CHAPTER 1

STRUCTURAL CERAMICS - RECENT ADVANCES AND MODERN FABRICATION TECHNIQUES

1.1 OVERVIEW

In this introductory chapter, recent developments on structural ceramic materials, their properties and potential areas of applications are briefly presented. The various modern ceramic fabrication techniques, their principle and associated practical limitations are presented. The purpose for the present investigation, statement of the problem and the objectives of the research have also been clearly mentioned.

1.2 CERAMICS

In the most general terms ‘ceramics’ are defined as inorganic, non-metallic materials. Naturally occurring materials, such as rocks and minerals, are usually excluded. Inorganic glasses can be considered to be a subset of ceramics, but they differ in that they do not display long-range order in their structure. Ceramics are typically oxides, carbides, nitrides and borides. In most applications they are used in polycrystalline form rather than as single crystals. Modern ceramic materials have a tremendous range of properties that are necessary for mechanical, electrical, optical and thermal applications (Subba Rao 1987). They have now become well-recognized candidate materials in electrical and electronic circuits because of their dielectric, piezoelectric, magnetic and superconducting properties. Abrasive wheels, cutting tools, grinding media and refractory bricks and slabs are the most popular structural ceramic parts. The advanced structural ceramics are increasingly important for the development of ceramic engines, ultra and nano-filtration supports, artificial bio ceramics etc., and research is still in progress to identify most effective processing
methods (Michael Cima 1991). Table 1.1 presents few important structural ceramics and their different areas of applications.

Table 1.1  Potential structural ceramics and their applications (Bengisu 2001)

<table>
<thead>
<tr>
<th>Sectors</th>
<th>Structural Ceramic Materials</th>
<th>Area of Applications</th>
<th>Potential Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>$\text{Al}_2\text{O}_3$, $\text{ZrO}_2$, $\text{Si}_3\text{N}_4$, $\text{SiC}$, Mullite-$\text{SiC}$, $\text{MgO}$, $\text{Al}_2\text{TiO}_5$, $\text{AIN}$, perovskite oxide systems.</td>
<td>Fuel cells and batteries, gas turbine and reciprocating engines, heat recovery systems</td>
<td>Heat exchanger tubes and shells, valves, turbocharger rotors, pre-combustion chambers, port liners, solid electrolytes, etc.,</td>
</tr>
<tr>
<td>Automobile and transportation</td>
<td>$\text{Al}_2\text{O}_3$, $\text{ZrO}_2$, $\text{Al}_2\text{O}_3$-$\text{SiC}$, $\text{Si}_3\text{N}_4$, carbon-carbon composites, carbon-$\text{SiC}$ composites</td>
<td>Heat shield and engine components, spacecraft structures</td>
<td>Brakes, bearings, exhaust valves, piston rods, turbine valves, sensors</td>
</tr>
<tr>
<td>Environmental</td>
<td>Silica, Mullite, Zirconia - $\text{TiO}_2$, $\gamma$-$\text{Al}_2\text{O}_3$, SnO$_2$</td>
<td>Filters, membranes, sensors</td>
<td>Substrates, thin and thick film membranes, gas sensors and monitoring devices.</td>
</tr>
<tr>
<td>Engineering</td>
<td>$\text{Al}_2\text{O}_3$, $\text{ZrO}_2$, $\text{BN}$, $\text{SiC}$, $\text{Al}_2\text{TiO}_5$</td>
<td>Mechanical and thermal applications</td>
<td>Cutting tools, ceramic sheathed thermocouples, rolling bearings in machine tools, sliding bearings in water pumps.</td>
</tr>
</tbody>
</table>

1.2.1 Structural Ceramics

Structural ceramics possess high load bearing capacity and are meant for working in applications where high mechanical stress is developed during service. Compared to structural metals, ceramics are attractive because of their lower densities, higher strength and toughness and excellent creep resistance. As the service temperature increases, ceramics become more attractive because they retain their mechanical properties at higher temperatures than the metals do (Noboru Ichinose 1983, Evans 1990 and Rishi Raj 1993).
At present, the ceramics that are carefully designed with a view to impart high reliability and long-term service ability in severe operating conditions and processed under strictly controlled method of shaping and firing are classified as 'advanced structural ceramics'. They are also known as “engineering ceramics” or “technical ceramics” (Shiroku Saito 1988). Apart from the usual material characteristics, they should embody the properties such as good corrosion, erosion and wear resistances, non-wettability, and low thermal conductivity at high temperatures, high refractoriness and high creep deformation resistance.

