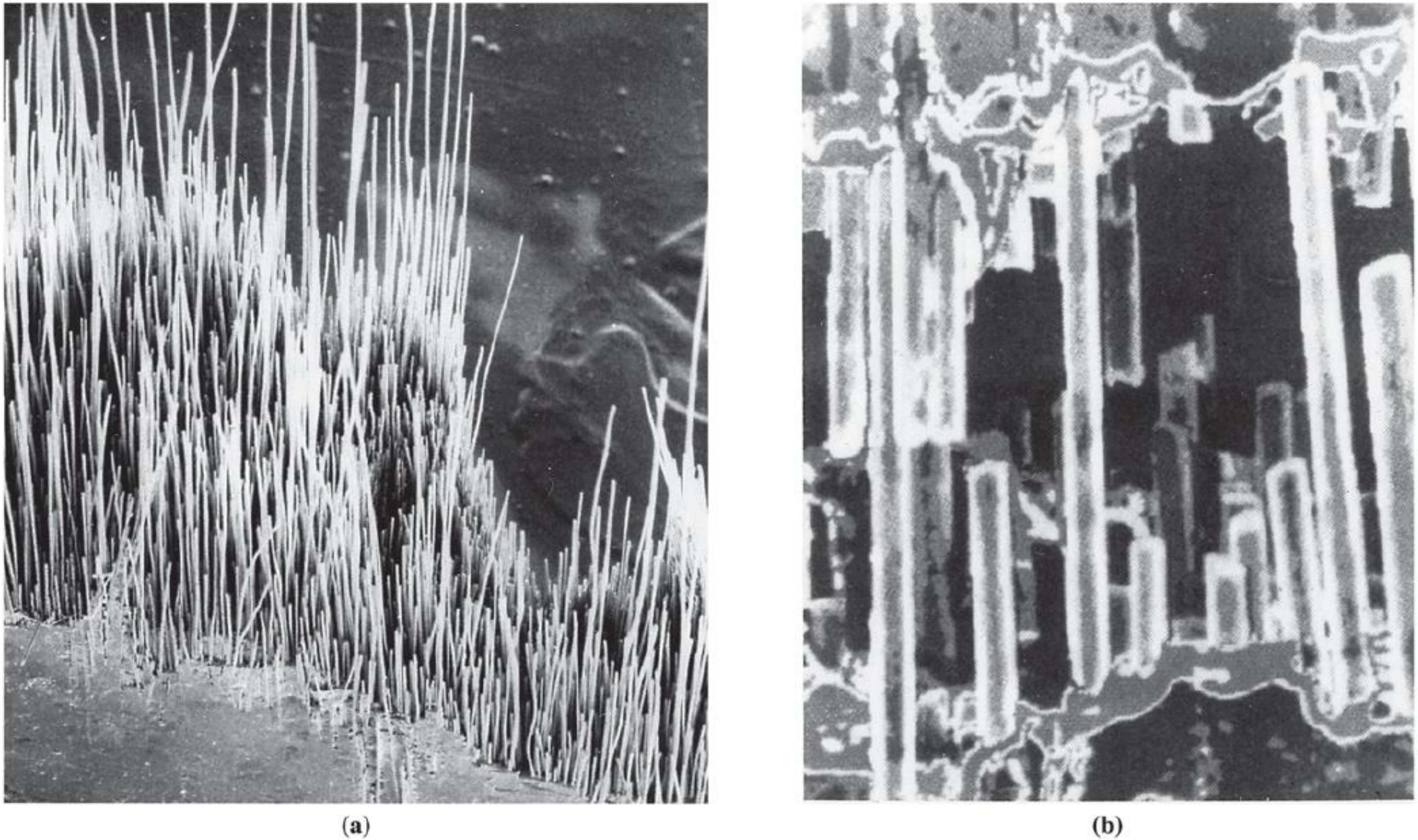
CMCs



Effect of SiC-reinforcement fibers on the properties of selected ceramic materials

