CHAPTER I

INTRODUCTION AND SCOPE OF THE PRESENT WORK

I.1 Ceramics

Materials for advanced structural applications, especially for elevated temperatures have been until recently largely restricted to advanced metallic alloys. However, it seems that for certain applications involving very high temperature, metallic materials have reached a limit to their potential for development for example, in combustion engines and other energy generating equipment, the development is necessarily limited by the melting point of the alloys. Ceramics offer significant increase in service temperature. Their low density, chemical inertness and high hardness offer additional potential for extending performance limits as compared to those metallic materials.

The term “ceramics” come from the Greek word keramikos, which means “burnt stuff”, which is an appropriate name since desirable properties in ceramics are normally achieved through high-temperature heat treatment called firing. Ceramics are compounds between metallic and non-metallic elements. Ceramics are many times composed of clay materials, cement and glass. Ceramics are insulative to the passage of electricity and heat. Ceramics are more resistance to high temperatures and harsh environments than metals and polymers. When looking at the material behaviour of ceramics, these are generally hard and brittle. On the other hand glass is an amorphous vitreous silicates material but unlike many of the more common liquids, glass has a three-dimensional frame work containing covalent bonds.

Ceramics are composed of at least two elements, thus the crystal structures are generally more complex than those of metals. One of the key characteristics of the ceramic is that these exhibit atomic bonding either through covalent or ionic bonding.
Ceramics exhibit predominantly ionic bonding and can be thought of as being electrically charged ions instead of atoms. In ionic bonding of ceramic structure, the metallic ions or cations (+ve charge) gives up their valence electrons to the non-metallic ions, or anions (-ve charge). This causes the crystal structure to become electrically neutral.

**I.2 Properties and Applications for Ceramics**

The applications of these materials are diverse from bricks and tiles to electronic and magnetic components. Some of the applications are shown in fig. I.1.

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**Fig. I.1 Spectrum of Ceramics Uses**

These applications use wide range of properties exhibited by ceramics. Some of these properties are listed in Table I.1 together with examples of specific ceramics and applications. The functions of ceramic products are dependent on their chemical
composition and microstructure, which determines their properties. It is the interrelationship between structure and properties that is a key element of materials science and engineering.

Table I.1 Properties and Applications for Ceramics

<table>
<thead>
<tr>
<th>Property</th>
<th>Example</th>
<th>Application</th>
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<tbody>
<tr>
<td>Electrical</td>
<td>B_{2}RuO_{3}</td>
<td>Conductive component in thick-film resistors</td>
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<td></td>
<td>Doped ZrO_{2}</td>
<td>Electrolyte in solid-oxide fuel cells</td>
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<td></td>
<td>Indium tin oxide (ITO)</td>
<td>Transparent electrode</td>
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<td></td>
<td>SiC</td>
<td>Furnace elements for resistive heating</td>
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<td></td>
<td>YBaCuO_{7}</td>
<td>Superconducting quantum interference devices (SQUIDs)</td>
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<td></td>
<td>SnO_{2}</td>
<td>Electrodes for electric glass melting furnaces</td>
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<tr>
<td>Dielectric</td>
<td>α-Al_{2}O_{3}</td>
<td>Spark plug insulator</td>
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<td></td>
<td>PbZr_{0.5}Ti_{0.5}O_{3} (PZT)</td>
<td>Micropumps</td>
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<td></td>
<td>SiO_{2}</td>
<td>Furnace bricks</td>
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<tr>
<td></td>
<td>(Ba,Sr)TiO_{3}</td>
<td>Dynamic random access memories (DRAMs)</td>
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<td></td>
<td>Lead magnesium niobate (PMN)</td>
<td>Chip capacitors</td>
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<tr>
<td>Magnetic</td>
<td>γ-Fe_{2}O_{3}</td>
<td>Recording tapes</td>
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<td></td>
<td>Mn_{0.5}Zn_{0.5}Fe_{3}O_{4}</td>
<td>Transformer cores in touch tone telephones</td>
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<td></td>
<td>BaFe_{12}O_{19}</td>
<td>Permanent magnets in loudspeakers</td>
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<td></td>
<td>Y_{5.66}Gd_{2.34}Fe_{12}Al_{0.5}Mn_{0.04}O_{12}</td>
<td>Radar phase shifters</td>
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<tr>
<td>Optical</td>
<td>Doped SiO_{2}</td>
<td>Optical fibers</td>
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<tr>
<td></td>
<td>α-Al_{2}O_{3}</td>
<td>Transparent envelopes in street lamps</td>
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<td></td>
<td>Doped ZrSiO_{3}</td>
<td>Ceramic colors</td>
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<td></td>
<td>Doped (Zn,Cd)S</td>
<td>Fluorescent screens for electron microscopes</td>
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<td></td>
<td>Pb_{2}La_{1-x}Zr_{x}Ti_{2}O_{5} (PLZT)</td>
<td>Thin-film optical switches</td>
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<td></td>
<td>Nd doped Y_{3}Al_{2}O_{12}</td>
<td>Solid-state lasers</td>
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<tr>
<td>Mechanical</td>
<td>TiN</td>
<td>Wear-resistant coatings</td>
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<td></td>
<td>SiC</td>
<td>Abrasives for polishing</td>
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<tr>
<td></td>
<td>Diamond</td>
<td>Cutting tools</td>
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<td></td>
<td>Si_{3}N_{4}</td>
<td>Engine components</td>
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<td></td>
<td>Al_{2}O_{3}</td>
<td>Hip implants</td>
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<tr>
<td>Thermal</td>
<td>SiO_{2}</td>
<td>Space shuttle insulation tiles</td>
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<td></td>
<td>Al_{2}O_{3} and AlN</td>
<td>Packages for integrated circuits</td>
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<td></td>
<td>Lithium-aluminosilicate glass ceramics</td>
<td>Supports for telescope mirrors</td>
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<td></td>
<td>Pyrex glass</td>
<td>Laboratory glassware and cookware</td>
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I.3 Classification of ceramics

The ceramics are classified into two classes:

1) Traditional ceramics

2) Technical ceramics/ Advanced ceramics
   - Oxide ceramics
   - Non-oxide ceramics

I.3.1 Traditional ceramics

In addition to dividing ceramics according to their properties and applications, it is common to class them as traditional or technical ceramic (fig. I.2). Traditional ceramics include high-volume items such as bricks and tiles, toilet bowls (whitewares), and pottery. Advanced ceramics include newer materials such as laser host materials, piezoelectric ceramics, ceramics for dynamic random access memories (DRAMs), etc., often produced in small quantities with higher prices.

There are other characteristics that separate these categories. Traditional ceramics are usually based on natural occurring clay and silica. There is sometimes a tendency to equate traditional ceramics with low technology; however, advanced manufacturing techniques are often used. Competition among producers has caused processing to become more efficient and cost effective. Complex tooling and machinery is often used and may be coupled with computer-assisted process control.
Advanced ceramics are also referred to as “special,” “technical,” or “engineering” ceramics. They exhibit superior mechanical properties, corrosion/oxidation resistance, electrical, optical, and/or magnetic properties. While traditional clay-based ceramics have been used for over 25,000 years, advanced ceramics have generally been developed within the last 100 year[1].