Some of the most important monolithic structural ceramics for high temperature applications are silicon nitride (Si₃N₄), silicon aluminium oxynitride (SIALON), silicon carbide (SiC), partially stabilized zirconia (PSZ), alumina (Al₂O₃), and mullite (3Al₂O₃.2 SiO₂). These materials exhibit high strengths (>500 MPa), moderate to high fracture toughness (between 4 to14 MPam¹/²) and low creep rates (<10⁻⁹ s⁻¹) at temperatures below 1300°C. Table 1.2 presents the properties of these widely used popular monolithic structural ceramics.

1.2.2 Structural Ceramic Composites

Structural ceramic composites that are developed recently show broader diversity, and designed to have improved damage tolerance or increased toughness. The monolithic ceramic matrix is mixed with a suitable second-phase reinforcing agent, mostly oxide particulates, whiskers and fibers and is converted to make the composites (Marshall and Ritter 1987). Mechanisms pertinent to the second phase reinforcement are, transformation toughening, micro-cracking, crack deflection, crack branching and crack bridging. The improvement in fracture toughness and associated toughening mechanisms in ceramic composites have been extensively studied by many researchers (Rice 1985a, Swain 1990 and John Wachtman 1996). Figure 1.1 presents the different types of structural ceramic composites that are obtained with the various reinforcement phases.
<table>
<thead>
<tr>
<th>Properties</th>
<th>Alumina</th>
<th>Partially Stabilised Zirconia</th>
<th>Sintered Silicon Carbide</th>
<th>Hot Pressed Silicon Nitride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus of Rupture, MPa</td>
<td>380</td>
<td>610</td>
<td>483</td>
<td>896</td>
</tr>
<tr>
<td>Tensile Strength MPa</td>
<td>210</td>
<td>466</td>
<td>299</td>
<td>~580</td>
</tr>
<tr>
<td>Compressive Strength, MPa</td>
<td>2750</td>
<td>1850</td>
<td>2000</td>
<td>&gt;3500</td>
</tr>
<tr>
<td>Weibull Modulus</td>
<td>10</td>
<td>10-20</td>
<td>10</td>
<td>10-15</td>
</tr>
<tr>
<td>Young's Modulus MPa, x 10^5</td>
<td>3.6</td>
<td>2.0</td>
<td>4.1</td>
<td>3.1</td>
</tr>
<tr>
<td>Hardness at 500gms, kg/mm^2</td>
<td>1600</td>
<td>1500</td>
<td>2500</td>
<td>2200</td>
</tr>
<tr>
<td>Fracture toughness MPa m^1/2</td>
<td>1.75</td>
<td>9.5</td>
<td>3.0</td>
<td>5</td>
</tr>
<tr>
<td>Poisson's ratio</td>
<td>0.27</td>
<td>0.30</td>
<td>0.24</td>
<td>0.27</td>
</tr>
<tr>
<td>Density gm/cm^3</td>
<td>3.98</td>
<td>5.78</td>
<td>3.1</td>
<td>3.2</td>
</tr>
<tr>
<td>Thermal expansion co-efficient 0-1000°C (1/K), x10^-6</td>
<td>9.0</td>
<td>10.6</td>
<td>4.3</td>
<td>3.2</td>
</tr>
<tr>
<td>Specific Heat J.kg^-1.K^-1</td>
<td>1040</td>
<td>543</td>
<td>1040</td>
<td>710</td>
</tr>
<tr>
<td>Thermal conductivity W.m^-1.K^-1</td>
<td>8.3</td>
<td>2.0</td>
<td>83.6</td>
<td>25</td>
</tr>
<tr>
<td>Thermal shock resistance (K)</td>
<td>200</td>
<td>~500</td>
<td>300-400</td>
<td>500-700</td>
</tr>
</tbody>
</table>
Figure 1.1 Classification of ceramic composites based on the types of reinforcements
A composite alumina exhibits high toughness on reinforcement with zirconia, mullite, SiC particulates, fibres, platelets and whiskers. Zirconia toughened alumina has been initially studied as a cutting tool material (Burden 1982 and Wang and Stevens 1990) and in recent years, it has received further attention because of its superplastic behaviour (Maehara and Langdon 1990). The zirconia stabilized with Y$_2$O$_3$, MgO, SrO$_2$ and CeO$_2$ additives is used for making the zirconia toughened Al$_2$O$_3$ composites (ZTA). Zirconia with respect to the amount of its monoclinic and tetragonal crystalline phases, the sintered composites have improved strength and toughness. Table 1.3 presents the toughness and strength improvements of alumina–zirconia composites that are developed and reported in the literatures. A high creep resistance at relatively low strain rates and high working temperatures have also been found for alumina / zirconia laminated composites (Chen and Xue 1990).