Material	Flexural Strength (psi)	Fracture Toughness (psi $\sqrt{\text{in.}}$)
Al_2O_3	80,000	5,000
Al_2O_3/SiC	115,000	8,000
SiC	72,000	4,000
SiC/SiC	110,000	23,000
ZrO_2	30,000	5,000
ZrO_2/SiC	65,000	20,200
Si_3N_4	68,000	4,000
Si_3N_4/SiC	115,000	51,000
Glass	9,000	1,000
Glass/SiC	120,000	17,000
Glass ceramic	30,000	2,000
Glass ceramic/SiC	120,000	16,000

CMCs



Two failure modes in ceramic-ceramic composites: (a) Extensive pull-out of SiC fibers in a glass matrix provides good composite toughness. (From Metals Handbook, American Society for Metals, Vol. 9, 9th Ed., 1985.) (b) Bridging of some fibers across a crack enhances the toughness of a ceramic-matrix composite. (From Journal of Metals, May 1991.)

CMCs

Unlike polymer and metal matrix composites, poor bonding-rather than good bonding-is required. Consequently, control of the interface structure is crucial.

In a glass-ceramic reinforced with SiC fibers, an interface layer containing carbon and NbC is produced that makes debonding of the fiber from the matrix easy.

If, however, the composite is heated to a high temperature, the interface is oxidized; the oxide occupies a large volume, exerts a clamping force on the fiber, and prevents easy pull-out. Fracture toughness is then decreased.

Applications of CMCs

Ceramic fibres such as SiC and Si_3N_4 use polysilane as the base material. CMCs, in which ceramic or glass matrices are reinforced with continuous fibres, chopped fibres, whiskers, platelets or particulates, are emerging as a class of advanced engineering structural materials. They currently have limited high-temperature applications but a large potential for much wider use in military, aerospace and commercial applications such as energy-efficient systems and transportation.

There are also other specialty CMCs such as nanocomposites (made from reactive powders) and electroceramics. CMCs are unique in that they combine low density with high modulus, strength and toughness (contrasted with monolithic ceramics) and strength retention at high temperatures. Many have good corrosion and erosion characteristics for high temperature applications. CMCs have been used in jet fighters. Industrial uses of CMCs include furnace materials, energy conversion systems, gas turbines and heat engines.

Applications of CMCs

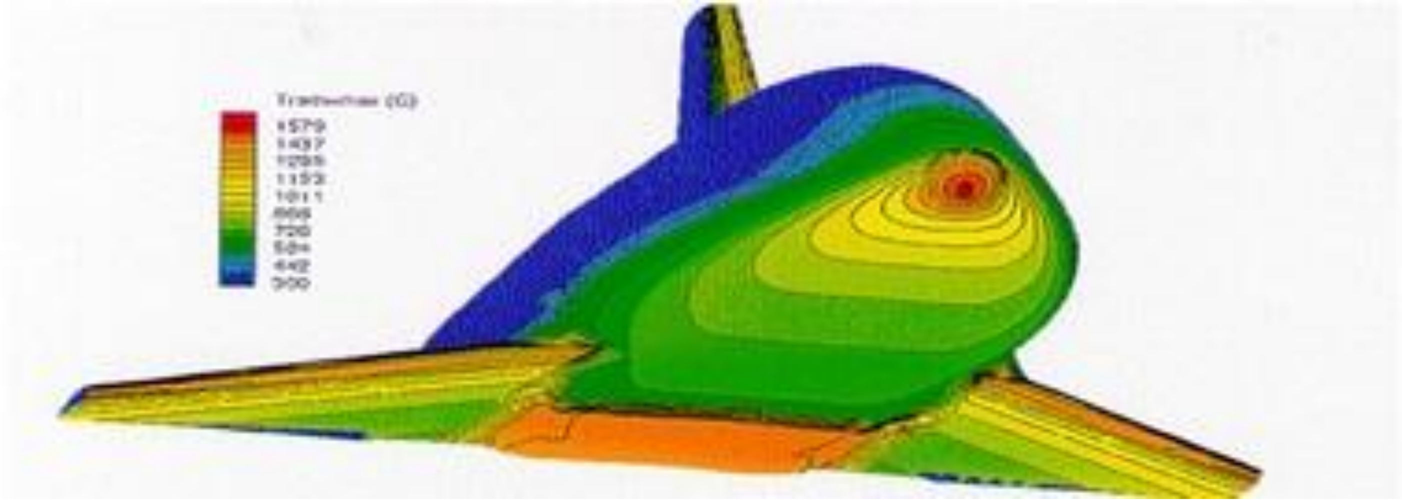
- Automotive industry.
- Heat exchangers
- Aerospace and military applications.
- Bearings in missiles.
- Other applications include wear parts, such as seals, nozzles, pads, liners, grinding wheels, brakes, etc. For instance, carbon fiber reinforced carbon composites are being used in aircraft brakes.
- They are also used in dies and tool bits, medical implants and land-based power and transport engines.
- …