I.3.2 Technical Ceramics

I.3.2.a Oxide ceramics

The oxide based ceramics can be designed for structural or functional applications. These include pure oxides such as SiO$_2$, Al$_2$O$_3$, TiO$_2$, ZrO$_2$, Y$_2$O$_3$, ZnO, UO$_2$, BeO, MgO and mixed oxide as MgO.SiO$_2$ (magnesium silicate), 3Al$_2$O$_3$.2SiO$_2$ (mullite) Al$_2$O$_3$.TiO$_2$ and porcelain. The complex oxides processed by solid state reactions (titanates, ferrites etc.), and silicate ceramics (including mullite-based ceramics) are usually not treated in this group [2-5].
Apart from alumina and zirconia, the other important oxide ceramics are BeO used as a nuclear ceramics as well as for high-temperature crucibles, insulating parts and chip carriers; CaO used as refractory bricks; compounds and fibre; CeO$_2$ used as ion conductors, crucibles and oxygen sensors; MgO used for melting crucibles, insulators and refractory bricks; TiO$_2$ used for high frequency capacitors and photo catalytic devices; UO$_2$ used as a nuclear ceramic; Y$_2$O$_3$ used for crucibles; ZnO used for varistors in voltage surge protectors etc. [6]

**I.3.2. b Non–oxide ceramics**

Ceramics have achieved wide spread use worldwide as their properties are enhanced and verified through the efforts of materials scientists. Of particular interest is use of ceramic materials for high temperature structural application. Non-oxides ceramics offer the most promising candidates for structural application and superior substitute for conventional refractoriness [7,8]. Fig. I.3 shows the classification of non-oxide ceramics. SiC, Si$_3$N$_4$, BN, B$_4$C, ZrC, WC and TiC are widely used as non-oxides ceramics.
Non-oxide ceramics

- **Carbides** - SiC, ZrC, TiC, WC, etc.
- **Silicides** - MoSi₂, TaSi₂, WSi₂, etc.
- **Borides** - TiB₂, ZrB₂, LaB₆, etc.
- **Nitrides** - Si₃N₄, AlN, TiN, ZrN, etc.
- **Sulfides** - ZnS, CdS, CuS, MoS₂, etc.
- **Others** - Phosphides (BP)

**Fig. I.3 Classification of non-oxide ceramics**

The non-oxide ceramics possess reasonably high strength, hardness, elastic modulus, fracture toughness, creep resistance and wear resistance. There is very attractive combination of thermo mechanical as well as tribological properties that support their candidature for various engineering application. Metal carbide TiC and WC are used in cutting tools application. SiC, Si₃N₄ and ZrC are used for high temperature and high performance structural materials [9,10]. As high temperature structural materials silicon carbide ceramics offer many advantages including high melting point, low density, high elastic modulus and strength, good resistance to creep, oxidation and wear[6-9]. Due to their outstanding thermo-mechanical properties, SiC is used as reinforcement as well as matrix in various high temperature composite materials[11-13].
Ceramic materials are somewhat inferior to metals or polymers when their fracture toughness is compared with ceramics. The principal drawback is that fracture or total failure will occur before any plastic deformation. However, under compressive loads, ceramics are very strong. This difference is due to presence of elliptical micro cracks on their surface and existence of atomic defects in ceramics. The porosity of ceramic plays a major role in the strength. Ceramics are generally very porous, enhancing their ability to insulate but limiting its tensile strength. When the material is under a tensile load, the cracks become larger and spread further. When the material is under a compressive load, the cracks are forced together, which makes the material act as if no cracks were present.

I.4 Phase diagram of Si-C system

SiC is formed from the reaction between silica and carbon below the melting point of silicon through an intermediate of silicon oxycarbide (Si-O-C)[14]. The phase diagram of Si-C system is shown in fig.I.4. It can be seen that SiC is the only compound of silicon, carbon formed in the condensed state in addition to elemental silicon and carbon. An eutectic point between silicon and SiC exists at 1402°C with 0.75 atom % carbon. The liquids curve between Si and SiC is seen at 2600°C with 27 atom % C. A peritectic point is located at 2540°C with 27 atoms % C under normal conditions.
I.5 Methods for Synthesis of SiC Ceramics

A number of manufacturing approaches have been used to fabricate ceramic materials, including hot pressing/hot isostatic pressing (HIP), sintering, reaction bonding/reaction forming, polymer pyrolysis, and chemical vapor deposition. Hot pressing and sintering approaches require significant consumption of energy while CVD and polymer pyrolysis techniques generate liquid and gaseous chemical by-products. The reaction bonding technique typically utilizes silicon carbide and carbon powder combined with polymer binders while resin/pore former derived preforms are used in the reaction forming techniques.

Fig. I.4 Phase Diagram of SiC
I.5.1 Acheson process

The Acheson process is the first developed process for the mass production of SiC powder. It is based on carbothermal reduction. In this process silica and carbon reacts to produce silicon carbide at 1700-2500°C temperatures [15].

\[
\text{SiO}_2 + 3\text{C} \rightarrow \text{SiC} + 2\text{CO} \quad (1)
\]

The raw material of carbon and silica precursors is loaded around the graphite electrode and heat treated at temperature beyond 1350°C. Silicon carbide is formed as a mixture of $\alpha$-SiC and $\beta$-SiC ingot of solid cylindrical shape around an electrode. Coarse crystals of $\beta$-SiC is formed in the inner region having the highest temperature.

I.5.2 Chemical Vapour Deposition (CVD)

Chemical vapor deposition (CVD) is a gas phase process of volatile compounds reacting, producing a non-volatile solid film that deposit automatically on a substrate [16]. CVD is a versatile process suitable for manufacturing of coatings, powders, fibers, and monolithic components. This method can deposit single layer, multilayer, composite, nanostructure and functionally graded coating materials of high purity and good conformal coverage in single-crystal, polycrystalline and amorphous forms at a relatively low processing temperature and in general under vacuum. The CVD technology combines several scientific and engineering disciplines, including thermodynamics, plasma physics, kinetics, fluid dynamics, and of course chemistry. While used for making ceramic powders, this method is also used quite extensively for making ceramic coatings, as well as monolithic components. Typically, inorganic and related precursors, which are substantially less expensive, are utilized for bulk, as in structural bodies, with processing temperatures commonly in the 1000 - 1500°C range.
The CVD process for the synthesis of SiC is based on the reaction of silane and hydrocarbon gases below 1500°C temperature. The precursors decompose on a hot substrate in suitable reaction chamber resulting in formation of carbides. The most essential requirements of the precursor are sufficient volatility at low temperature and sufficiently high decomposition temperature [17]. Silicon carbide fibers can be made by CVD on a substrate heated to approximately 1300°C. Silicon carbide fibers produced by the chemical vapor deposition (CVD) technique usually having larger diameters ranging from 100 to 150 μm and their microstructures are very sensitive to the detailed conditions of the CVD process. The resulting structure of fibers as well coating is strongly dependent on the composition, pressure and supply rate of the vapor mixture and deposition temperature [18-20]. Thus, the composition and microstructure may vary from fiber to fiber due to different deposition conditions employed during the CVD process.

1.5.3 Carbothermal Reduction

In the carbothermal reduction, the mixture of silica and carbon powder are heated below 1700°C in the inert atmospheres to form β-SiC. Unreacted silica and carbon are removed by the subsequent refining processes. In this process β-SiC formation takes place at 1700°C [21]. The shape and particle size depends on parent materials. Rapid carbothermal reduction is a way of producing ultra fine silicon carbide particles. This reaction can be represented by the equation (2)

$$\text{SiO}_2 (s) + 3\text{C} (s) \rightarrow \text{SiC} (g) + 2\text{CO} (g) \quad (2)$$

It has been identified that the formation of silicon carbide involves a complex mechanism. An intermediate SiO gas further reacts with solid carbon and converts into silicon carbide as shown in equation (3 and 4) [22].
\[
\text{SiO}_2 (s) + C (s) \rightarrow \text{SiO} (g) + \text{CO} (g) \quad \text{(3)}
\]
\[
\text{SiO} (g) + C (s) \rightarrow \text{SiC} (s) + 2\text{CO} (g) \quad \text{(4)}
\]

I.5.4 Chemical vapour reaction (CVR)

Chemical reaction for materials synthesis can be carried out in a solid, liquid or gaseous state. The more conventional solid-state synthesis route is to bring solid precursors into close contact by grinding, mixing and subsequent heat treatment with or without pressure to facilitate diffusion of atoms and ions in chemical reaction. The rate of diffusion of atom and ions depends on morphology of precursor materials and reaction conditions. As compared to total solid-state reaction, diffusion of matter in gas phase is typically and advantageously many orders of magnitude larger than in solid and liquid phase. The synthesis of materials can be achieved at lower temperatures with high-purity [23-27]. CVR reaction is based on carbothermal reduction. In the carbothermal reduction, first stage, the silicon reacts with silica leading to the formation of silicon monoxide.

\[
\text{Si} (s) + \text{SiO}_2 (s) \rightarrow 2\text{SiO} (g) \quad \text{(4)}
\]

In second stage, gaseous silicon monoxide reacts with a carbon substrate and SiC is formed.

\[
\text{SiO} (g) + C (s) \rightarrow \text{SiC} (s) + \text{CO} (g) \quad \text{(5)}
\]
\[
\text{SiO}_2 (g) + 3C (s) \rightarrow \text{SiC} (s) + 2\text{CO} (g) \quad \text{(6)}
\]
\[
\text{SiO} (g) + \text{CO} (g) \rightarrow \text{SiC} (s) \text{ (whisker)} \quad \text{(7)}
\]

Reactions (6) and (7) show another possibility for formation of SiC particles and whiskers on Carbon substrate respectively.
I.5.5 Preceramics Polymer Route

Preparation of ceramics by pyrolysis of organometallic polymers or other precursors has begun to attract considerable attention in last two decades. Preceramics are primarily inorganic polymers and the early literature on these materials is compiled in the books edited by Lappert and Leigh [28] and by Haidue [29].