Mullite matrix ceramic composites are well-recognized high temperature structural materials because of their excellent creep properties. However, mullite has comparatively poor strength and therefore zirconia, alumina and SiC are used as second phase reinforcing agents. The addition of zirconia into mullite matrix retard grain growth and promote densification and results in high-grade mullite composites (Moya and Osendi 1984). The mullite-zirconia composite fabricated by iso-static pressing followed by sintering showed the flexural strength of 400 MPa and toughness of 4.5 MPam$^{1/2}$. The studies conducted on mullite-alumina particulate composites also showed a very marked effect on the microstructures. The composites made of 15 vol. % mullite showed fine-grained alumina composites with grain size less than 2 μm (Basil Marple and David Green 1989 and Stuart Blackburn and Lawson 1992).

Silicon carbide is an efficient reinforcement phase for many oxide matrix structural ceramics and is studied extensively with alumina, mullite and silicon nitride matrices. The development of ceramic heat exchangers demands for silicon carbide reinforced oxide composites. Such ceramics have high temperature stability, corrosion and erosion resistance and wear properties in addition to the high strength and
toughness. The high fracture toughness in alumina composites is believed to be due to a strong residual stress in the interface between Al₂O₃ and SiC, arising from the thermal expansion mismatch of the alumina and SiC phases. Although, fibre and platelets reinforced composites have showed excellent performance, the problems associated in uni-directional fibre alignment, fibre degradation, large size variation and distribution of the platelets, the whisker and particulate composites have been now preferred. Table 1.4 shows the results on the properties of alumina - SiC reported in the literature.

Table 1.3 Properties of alumina-zirconia structural ceramic composites (Rice 1990)

<table>
<thead>
<tr>
<th>Composites Type</th>
<th>Fabrication Conditions</th>
<th>Toughness, $K_{IC}$ (MPam$^{1/2}$)</th>
<th>Strength (MPa)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina / ZrO₂ 2-20 vol. %</td>
<td>Hot pressed at 1400-1500°C/30 min</td>
<td>10</td>
<td>&lt;550</td>
<td>Claussen et al (1977)</td>
</tr>
<tr>
<td>Alumina -30 vol. % ZrO₂</td>
<td>Colloidal filtration 1600°C/2 h</td>
<td>-</td>
<td>900</td>
<td>Aksay et al (1983)</td>
</tr>
<tr>
<td>Alumina - 2 mol. %Y₂O₃ stabilized ZrO₂</td>
<td>Dry pressing sintered &lt;1450°C and hot iso-static pressing at 1500°C at 100 MPa</td>
<td>-</td>
<td>2200</td>
<td>Tsukuma et al (1985)</td>
</tr>
<tr>
<td>Alumina -30 vol. % ZrO₂</td>
<td>Slip casting 1600°C</td>
<td>-</td>
<td>850</td>
<td>Wilfinger and Cannon (1986)</td>
</tr>
<tr>
<td>Alumina / ZrO₂ (0-7.5 mol. % Y₂O₃ added as nitrates)</td>
<td>Precipitation and dry pressing</td>
<td>8</td>
<td>1100</td>
<td>Lange (1982)</td>
</tr>
</tbody>
</table>
Table 1.4 Properties of SiC reinforced structural Ceramic Composites (Rice 1990)

<table>
<thead>
<tr>
<th>Composites Type</th>
<th>Fabrication Methods and Conditions</th>
<th>Toughness $K_{IC}$ (MPa m$^{1/2}$)</th>
<th>Strength (MPa)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3 + 30$ vol. % SiC whiskers</td>
<td>Hot pressing, 1850-1900°C</td>
<td>9</td>
<td>800</td>
<td>Becher and Wei (1984)</td>
</tr>
<tr>
<td>Mullite+20 vol. % SiC whiskers</td>
<td>Hot pressing, 1600°C</td>
<td>4.6</td>
<td>440</td>
<td>Wei and Becher (1985)</td>
</tr>
<tr>
<td>$\text{ZrO}_2 + 30$ vol. % SiC whiskers</td>
<td>Hot pressing, 1450°C</td>
<td>1200</td>
<td></td>
<td>Claussen et al (1986)</td>
</tr>
<tr>
<td>$\text{Si}_3\text{N}_4 + 30$ vol. % SiC whiskers</td>
<td>Hot pressing, 1750°C</td>
<td>7</td>
<td>700</td>
<td>Shalek et al (1986)</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3 + 10$ vol. % SiC with MgO and $\text{Y}_2\text{O}_3$ additives</td>
<td>Iso static pressing and sintering 1700-1800°C</td>
<td>7</td>
<td>330</td>
<td>Tiegs and Becher (1987)</td>
</tr>
</tbody>
</table>