Applications of CMCs

Carbon-Ceramic Matrix Rotors

http://www.tunemytoyota.com/forum/showthread.php?t=2991

Applications of CMCs



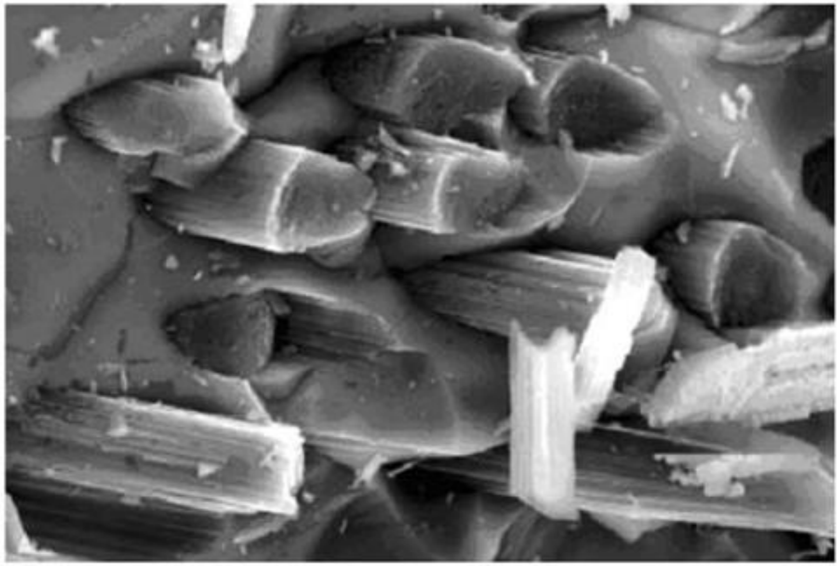
Multiple-mission spacecrafts necessiate reusable heatshields and heatexposed elements. Ceramic Matrix Composite (CMC) are the most suitable structural heatdurable materials for these functions, carbon fibre reinforced silicon carbide (C/SiC) in particular.

For producing these composites, the carbon fiber mats are imprignated with the Fast-Sol-Gel, a resin based on rapid hydrolysis and polymerization of a mixture of $(Me)_xSi(O\text{-}Me)_{4-x}$ monomers. After a gradual heat-pressure process under inert atmosphere the green composites are converted into C-SiC composites. Schematic reaction: $(SiRO_{3/2})_n \rightarrow SiC + CO_2 + H_2O$