Polymer derived precursors obtainable through hydrolysis of substituted silanes or siloxanes offer the possibility of introducing carbon at a low temperature in the matrices. Organo silicon gels as precursors of black glasses have been prepared through hydrolysis of alkyl or aryl substituted alkoxy or chlosilanes [30-33]. The non hydrolysable carbon groups in the substituted polymers give rise to the presence of carbon in the glass as oxycarbide as well as separate carbon phase. Although no equilibrium solid phases are known between SiC and SiO$_2$, evidence for the existence of a metastable silicon oxycarbide in the back glasses at low temperature and low pressure of oxygen has been presented by numerous researches [34-38] using IR and NMR techniques. The silicon oxycarbide has an amorphous covalent structure described as a combination of Si-C and Si-O bonds approaching a random distribution.

Carbon is also introduced in the network through pyrolysis of a mixture of silica gel and a carbonaceous source, usually a thermosetting resin or pitch derived carbonaceous sol. Smith and Crandall [39] added up to 1.2% carbon in silica by hot pressing powders silica containing carbowax at 1000$^\circ$C to 1500$^\circ$C. Elmer and Meissner [40-42] added furfuryl alcohol [43] to vycor glass, which decomposed to carbon on firing the glass in a hydrogen/ nitrogen atmosphere to 1245$^\circ$C.
Ceramics prepared by polymer pyrolysis have a variety of potential applications. Some examples of different forms and applications of ceramics from polymer pyrolysis are compiled in Table I.2 [34].

Table I.2 Forms and application examples of ceramics from polymer pyrolysis

<table>
<thead>
<tr>
<th></th>
<th>Fibers Reinforcement, Filters, Insulation</th>
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<tbody>
<tr>
<td>2.</td>
<td>Coating, Sealing (e.g. for oxidation resistance)</td>
</tr>
<tr>
<td>3.</td>
<td>Joining</td>
</tr>
<tr>
<td>4.</td>
<td>Foams (e.g. for filtering or heaters)</td>
</tr>
<tr>
<td>5.</td>
<td>Bulk bodies (a) from powders from pyrolysis (b) using product producing polymers as binders (c) directly via pyrolysis (d) composites</td>
</tr>
</tbody>
</table>

Thermolysis of organometallic polymers in controlled atmosphere and heat treatment conditions is a comparatively simple and inexpensive process for producing oxide and nonoxide ceramics. It provides means for controlling and adjusting microstructure design and shape of ceramic components, which often cannot be achieved using “classical” techniques such as melting, sintering, or chemical vapor deposition (CVD). Fig. I.5 Shows flow diagram of the individual steps involved in the preparation of ceramics by polymer pyrolysis [44].
As a consequence of being mostly reaction controlled, precursor thermolysis is especially valuable for the production of nonoxide ceramics, which possess a high degree of covalent bonding. The main disadvantage of this concept of producing ceramics from molecular precursor over sintering and melting is the possibility of realizing the shapes that are impossible or difficult to achieve using a classical procedure. Possible approaches are shown in fig. I.6 [45].

Fig. I.5 Shows flow diagram of the individual steps involved in the preparation of ceramics by polymer pyrolysis [44].
Composites materials are amongst the oldest and newest of the materials. Composites materials being used by mankind since early civilization both for shelter and protection with the empirical knowledge that when two or more individual constituent materials used in combination, the resultant material does a better job than the individual’s constituent. Nature has also created many materials that are natural composites. Wood, for example, is a composite material constituting of cellulose fibers embedded in a matrix of lignin [46].

Fig I.6 Preparation of ceramic materials by preceramic polymer route [45]
The use of natural composites and of manmade composites has broadened in all facets of life [40]. The increased use of composite materials has been at least partially due to reduced manufacturing costs of reinforcements and superior performance of these materials. Performance of composites characterized by high strength to weight ratio or the capability of structural integrity at very high temperatures has made the composites well suited for many diverse applications ranging from sport goods such as tennis rackets, baseball bats and boats, auto motive parts, including piston rings, engine blocks and advanced aerospace applications such as national aerospace plane, cargo plane and fighter jets and bombers [47].

The properties and behavior of a composite can be determined by two factors, viz, (i) the nature of the constituents and (ii) the relation and interactions between the constituents. While micro structural nature and the geometrical characteristic of the constituents determine largely the range of properties that a composite will finally have. The size and shape of constituent elements and relative amounts of the constituent phase can be varied to provide specific values in terms of properties. Another factor of importance in determining a composite’s performance is the distribution and arrangement of structural constituents in the body of composites [46]. The wide range of these possible variations gives composite much of its versatility to have desirable properties for specific applications.

The composites are made by the combination of two or more dissimilar materials in order to achieve properties that the constituent materials cannot provide by themselves individually. In fact, the development of composite is based on idea of combining materials to utilize jointly the best characteristic of each. The dimensions of one of the constituents of composites materials are smaller than those of the second [47], where the first being known as reinforcement and the other as a matrix.
Certain properties of a composite depend only on relative amount and properties of the individual constituents. The rule of mixtures can accurately predict these properties; the density of a particulate composite e.g.

$$\rho_c = \sum f_i \rho_i = f_1 \rho_1 + f_2 \rho_2 + \ldots + f_n \rho_n \quad (8)$$

where, $\rho_c$ = Density of composite,

$\rho_1, \rho_2, \ldots, \rho_n$ are densities of each constituent in the composite and

$f_1, f_2, \ldots, f_n$ are volume fractions of each constituent.

The strength of fiber-reinforced composites can be predicted, to some extent by the rules of mixtures. Also it predicts the electrical and thermal conductivity if the fibers are continuous and unidirectional. With the exception of density, these properties are much more difficult to predict if the fibers are not continuous and unidirectionally aligned. Certain properties such as hardness cannot be predicted by the rules of mixtures [48,49].

Different materials, e.g. metals, ceramics, glasses and polymers may be combined in different forms in composite materials. The effective method to increase strength properties is to incorporate high-strength materials as dispersed phases into the matrix, which can be a particulate matter, organic or glass fibers in continuous or short length’s metal wires, metal or ceramic whiskers or ceramic filaments such as boron or carbon.

### 1.7 Types of Composites

The first group of composites are known as “filled materials.” The main feature of these materials is the existence of some basic or matrix material whose properties are improved by filling it with some particles. Usually the matrix volume fraction is more than 50% in such materials and properties being modified by the
addition of fillers governed mainly by the matrix. These filled materials can be treated as homogeneous and isotropic.

The second group of composite materials are called “reinforced materials.” The basic components of these materials are long and thin fibers possessing high strength and stiffness. The fibers are bound with a matrix material whose volume fraction in a composite is usually less than 50%. The main properties of advanced composites due to which these materials find a wide application in engineering are governed by fibers. The composite materials are divided into several categories e.g.,

I.7.1 Polymer matrix composites
I.7.2 Metal matrix composites
I.7.3 Carbon matrix composites
I.7.4 Ceramic matrix composites

I.7.1 Polymer matrix composites

Polymer matrix composites have established themselves as engineering structural materials, not just as for making chairs and tables. This came about not only because of the introduction of high-performance fibers such as carbon, boron and aramid, but also because of some new and improved matrix materials also. The glass fiber reinforced polymers represents the largest class of polymer matrix composites. Carbon fiber reinforced polymer matrix composites are perhaps the most important structural composites.