Alumina matrix composites consisting of metallic particulates and fibres (inter-metallic, interpenetrated continuous/semi-continuous, e.g. Al/Al$_2$O$_3$, Ni/Al$_2$O$_3$ etc.) have also been receiving much attention in recent years because of their functional properties (Tohru Sekino et al 1996).

1.2.3 Micro / Nano Structural Ceramic Composites

New generation composites consisting of ‘micro-micro’ and ‘micro-nano’ grains in the sintered ceramics have received much attention and are highly preferred for structural and electronic applications. In such composites, micron sized ceramic particles are covered with a thin layer of nano scale second phase additive and subjected to usual processing. For example, when alumina particles are covered with a thin layer of silica, mullite inter-phase during sintering results and one can get alumina-mullite composites (Sacks et al 1986). In such composites, uniform
must therefore be based on the probability of the existence of a given flaw distribution in the parts. This is a very different design approach to the traditional approach used for metal parts and because of this, designers need to adapt their design strategies to ceramics.

- **Cost**: Ceramic parts are expensive because of the high purity starting materials and the carefully controlled processing steps involved.

### 1.4 CERAMIC FABRICATION TECHNIQUES

Figure 1.2 shows a general process flow sheet and the unit operations involved in the fabrication of ceramic parts. Typically, the fabrication is carried out in two stages. First the ceramic powders are formed into green parts and in second stage the green parts are subjected to high temperatures, where the powder particles fuse together and produce a strong, dense ceramic part (Reed 1995). Green parts are porous bodies consisting of tightly packed ceramic powder particles.

For advanced ceramics the starting ceramic powders are highly pure with particle sizes in the range of one micron or less. A very small particle size is preferred because the mechanical properties of ceramics improve with decreasing grain size. Finer powders also sinter faster at lower temperatures (Wolfgang Sigmund 2000). Wide ranges of forming processes are in practice. Table 1.5 shows the major ceramic fabrication techniques. However, an efficient forming technique should have the following characteristics.

- Maximum packing density (Green density >55%TD)
- Absolutely no cracking and warping during drying and sintering
- Near net-shape products
- Minimum binder and organic processing additives requirements
- Densification at lower sintering temperatures
- High degree of microstructural uniformity
- Increased production rate and cost efficient
Figure 1.2 Ceramic fabrication - Process flow sheet

Table 1.5 Ceramic fabrication techniques

<table>
<thead>
<tr>
<th>Dry processing</th>
<th>Suspension processing</th>
<th>Special processing</th>
<th>Plastic forming</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uni-axial pressing</td>
<td>Slip casting</td>
<td>Tape casting</td>
<td>Extrusion</td>
</tr>
<tr>
<td>Isostatic pressing</td>
<td>Drain casting</td>
<td>Doctor blade</td>
<td>Roll forming</td>
</tr>
<tr>
<td>Hot pressing</td>
<td>Pressure casting</td>
<td>Solid free form fabrication</td>
<td>Injection molding</td>
</tr>
<tr>
<td>Hot isostatic pressing</td>
<td>Centrifugal casting</td>
<td>Sol gel</td>
<td>Compression molding</td>
</tr>
<tr>
<td>Dynamic consolidation</td>
<td>Vacuum casting</td>
<td>Electrophoretic casting</td>
<td>-</td>
</tr>
<tr>
<td>Self propagating high temperature synthesis</td>
<td>Freeze casting</td>
<td>Thermally reversible casting</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Gel casting</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Gel casting | - | - |
The ceramic forming processes that are reported in the literature are briefly described in the following sections. The principle and limitations of the various processing techniques within the scope of this thesis have been presented.