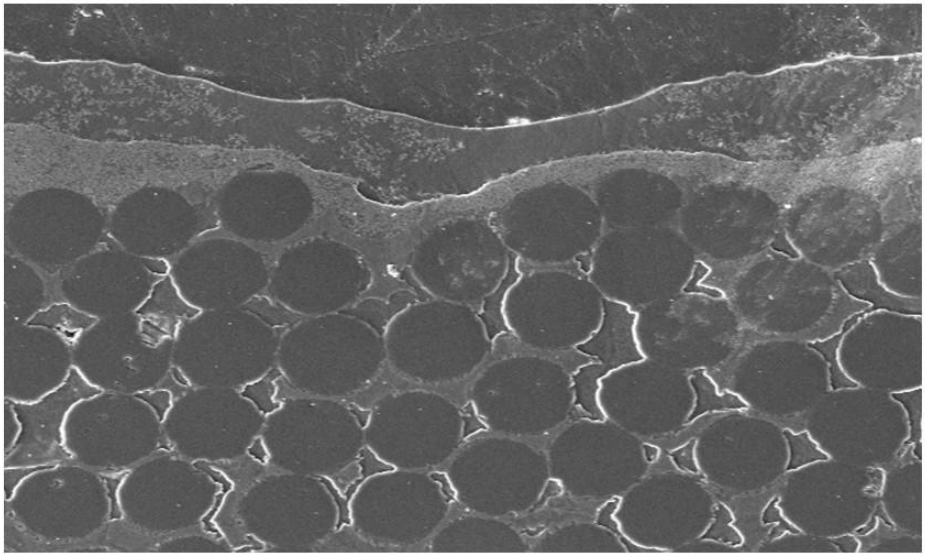
http://www.aac-research.at/products/products_AAC_Service_CeramicMatrix_en.html

Applications of CMCs

In addition such materials require an Oxidation Protection System (OPS) to prevent oxidative damage to the carbon fibres during re-entry. These OPS should reliably protect the C/SiC structures at temperatures up to 1600°C and must remain crack-free over the whole temperature range from approx. 450 to 1600°C. This system consists of the Fast-Sol-Gel resin and ceramic filler like n-Al_2O_3 or n-ZrO_2.



SEM view of hot-pressed (1600°C 30MPa) Fast-Sol-Gel-derived carbon-fabric composites: Fibers extending from molten glass.



SEM view of C/SiC composite with two layers of OPS.