I.7.2 Metal matrix composites

Metal matrix composites consist of a metal or an alloy as the continuous matrix and reinforcement that can be particle, short fiber or whisker or continuous fiber. There are three kinds of metal matrix composite depending upon physical characterization of reinforcement,
- Particle reinforced metal matrix composites
- Short fiber reinforced metal matrix composites
- Continuous fiber or sheet reinforced metal matrix composites

I.7.3 Carbon-carbon composites

Carbon-carbon composites are used for application ranging from in the space shuttle as nose cone, leading edges of the wings, heat shields, nose tips for re-entry vehicles to throat inserts for advanced solid motors, etc. [50-52]. Carbon-carbon composites can operate at temperatures of up to 3000°C and in fact, are stronger at higher temperatures than low temperatures. Due to high thermal conductivity and low coefficient of thermal expansion, carbon-carbon composites are most suitable as brake disk materials for supersonic and military aircrafts [53,54]. Some European racing cars are also equipped with carbon brakes.

I.7.4 Ceramic matrix composites

Carbon-carbon composites can retain their mechanical properties at high temperatures in inert atmosphere only as like any other carbon material as these have poor oxidation resistance. The oxidation problem in carbon-carbon composites can be overcome either by coating the composite with oxidation resistant ceramic materials or by making ceramic matrix composite having high oxidation resistance of matrix and reinforcement.

Ceramic composites are applicable to mechanically loaded parts at highest operating temperatures. Due to brittleness, stiffness and high-tensile strength, the ceramic matrix behaves differently than tough polymeric and metallic matrices. The toughness of ceramic matrix composite is improved by the fibers by using the energy for crack propagation on fracturing, separating and pulling out the fibers from the matrix. The thinner the fibers and better designed net structure (3-D pattern), the
better the overall mechanical properties expected. Their low density and thermal conductivity make them attractive for applications in thermal engines, aircraft and space devices subjected to high temperatures. With economic processes of fabricating CMC products, they would be ideal for application at high temperatures (> 2000° C) in the conditions of chemically aggressive environment, and abrasion wear. These composites are more difficult to fabricate than others, since higher temperatures and pressures are needed and the ceramic matrix adapts with greater difficulty to the reinforcing material than polymeric or metallic matrices. Various types of ceramic matrix composites are available depending on open reinforcement and matrix systems for high technological application. Based on a matrix system the ceramic materials are divided into four major groups describe as below

- Carbon matrix composites (Reinforcements- Carbon, SiC)
- Carbide matrix composites (Reinforcements- Carbon, SiC)
- Oxides matrix composites (Reinforcements- Silica, Quartz, Alumina, Mullite, Al₂O₃-ZrO₂-SiO₂, ZrO₂)
- Nitride matrix composites (Reinforcements- Carbon, Nitrides, Al₂O₃-ZrO₂-SiO₂)

The ceramic matrix composites are possessing very high thermal resistance. The stiffness of the fibers which are usually metals e.g. steel, tungsten, molybdenum, niobium, carbon, boron, non metallic and the ceramic matrices (oxides, carbides, nitrides and carbon) are not very different, and the fibers do not carry the main fraction of the load in ceramic composites. The function of the fibers is to provide strength and mainly toughness (resistance to cracks) to the composite because non-reinforced ceramic is very brittle. Ceramic composites can operate under very high temperatures depending on the melting temperature of the matrix that varies from
1200°C to 3500°C. Naturally, the higher is this temperature the more complicated is the manufacturing process. The main shortcoming of ceramic composites is associated with a low ultimate tensile elongation of the ceramic matrix resulting in cracks appearing in the matrix under relatively low tensile stress applied to the material.

I.8 Processing of Ceramic Matrix Composites

Depending upon the type of reinforcements, various classes of ceramic matrix composites can be processed having different values of toughness, fracture strain, fracture stress, residual strength after uploading and damage tolerance, which indicates large differences in fracture potential. On the other hand various classes of composites such as long fiber reinforced and complex shape composites expanded for processing technological problems and fabrication complexity and the cost.

Continuous fiber reinforcement has the highest potential for improving stress-strain behavior and damage tolerance, but has the highest fabrication complexity and cost. One serious problem in processing continuous fiber reinforced ceramic composite is the limited temperature stability of the fibers. Philips [35] have reviewed the ceramic matrix composites manufacturing techniques. An additional consideration is the chemical attack on the fibers, which is due to reaction with matrix material or with gaseous media of the sintering atmosphere. The interfacial characteristic of the fiber matrix has to be optimized in such a way that during loading in the first step load transfer from the matrix to the fiber is possible.

However, in the second step, debonding and post deboned friction with subsequent fiber pull out can be initiated. To meet all these conditions, strong efforts are being undertaken to avoid high processing temperature.
I.8.1 Cold Pressing and Sintering

Cold Pressing of matrix powders and fibers followed by sintering is adopted from traditional processing of ceramic materials. The method of sintering is typically used to consolidate ceramic powders. This technique of densification requires atomic diffusion. The green compact consisting of various powders and fibers is first fabricated by a sintering process [37,38], i.e., the compact is heated to an elevated temperature range where atomic diffusion takes place.

Disadvantages

- The matrix shrinks greatly.
- High aspect ratio of fibers and whiskers makes the sintering process difficult.
- The sintered density of silicon carbide reinforced alumina decreases with an increasing aspect ratio of the whiskers.
- The difference in the coefficient of thermal expansion between the reinforcement and the matrix may introduce a hydrostatic tensile stress in the matrix.

I.8.2 Gas Infiltration (CVI)

In the CVI process, the desired matrix in the vapor form is deposited within a porous preform, to produce the composite material.

Rather expansive approach relies on CVI of gaseous precursors of ceramic into ceramic fibrous preform [55,56]. This technology has been used to produce tough SiC/SiC engine elements for aerospace applications [57]. CVI relies on gaseous precursor decomposition inside fiber preform, for example: Methane (CH$_4$) and Methyltrichlorosilane (CH$_3$Cl$_3$Si) decompose according to reactions given below to produce carbon and silicon carbide where are deposited onto the substrate:
CVI uses low pressure (e.g. 25 torr), low temperature (e.g. 1200°C), and low reactant concentration in H₂ carrier gas flow.

**Advantages**

CVI is a low temperature process, shorter process time (≈ 1 day) for thermal and pressure gradient, size and shape versatility, adaptable to produce many fibers and matrices, amenable to 1-D, 2-D, 3-D woven and braided perform, forms dense deposit yields of high strength and high toughness composites can be molded/automated.

**Disadvantages**

In the CVI process, evolution of hazardous gases, long process time (> 3 weeks) for isothermal process, typically 90% dense & graded, thickness usually limited to 25mm can be deposited. The process requires accurate. It is an expansive method requiring multi cycle process while near net shape products are not achieved.

**I.8.3 Liquid infiltration**

The method produces high density matrix with no voids in the matrix. The key to liquid infiltration is the proper control of the fluidity of the liquid matrix [58]. A special variant of the liquid infiltration method often employed to fabricate carbon/carbon composites is called high pressure impregnation of carbon (HPIC). A schematic of the HPIC method to fabricate C/C composites by liquid infiltration is presented the fig.I.7.

\[
\begin{align*}
\text{CH}_4(g) & \rightarrow C(s) + 2H_2(g) \quad \text{(9)} \\
\text{CH}_3\text{Cl}_3\text{Si}(g) & \rightarrow \text{SiC}(s) + 3\text{HCl}(g) \quad \text{(10)}
\end{align*}
\]
I.8.4 Slurry Infiltration and hot pressing

The hot pressing method involves simultaneous applications of pressure and high temperature [59]. An alternative technique developed from hot pressing method is the slurry infiltration. The slurry infiltration may be the most important technique used to fabricate continuous fiber reinforced glass and glass-ceramic composites.

The reinforcing fibers are incorporated into an unconsolidated matrix. The composite is consolidated by hot pressing. A schematic of the slurry infiltration method followed by hot pressing for making a fiber reinforced glass and glass-ceramic composite is presented in fig1.8.