http://www.aac-research.at/products/products_AAC_Service_CeramicMatrix_en.html

Applications of CMCs

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

http://www.oppracing.com/category/808-braketech-brake-rotors/

Applications of CMCs

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

Ceramic Matrix Composite Turbine Blade

Applications of CMCs

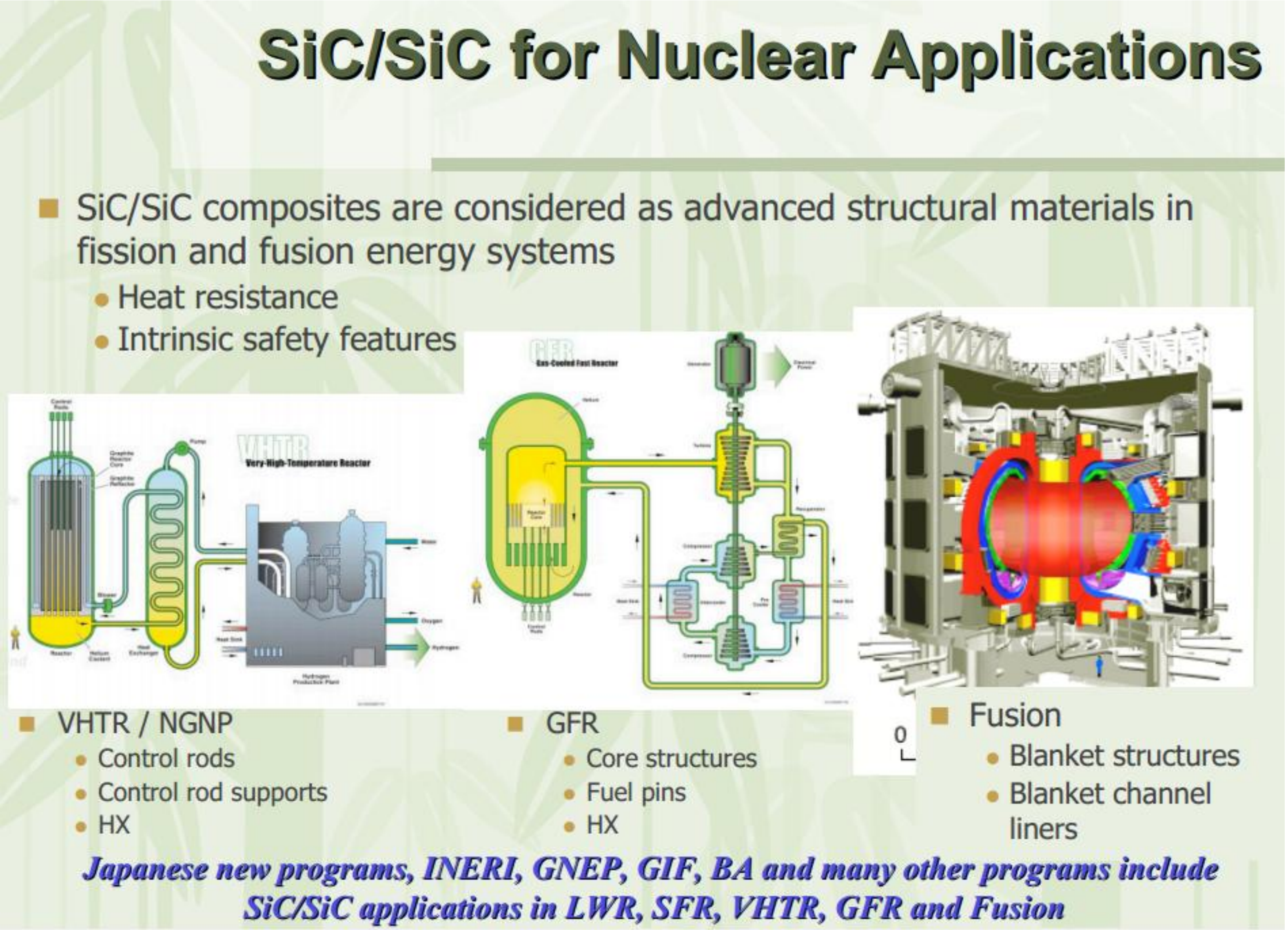
An F-16 Fighting Falcon F100 engine exhaust nozzle with five A500 ceramic matrix composite divergent seals, identified by the yellow arrows. (Air Force photo)

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.

http://www.wpafb.af.mil/news/story.asp?id=123116097

Applications of CMCs



SiC/SiC for Nuclear Applications

- SiC/SiC composites are considered as advanced structural materials in fission and fusion energy systems
  - Heat resistance
  - Intrinsic safety features

- VHTR / NGNP
  - Control rods
  - Control rod supports
  - HX

- GFR
  - Core structures
  - Fuel pins
  - HX

- Fusion
  - Blanket structures
  - Blanket channel liners

Japanese new programs, INERI, GNEP, GIF, BA and many other programs include SiC/SiC applications in LWR, SFR, VHTR, GFR and Fusion