The reinforcing fibers are passed through slurry, which penetrates into the porous structure of the reinforcing phase. The driving force of the infiltration is capillary effect but the process may be enhanced by vacuum or pressure. The prepreg (infiltrated fibers) is wound onto a mandrel. These are dried, cut and laid-up. After drying these are cut and laid-up on a tooling mold. Hot pressing including sintering,
densification are performed at high temperature and increased pressure, which enhance the diffusion of the ceramic material between the particles incorporated into the fibers structure. The particles consolidate resulting in a low porosity densified composite.

Fig. I.8 A Slurry Infiltration Process followed by hot pressing for making a fiber reinforced glass ceramic composite

Disadvantages

- Composites with complicated shapes are difficult to fabricate
- Clusters of fibers and matrix-rich regions are typically observed in the composite, which degrade the mechanical properties of the composite
- The process is expansive even though the composites produced are generally of good quality
I.8.5 Reaction bonding process

Another variant of CMC processing includes the traditional reaction bonding (RB) [60]. This technique is derived from fabricating monolithic ceramics. The material is manufactured by a chemical reaction, i.e. conversion of a compacted powder (porous) preform composed of one element of a ceramic (i.e. metal or nonmetal) to the final ceramic compound through reaction with the environment usually in a liquid or gaseous form. The classical example includes silicon matrix that is converted to silicon nitride by holding it in nitrogen for a couple of days at 1400°C. Reaction bonded SiC is usually produced by infiltration of a carbon preform with molten silicon.

Advantages

In the resulting composite there is little or no matrix shrinkage. Very good results are obtained with high modulus carbon fibers and chemical vapor deposition SiC fibers. It is single step consolidation process having short time processing (≈ 1 day) for SiC, complex near net shapes.

Disadvantages

It requires very high temperature vacuum equipment. During the process probable fiber damage can have improper fiber wetting. Usually it takes long processing time even in the homogeneous matrix e.g. silicon nitride.

I.8.6 Sol-Gel Method

I.8.6.a Sol-Gel Techniques

Sol-gel processing is a rapidly growing method for synthesis of oxide ceramics [50,61]. The processing conditions allow the synthesis of a wide variety of materials including semiconductors, insulators, ferroelectrics, and superconductors (fig.I.9 and fig.I.10). A significant advantage of sol-gel science over more
conventional materials processing routes are the mild conditions that can be employed. This allows thermally unstable inorganic compounds to be entrapped or covalently bonded within sol-gel matrix. It is more economical way to synthesis of ceramic powders, glasses as well as films and composites (Fig.I.11). For instance, glasses with high purity and crystalline oxides ceramic materials can be synthesized by sol-gel processing of metal alkoxide derivatives. Sol-gel process is based on the possibility of forming disordered network of the glass at low temperature from the suitable compounds by chemical polymerization in a liquid phase. The termed “sol” as dispersion of colloids in liquid. Colloids are the solid particles with diameters in the range of 10-1000 Å [62]. Each contains $10^3$-$10^9$ atoms in a molecule. Because of small sizes, Brownian motions colloidal sol is stable against sedimentation. When viscosity of the sol increases sufficiently it becomes rigid. This rigid material is known as “Gel”. However, in the field of ceramics and glasses sol-gel have broad meaning. It also includes the use of organometallic such as alkoxide, which can be partly hydrolyzed and then polymerized into a uniform gel.
Fig. I.9 Different types of sol-gel processing

Fig. I.10 Formation of sols and gels.
I.8.6.b Factors in Sol-Gel Process

Sol-gel; process involves following steps (a) preparation of solution, (b) hydrolysis of sol at suitable temperature, (c) casting, (d) drying and (e) firing.

The physical aspects of the solid gel are strongly influenced by the drying stage. Depending on the experimental conditions of solvent evacuation, powder, large grains or monoliths can be obtained. Molar ratio of water to the metal alkoxide used for the hydrolysis reaction significantly influences the conversion of dried gel to fully dense materials [63-67].
- Various parameters in sol-gel processing
  - Choice of precursors
  - Concentration of precursors
    - I.e. addition of water, organic solvent
  - Water/alkoxide mole ratio
  - Type and amount of catalyst
  - Control of hydrolysis reaction etc.

Certain parameters such as volatile evolution rate, variant in ambient condition, small impurities in sol, rate of change of viscosity etc though affect kinetics of sol-gel process but are controllable.

The hydrolysis of organometallic compound is very slow reaction. To enhance the rate of hydrolysis reaction, various catalysts both acidic and basic have been used.

Advantages of sol gel process:
  - Better homogeneity – from raw materials
  - Better purity – from raw materials
  - Low temperature for preparation:
    - (a) Save energy
    - (b) Minimize evaporation losses
    - (c) Minimize air pollution
    - (d) No reaction with containers, thus purity
    - (e) Bypass phase separation
    - (f) Bypass crystallization
  - New nanocrystalline solids outside the range of normal glass formation
  - New crystalline phases from new crystalline solids
  - Better glass products from special properties of gel
Special products such as films

- Disadvantage of sol gel process:
  - Large shrinkage
  - High cost of reactant
  - Multiple impregnation required

### I.8.7 Freeze Gelation Method

A sol-gel process involving rapid “freeze gelation” permits the fabrication of ceramic-matrix composite components at low sintering temperatures to near net shape and with low shrinkage. In the high temperature processing of CMCs, there may be chances of fiber damage and involves interfacial reactions between fiber and matrix, which result into brittle, low strength composites. The freeze gelation process involves rapidly freezing a sol to produce a porous, easily handled green body, which then may be infiltrated and sintered. The procedure of gelation is as shown in fig.I.12.

The silica sol, filler and reinforcements are rapidly frozen to liquid nitrogen temperature. The freezing process causing the formation of ice crystals of aqueous solvents, with a small increase in volume occupied by the water. A gel is formed in the regions between the ice crystals. On warming back to room temperature and
drying of water, the solid produced, may be readily handled and it exhibits minimum shrinkage. Residual porosity in the regions previously occupied by the ice crystals is large and open, representing the possibility of infiltration of gas or liquid phase followed by sintering to densify the formed bodies [68].

The process has several advantages. It is a low cost method for fabrication of ceramic matrix composites. Shrinkage level is low along with low sintering temperature. This method is applicable to both continuous and short fiber reinforcements systems. Using this method near net shape and similar size of products can be fabricated with ease.

### 1.9 High Tech applications of ceramics and ceramic matrix composites

The processing temperatures for high tech ceramics are also higher. Therefore, two factors add together to make hi-tech ceramics cost prohibitive materials. High cost of reinforcing materials add to the cost of fiber reinforced ceramic materials and production routes coupled with low demand patterns have restricted the applications of high tech ceramics and ceramic composites to only narrow areas such as aerospace, nuclear and hi-tech programmers. More emphasis has been on aerospace programs, where increased materials capabilities and decrease weight can result in tremendous increase in the performance and hence can pay back the cost. For such applications, the brittle failure mode of monolithic ceramics or even whiskers reinforced ceramic can ordinarily not be tolerated. The major developmental efforts have involved CVI produced silicon carbide matrix composites for a variety of components for aerospace vehicles, which include nose cones, leading edges, fins and rudders [62]. A prototype turbine blade produced by sol-gel processing has also been demonstrated [69].
Other applications include

- Inorganic membranes for liquid separations: the purification of polluted water has been achieved using alumina membranes in an ultra filtration process [70].

- Boron nitride is superior to Al₂O₃ concerning the thermal conductivity. BN is not wetted by most molten metals and salts. It can be used as crucible material, coating agent or break rings for horizontal continuous casting. BN powder is used as a high temperature lubricant [67].

- Ceramic gas burners are used to maintain high temperature in the steel manufacturing process. The ceramic heat exchanger will endure material temperature; whereas the application of metallic heat exchanger may cause problems. Hexoloy SA silicon carbide tubes are known [68] to withstand elevated flue gas temperatures and highly corrosive conditions.

- Silicon carbide is normally used as heating elements for furnaces in temperature range of 800°C to 1500°C. Elements are available in the form of rods or spiraled tubes. Elements have excellent hot strength and are easy to install. Typical uses are in furnaces for firing, crystal growing homogenization and testing.

- Molybdenum disilicide based elements are used at temperatures between 800°C to 1700°C. Elements are characterized by zero electrical aging, excellent oxidation resistance and thus extremely long service life. If offers solution to rapid heating, easily adjusted and accurately controlled temperatures and excellent condition for cycling.

- Materials with good chemical resistance, wear resistance and hardness are used as cutting tools, pump and valve components, nozzle and human implants. Materials with excellent high temperature mechanical properties are used as engine parts, turbine, coating and kiln furniture.
Numbers of areas, where ceramic materials are being considered for advanced heat engines components, are valves, valve guides, piston insert, and piston. Wrist pins, cylinder, turbine stator, turbine housing and heat exchanger etc. thermal barrier coatings are developed because of wear, corrosion and heat insulation.

Many other potential applications for continuous fiber reinforced ceramic composites have been summarizes in Table I.3 [69].
Table I.3 Potential Industrial applications for ceramics and continuous fiber reinforced ceramic composites [69]

<table>
<thead>
<tr>
<th>Product area</th>
<th>Examples</th>
<th>Likely industrial market</th>
</tr>
</thead>
<tbody>
<tr>
<td>Advanced heat engines</td>
<td>Combustors, Liners, Wear parts etc.</td>
<td>Primarily high temperature as turbine, possible adiabatic diesels</td>
</tr>
<tr>
<td>Heat recovery equipment internals</td>
<td>Air preheaters recuperators</td>
<td>Any indirect heating uses, energy intensive industrial process (e.g. Aluminium remelters, steel reheaters, glass melters)</td>
</tr>
<tr>
<td>Burners and combustors</td>
<td>Radiant tube burners</td>
<td>Potentially any indirect fired, high temperature or controlled atmosphere/ heating/ melting/ heat treating industrial applications</td>
</tr>
<tr>
<td>Burners and combustors</td>
<td>Catathermal combustors</td>
<td>Low NOx clean fuel heating applications- including gas turbine combustors, industrial process heat.</td>
</tr>
<tr>
<td>Waste incineration systems</td>
<td>Handling equipment, internals clean up</td>
<td>Chemical process industry, petroleum refining, conventional MSW/RDF facilities, advanced toxic/ hazardous waste facilities, with or without energy recovery.</td>
</tr>
<tr>
<td>Separation/ filtration systems</td>
<td>Filters, substrates, centrifuges</td>
<td>Gas turbine, combined cycle and IGCC configuration, particulate taps for diesel exhausts, molten metal filters, sewage treatment.</td>
</tr>
<tr>
<td>Refractory and related</td>
<td>Furnace lining, crucibles, flasks etc.</td>
<td>High temperature industrial heating/ melting</td>
</tr>
<tr>
<td>Structural components</td>
<td>Beams, Panels, Decking, containers</td>
<td>Possible for EMI shielding, corrosive/ abrasive environments, fire protection, missile protection</td>
</tr>
</tbody>
</table>
I.10 Overview of Literature Survey

On high reactivity precursors and carbothermal reduction reaction to increase the SiC production yield. Two approaches were formed in the literature. One approach to accelerate the carbothermal reduction of silica and to increase the yield was performed by Julbe et al[70]. Crystalline β-SiC was prepared after pyrolysis at about 1580°C with a 3h hold time using colloidal silica sol and saccharose (C\textsubscript{12}H\textsubscript{22}O\textsubscript{11}) as silicon and carbon sources respectively. Boric acid (H\textsubscript{3}BO\textsubscript{3}), soluble in aqueous solutions, was directly introduced in the sol. The SiC powders having 100nm grain size were obtained as homogeneous product. Moreover, boric acid added in the original colloidal sols improved significantly the carbothermal reduction yield as well as the conversion rate and the powder crystallinity.

Another approach to enhance carbothermal reduction yield of SiC consists in increasing the reactivity of the precursors by using boric acid as additive, Researchers [71] synthesised β-SiC by heat treatment at 1550°C by reductive heating of gel precursors prepared from silica sol and saccharose or activated carbon as carbon sources. It was proved that for SiC formation starting with silica and with saccharose being the carbon source, formation of SiC started at 1300°C and became intensive at 1400°C. In contrast, in the case of gels prepared from activated carbon, the crystallization of β-SiC started at 1400°C and progressed via carbothermal reduction of SiO\textsubscript{2} with a high crystallinity. These differences are due to the close contact between SiO\textsubscript{2} and C molecules obtained only if the gels are prepared using saccharose as carbon source. The same behaviour was also observed [72,73] for SiC powder synthesized starting from organosilicon polymers as silicon and carbon precursors. The molecular intimacy of SiO\textsubscript{2}/C mixture resulted in lower temperatures of synthesis and higher surface areas of the produced SiC powders.
It was also established that even though the synthesis of SiC from gels with activated carbon progressed with greater conversion rate than when using saccharose and boric acid addition was found to be advantageous.

V. Raman [74] synthesized SiC via the sol-gel process from various silicon alkoxides and various carbon sources. Tetraethoxysilane (TEOS), methyltriethoxysilane (MTES) and a mixture of TEOS and MTES were used as silicon precursors whereas, phenolic resin, ethylcellulose, polyacrylonitrile and starch were used as carbon sources. After hydrolysis, the sol was kept at 40 °C for gelling, ageing and drying. As obtained gels were then heat treated in order to synthesize silicon carbide by carbothermal reduction of silica. [75-76]. It was found that all products obtained from all these precursors were β-SiC. The colour of products ranged from light-green to greyish-black depending upon the amount of free carbon in the final product. Table I.4 summarizes the characteristics of obtained SiC materials as a function of the different silicon and carbon sources.

Table I.4 Properties of SiC prepared by sol-gel process from different silicon and carbon precursors. [74]

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Silicon Source</th>
<th>Carbon Source</th>
<th>Colour</th>
<th>Crystallite size (nm)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TEOS</td>
<td>Phenolic resin</td>
<td>Greyishblack</td>
<td>52.5</td>
<td>1.64</td>
</tr>
<tr>
<td>2</td>
<td>MTES</td>
<td>Phenolic resin</td>
<td>Grey</td>
<td>32.6</td>
<td>1.60</td>
</tr>
<tr>
<td>3</td>
<td>TEOS + MTES</td>
<td>Phenolic resin</td>
<td>Grey</td>
<td>52.5</td>
<td>1.86</td>
</tr>
<tr>
<td>4</td>
<td>TEOS</td>
<td>Ethylcellulose</td>
<td>Light-green</td>
<td>23.3</td>
<td>--</td>
</tr>
<tr>
<td>5</td>
<td>MTES</td>
<td>Ethylcellulose</td>
<td>Light-green</td>
<td>9</td>
<td>1.76</td>
</tr>
<tr>
<td>6</td>
<td>TEOS</td>
<td>PAN</td>
<td>Greyishblack</td>
<td>&lt; 32.6</td>
<td>1.38</td>
</tr>
<tr>
<td>7</td>
<td>TEOS</td>
<td>Starch</td>
<td>Greyishblack</td>
<td>21.3</td>
<td>1.80</td>
</tr>
</tbody>
</table>

J. Li [77] used two step sol-gel processes for synthesis of SiC precursors. The authors synthesized phenolic resin-SiO₂ hybrid gels by sol-gel technique that was
used as silicon source in the presence of hexamethylenetetramine (HMTA) as catalysts. In the first step for prehydrolysis, oxalic acid (OA) was added as catalyst and the ratio OA/TEOS was investigated. OA was considered to the promoting hydrolysis of TEOS. Moreover, it was established that the OA content as well as the prehydrolysis time determined whether gel instead of precipitate could form. For the second step of sol-gel process, that is gelation, HMTA was added as a catalyst that resulted in a considerable reduction of gelation time and condensation promoting. It was considered that the hydrolysis and condensation rates of TEOS were greatly dependent upon the catalyst and the pH value [78]. Thus, for pH values below 7, hydrolysis rate increased with decreasing pH but condensation rate decreased and reached its lowest point at pH-2, the isoelectric point for silica. In both steps in the previous work pH below 7 and subsequently decreased with increasing OA content. Given the fact that SiC is a refractory material which shows a high thermal conductivity and because of its properties of particle strength and attrition resistance, mesoporous SiC is expected to have extensive application in harsh environments such as catalyst, sorbent or membrane support [79-80].