Applications of CMCs

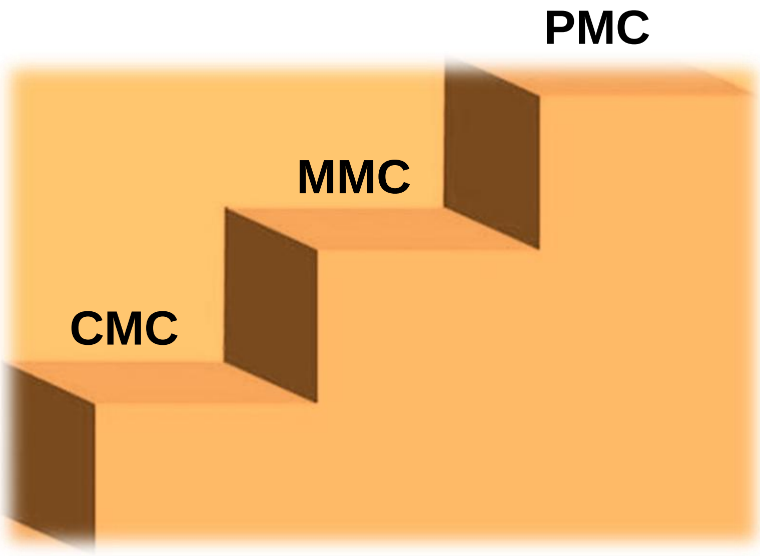
Braided and unidirectional S-2 Glass and carbon fibers are used to produce forks with different stiffness.

http://matse101.mse.uiuc.edu/

Ceramic Matrix Composites

Ceramic matrix composite (CMC) development has lagged behind other composites for two main reasons.

First more of the processing routes for CMCs involve high temperatures and can only be employed with high temperature reinforcements. It follows that it was not until fibres and whiskers of high temperature ceramics, such as silicon carbide, were readily available was there much interest in CMCs. The high temperature properties of the reinforcement are also of importance during service. A major attribute of monolithic ceramics is that they maintain their properties to high temperatures and this characteristic is only retained in CMCs if the reinforcements also have good high temperature properties. Hence, there is only limited interest in toughening ceramics by incorporation of reinforcements of materials, such as ductile metals, that lose their strength and stiffness at intermediate temperatures.



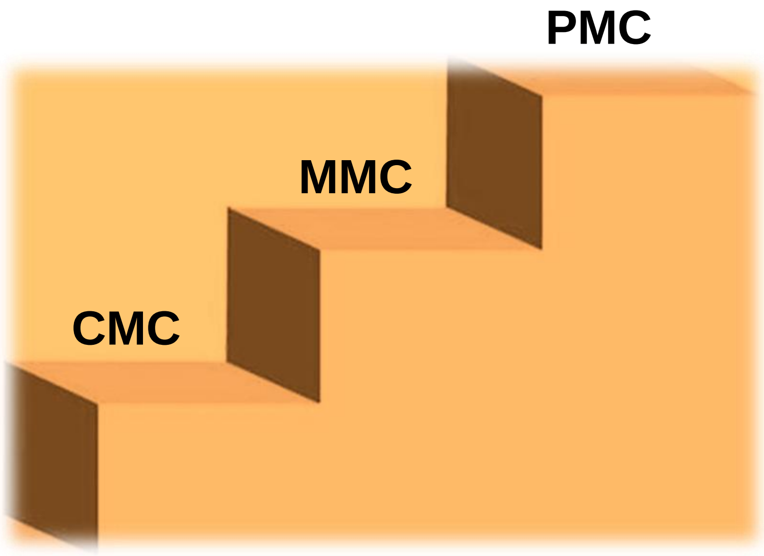
M. Rosso, Ceramic and metal matrix composites: Routes and properties, Journal of Materials Processing Technology 175 (2006) 364–375

Ceramic Matrix Composites

The second factor that has hindered the progress of CMCs is also concerned with the high temperatures usually employed for production. Differences in coefficients of thermal expansion, α, between the matrix and the reinforcement lead to thermal stresses on cooling from the processing temperature.

However, whereas the thermal stresses can generally be relieved in metal matrix composites by plastic deformation of the matrix, this is not possible for CMCs and cracking of the matrix can result.

The nature of the cracking depends on the whether the reinforcement contracts more or less than the matrix on cooling as their determines the character (tensile or compressive) of the local thermal stresses.



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Thanks for your kind attention

THE END

Any Questions