Nevertheless, SiC applications as a catalyst carrier was limited since the specific surface area reachable for this material was rather low. It was shown that the sol-gel process is a promising route to prepare high surface area SiC materials. G. Q. Jin [81] has investigated a modified sol-gel method to obtain mesoporous silicon carbide. As a first step, a binary sol was prepared starting from TEOS, phenolic resin and oxalic acid. Nickel nitrate was used in the sol-gel process as a pore-adjusting reagent. Secondly, a carbonaceous silicon xerogel was formed by the sol condensation with a small amount addition of hexamethylenetetramine in order to accelerate the condensation of the sol. Finally, mesoporous SiC was obtained with a surface area
112 m²/g and an average pore diameter of about 10 nm by carbothermal reduction of the xerogel at 1250°C in an argon flow for 20h. Even though, the mechanism of formation of mesoporous SiC is not yet well defined, interestingly, it was found that the surface areas and pore size distributions were nickel nitrate content dependent.

However, this process is very time consuming and necessitates special conditions, such as flowing argon (40cm³/min). Additionally, the carbothermal reduction of the xerogel is carried out at 1250°C for a relatively long holding time.

Y. Zheng [82] prepared a carbonaceous silicon xerogel starting from TEOS and saccharose as silicon and carbon sources respectively. Then the xerogel formed was treated for carbothermal reaction at 1450°C for 12h to prepare a novel kind of β-SiC. The characterization of purified sample revealed mesoporous material nature as a thornball-like structure and a higher surface area 141 m²/g. Moreover, the as obtained mesoporous SiC material, revealed two different kinds of pores, with 2-12 nm sized mesoporous in the thorn-like SiC crystalloids and 12–30 nm sized textural mesoporous in the thornball-like SiC.

R. Sharma [83] reported a new and simple sol-gel approach producing a simultaneous growth of nanocrystalline SiC nanoparticles with the nanocrystalline silicon oxide using TEOS, citric acid and ethylene glycol. After the gel development, a black powder was obtained after drying at 300°C. The powder was subsequently heat treated at 1400°C in hydrogen atmosphere. Interestingly, it was found that under these working conditions, crystalline silicon oxide was formed instead of amorphous silicon oxide which was normally found to grow during the gel growth technique.

On the other hand, SiC is considered to be one of the important microwave absorbing materials due to its good dielectric loss to microwave [84]. In microwave processing, SiC can absorb electromagnetic energy and can be heated easily. It has a
loss factor of 1.71 at 2.45 GHz at room temperature. And the loss factor at 695°C for the same frequency is increased to 27.99. This ability for microwave absorption is due to the semiconductivity of this ceramic material [85].

Moreover, SiC can be used as microwave absorbing materials with lightweight, thin thickness and broad absorbing frequency. Since pure SiC possess low dielectric properties that give barely the capacity to dissipate microwave by dielectric loss, therefore, doped SiC was used in order to enhance the aimed properties.

B. Zhang [85] synthesized nano-sized SiC powders by carbothermal reduction of SiO₂ and SiO₂–Al₂O₃ xerogel. The latter was prepared by mixing TEOS, saccharose and some Al₂O₃ powders. The xerogel were subsequently heated at 1550°C for 1h in argon or nitrogen atmosphere to synthesize SiC. It was found that aluminium and nitrogen have important effects on the polytypes of SiC powders. In the presence of aluminium, the polytypes of l2H SiC powders were obtained, whereas, 21R SiC was synthesized under the nitrogen atmospheres (Table I.5). During the synthesis of silicon carbide, Al₂O₃ is reduced by carbon and forms carbide. At the same time, aluminium dopes into SiC and forms solid solution. Thus, aluminium atoms replace atoms of silicon in the solid solution and induce vacancies of carbon. The lattice parameters were decreased with increasing aluminium content. On the contrary, when SiC powders are synthesized in nitrogen atmosphere, nitrogen atoms replace some carbon atoms and form silicon vacancies. The synthesized β-SiC powder has much higher relative permittivity (ε ’r = 30~50) and loss tangent (tg δ = 0.7~0.9) than all of the α-SiC powders, though the α-SiC powders with 5.26 mol% aluminium possess higher conductivities. In fact, it was established that for Al-doped SiC powders, the relative permittivity and loss tangents are in an opposite measure of the aluminium content. For the powders with the same aluminium content, the
samples synthesized in nitrogen atmosphere have smaller values for $\varepsilon'$ and $\tan\delta$ than those obtained in argon atmosphere in the frequency range of 8.2-12.4 GHz. The fundamental factor on these dielectric behaviours is ion jump and dipole relaxation, namely the reorientation of lattice defect pairs (VSi–VC, SiC–CSi). In fact, aluminium and nitrogen decrease the defect pairs that contribute to polarization. With the increase of the aluminium content and the doping of nitrogen, the conductivity of SiC rises, but the relative dielectric constant and loss tangent decrease.

Table I.5 DC resistivities and calculated loss tangent of SiC powders as a function of the alumina content [85]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atom ratio of Al-Si</th>
<th>Reaction atmosphere</th>
<th>SiC polytype</th>
<th>DC Resistivity (Ω cm)</th>
<th>Calculated loss tangent for 10 GHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>Argon</td>
<td>3C</td>
<td>557.9</td>
<td>8.00x10-2</td>
</tr>
<tr>
<td>2</td>
<td>2.63:100</td>
<td>Argon</td>
<td>12H</td>
<td>1803.5</td>
<td>8.78x10-2</td>
</tr>
<tr>
<td>3</td>
<td>5.26:100</td>
<td>Argon</td>
<td>12H</td>
<td>511.3</td>
<td>3.57x10-1</td>
</tr>
<tr>
<td>4</td>
<td>2.63:100</td>
<td>Nitrogen</td>
<td>21R</td>
<td>1181.7</td>
<td>1.84x10-1</td>
</tr>
<tr>
<td>5</td>
<td>5.26:100</td>
<td>Nitrogen</td>
<td>21R</td>
<td>77.5</td>
<td>4.06x10-1</td>
</tr>
</tbody>
</table>

Besides the p-type doping by Al, boron atoms can substitute preferably the silicon atoms of SiC lattice. Zhou et al [86] investigated the effects of different temperatures on the doping of SiC with B. The authors synthesized B-doped SiC powders by sol-gel process starting from the mixture sol of TEOS and saccharose as silicon and carbon sources, respectively, and tributyl borate as dopant at 1500°C, 1600°C, 1700°C and 1800°C. It was proved that $\beta$-SiC is completely generated when the temperature is 1700°C and SiC($\beta$) solid solution is generated when the temperature is 1800°C. The powders synthesized at 1700°C had fine spherical particles with mean size of 70 nm and narrow particle size distribution. On the contrary, few needle-like particles were generated in the powders synthesized at
1800°C. Thus it is considered that the formed SiC(β) solid solution suppresses the anisotropic growth of SiC whiskers.

The electric permittivity’s of SiC samples were determined in the frequency range of 8.2–12.4 GHz. Results showed that the SiC(β) sample has higher values in real part $\varepsilon'$ and imaginary part $\varepsilon''$ of permittivity. The average values of $\varepsilon'$ and $\varepsilon''$ for the sample synthesized at 1700°C were 2.23 and 0.10, respectively. It was also noticed that both $\varepsilon'$ and $\varepsilon''$ have increased for the sample synthesized at 1800°C, and particularly the $\varepsilon''$ was nearly 2.5 times greater than that of the sample synthesized at 1700°C. This can suggest an improved capacity of dielectric loss in microwave range.

The basic factor on these dielectric behaviours is that for a temperature heat of 1800°C, which generates the SiC(B) solid solution, there exist bound holes in SiC with acceptor doping. Under the alternating electromagnetic field, these bound holes will migrate to and fro to form relaxation polarization and loss, thus leading to higher $\varepsilon'$ and $\varepsilon''$ of the sample at 1800°C.

Wang [87] studied the effect of Y$_2$O$_3$ addition and the total oxide volume fraction (Y$_2$O$_3$ + Al$_2$O$_3$) on mechanical properties of pressure less sintered β-SiC ceramics at the low temperature. It was demonstrated that the increase in strength with yttria (Y$_2$O$_3$) content is directly related to an increase in relative density of sintered specimens, which in turn is related to the level of Y$_2$O$_3$ addition. The study of the fracture toughness of SiC ceramics with oxide addition revealed that with increasing oxide content, the fracture toughness increases and reached a maximum of about 4.3 MPa. m$^{1/2}$ achieved at ~14 vol.% of oxide added for samples sintered at 1850°C. This is mostly related to cracking deflection mechanisms toughening, which occurs when the crack changes its direction as it encounters the SiC grains and the grain boundary phase. Moreover, the mechanism of toughening is further enhanced by a thermal...
mismatch between SiC and the intergranular YAG phase at the grain boundaries and this leads to the crack’s progress along the grain boundaries [88].

An alternative promising strategy to improve the mechanical properties of β-SiC is to adjust the volume fraction and composition of the boundary phase so as to generate the microstructure with high density and resistance to crack propagation. The variation of the α-SiC and β-SiC proportions of the starting powders mixture are considered to be an efficient way of adjusting both the microstructure and the mechanical properties of the SiC ceramic [87]. According to this approach, Lee et al [89] investigated the effect of starting phase of the raw material on the microstructure and fracture toughness of SiC ceramic by varying the mixed ratio of α-SiC and β-SiC powders. The authors prepared several samples by altering the β/α phase ratio of SiC starting powder from 0 to 100 vol. % and adding 2 mol % of yttrium aluminium garnet and 2.5 wt. % polyethylene glycol (PEG). The mixtures were then compacted and hot pressed at 1850°C for 30 min at a pressure of 50 MPa and subsequently sintered at 1950°C for 5h. The densities of the resulting compacted powders were higher than 95 % of theoretical density regardless of the starting phase. Most sintered SiC specimens enclosed elongated grains with rod-like type. However, it was noticed that the amount of elongated grain and their aspect ratio was changed with the ratio of α- and β-SiC in the starting powder. Elongated grains were formed by the β→α phase transformation with a 4H polytype and anisotropic grain growth during heat treatment. It was concluded from this study, that specimen containing 50 vol.% β-SiC in the starting powder showed highest values of volume fraction, maximum length and aspect ratio for elongated grains. This specimen revealed also the highest fracture toughness of 6.0 MPa. m1/2 which is due to the elongated grains induced crack deflection during crack propagation.
Table I.6 Mechanical properties of LPS SiS as a function of different sintering aids.

<table>
<thead>
<tr>
<th>References</th>
<th>Technique</th>
<th>Sintering additives</th>
<th>Hardness H (GPa)</th>
<th>Fracture Toughness (MPa.m1/2)</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Chen, Zeng, 1995)</td>
<td>Pressureless sintering SiC</td>
<td>Al₂O₃ + HoO₃ (eutectic composition)</td>
<td>17.47</td>
<td>3.68</td>
<td>Up to 3.764 g/cm³</td>
</tr>
<tr>
<td>(Chen, 1993)</td>
<td>Pressureless sintering SiC</td>
<td>Al₂O₃ + SmO₃ (eutectic composition)</td>
<td>17.1</td>
<td>4.6</td>
<td>92.6 %</td>
</tr>
<tr>
<td>(Hidaka et al, 2004)</td>
<td>Hot pressing at 1950°C and P=39 MPa</td>
<td>(Al₂O₃ + Y ⟋ ions) /Polytitanocarb osilane by infiltration</td>
<td>19 - 21</td>
<td>5.9</td>
<td>95 – 98 %</td>
</tr>
<tr>
<td>(Scitti et al, 2001)</td>
<td>Hot pressing at 1850-1950°C Annealing (1900°C/3 or 2h)</td>
<td>Al₂O₃ + Y₂O₃</td>
<td>22</td>
<td>2.95 – 3.17</td>
<td>Up to 99.4 % (3.24g/cm³) 3.22 g/cm³</td>
</tr>
<tr>
<td>(Wang, Krstic, 2003)</td>
<td>Pressureless sintering β-SiC at 1850°C</td>
<td>Y₂O₃ in (Al₂O₃ + Y₂O₃)</td>
<td>22</td>
<td>4.3</td>
<td>~ 98 %</td>
</tr>
<tr>
<td>(Mulla, Krstic, 1994)</td>
<td>Pressureless sintering β-SiC at 2050°C</td>
<td>Al₂O₃</td>
<td>--</td>
<td>6</td>
<td>97-98 %</td>
</tr>
<tr>
<td>(Hirata et al, 2010)</td>
<td>Hot pressing at 1900-1950°C and P=39 MPa</td>
<td>Al₂O₃ + Y₂O₃</td>
<td>--</td>
<td>6.2</td>
<td>97.3-99.2</td>
</tr>
</tbody>
</table>

It could be concluded that, densities in excess of 99% of the theoretical limit can be easily achieved by carefully choosing the composition of liquid phase and the packing powder configuration [90]. On one hand, the sintering mechanism in the
pressureless liquid-phase sintering to full dense SiC with Al$_2$O$_3$ and Y$_2$O$_3$ additions is considered to be attributed to liquid-phase sintering via the formation of an eutectic liquid between Al$_2$O$_3$ and Y$_2$O$_3$ to yield yttrium aluminium garnet, or YAG, based liquid phase. On the other hand, the hardness was mainly related to reduction of secondary phases which generally decrease such property. Finally, the increase in toughness is related not only to grain morphology but also to second phase chemistry, thus a suitable choice of thermal treatment parameters that modify second phase chemistry without excessive grain growth can theoretically lead to a reinforced microstructure with slight or no strength decrease.

**Scope of the Present Work**

In recent years there have been increasing numbers of applications requiring more efficient and lightweight thermal management such as hybrid diesel-electric vehicles, communication satellites, advanced aircraft and fusion reactor systems [91]. The primary concerns in these thermal management applications are high thermal conductivity, low weight, and low coefficient of thermal expansion, high specific strength and high fracture toughness. Materials such as graphite, carbon/carbon composites, SiC/SiC, C/SiC composites used for high temperature and are particularly preferred for fusion reactor plasma facing components [92,93]. This is because of their high thermal conductivity, low coefficient of thermal expansion, superior thermal shock resistance and tolerance to neutron irradiation damage. Therefore, much work has been done and is in progress directing towards the improvement of the present composites either by modifying the type of fiber or matrix precursors. By choosing the right combination of reinforcements and matrix and processing conditions, new materials have been developed. More ever, there is a large range of ceramics, which can be used as matrices for ceramic matrix composites and hence
there is a great scope to develop ceramic matrix composites of desired properties by properly selecting the matrix and the method producing these matrices.

Fabrication technology for ceramic matrix composites is a quite recent one. Most of the development work has been carried out in United States of America, West Germany, France and England. The ceramic matrix composites fabrication utilizing organometallic polymers provide the unique advantages for processing refractory matrices in complicated shapes and composition as per designed performance requirements. This kind of work in India is of first of its kind and could be useful for fabrication of high performance, high temperature materials for structural applications. There is a great worldwide interest to develop carbides, oxycarbides, ceramics and nitridies. Oxycarbides are being developed through precursor polymers and sol-gel routes. There is a steady increase in the amount of work reported in the country. Therefore, the present research work was undertaken to develop silicon based ternary and multielement matrices containing Si, C, O through polymeric route such as modification of silica by incorporating carbon by using different carbon precursors sucrose, phenolic resin, furfuryl alcohol by sol-gel route

The research work was undertaken to develop ceramic matrix composites with silicon-oxygen-carbon based matrices and to study various parameters involved in fabrication of matrices, composites and fiber- matrix interactions. Therefore, the aim of present work was first to study the development of silicon oxycarbide/silicon carbide matrix system, their characterization and subsequently fabrication of fiber reinforced composites using developed copolymerized.
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