1.4.1 Pressing Techniques

In pressing techniques, the compaction of ceramic powders under application of pressure produces the green ceramics. A small amount of binder is added to the powder to hold the particles together so that the green body maintains its shape after removal of the pressure. In dry pressing, ceramic powders are compacted inside the dies by applying pressure in a uni-axial direction. Geometries are usually limited to prismatic shapes. Die wall friction and geometrical factors may result in different compaction stresses being exerted on different areas of the powder, resulting in non-uniform densities (Bruch 1967). These density variations can cause problems during sintering. Dry pressing offers the key advantages that ceramic parts can be made quickly to good dimensional tolerances in an automated process that involves no post forming drying step. However, it has limitation in the product shape and size, and required heavy metallic dies. The introduction of metallic impurities due to the wear of metal parts, variation in pressure gradients during compaction has also been observed in dry pressing and reported (Rahaman 1995). The powder is often fed in the form of micro granules, for the easy flow and uniform filling of the die cavity. The variation of bulk density of the powder granules results in localized compaction and may produce lamination (Walker and Reed 1999).

Cold isostatic pressing (CIP) is an improved dry pressing technique where more uniform compaction is achieved (Papen 1968). In this process the powder is placed inside a flexible mold that is sealed and placed inside a pressure chamber. Hydrostatic pressure is applied to the mold using a fluid. Advantage of this process is that it ensures uniform green densities and product diversity. The main disadvantage is poor shape and dimensional control because it is difficult to precisely control the flexible mold deformation during pressing.
Powder pressing is an economical process for producing relatively simple shapes in large quantities. Examples of parts made by pressing include spark plug insulators and grinding wheels.

1.4.2 Hot Pressing and Hot Iso-Static Pressing

Hot pressing (HP) and hot isostatic pressing (HIP) are mechanically similar to simple dry pressing and cold iso-static pressing except that these processes are performed at high temperatures. In both these cases, under the simultaneous application of pressure and heat to a powder system compaction and sintering take to form a dense ceramic part (Takao Fujikawa 1988). The application of pressure at the consolidation temperature accelerates densification kinetics by increasing the contact stress in a powder compact, finally densification takes place by the rearrangement of the particles or by stress – aided diffusion. The pressure increases the sintering rate allowing the material to be sintered at a lower temperature (Notis et al 1975). Lower temperature sintering can reduce the grain growth and this tends to produce stronger parts. Hot pressing is mostly performed at pressures between 20 to 70 MPa at temperatures 1300 to 1700°C and the commonly used die materials are graphite, refractory metals, super alloys, Al₂O₃ and SiC. Alumina hot pressing requires temperature less than 1400°C. Hot pressing of well sintered alumina with fine-grained microstructure can be achieved at 1300°C / 30 min at 20 MPa.

Similar to the conventional uni-axial pressing process, hot pressing also has product limitations and could be applied only to simple shapes like disks, rods and bars. The problem associated with the removal of sintered parts also restricts the success of hot pressing. The loosely packed green compact during hot pressing, due to the poor thermal conductivity of the regions in the vicinity of the dies may heat and consolidate faster, compared to the interior and ultimately cause microstructural variations. Hot iso static pressing overcomes the limitations of hot pressing and in this method the pressure is applied isostatically by an autoclave charged with inert gases (Janeway 1992). Oxygen is used for oxide ceramics and nitrogen to prevent
decomposition of non oxides at high temperatures. In HIP technique, temperatures up to 3000°C and pressure up to 300 MPa can be attained. This method is found to be well suited for producing whisker toughened ceramics, because in these the multi directional orientation of whiskers is possible, resulting in uniform microstructures and isotropic properties.

Hot pressing and hot iso-static pressing are very expensive processes, but produce the best mechanical properties and hence adopted for making high performance applications, such as engine components (Kennard 1986).

1.4.3 Dynamic Consolidation

Dynamic consolidation processes use energetic materials, i.e. explosives or other energy sources, to consolidate powders at high velocities. A high-pressure compaction setup usually made up of mild steel or copper is filled with ceramic powders and surrounded by an explosive. Detonation of the explosive generates shockwaves that travels downward and thereby rearranging the powder particles to denser packing and brings them into close contact and at high pressures the surface bonding occurs and finally produces dense compacts (Bengisu and Inal 1994). The technique is still at an experimental level. The defects such as micro/ macro cracks, stress development during compression and decompression stages, and fragmental density are being noticed. While the higher shock stress causes increased defects lower shock stress generally results in poor densification (Adair et al 1984).

1.4.4 Reaction Bonding

In reaction bonding or reaction sintering process, a solid pre-form of a desired shape is reacted with a liquid phase. Reaction bonded SiC (RBSC) is a classical example of this method and it is produced by infiltrating SiC-C bodies with liquid silicon near the melting temperature of silicon (1410°C) which is very low compared to hot pressing temperature (usually 1800°C). This is also called as ‘reactive
liquid phase sintering'. The development of alumina-aluminium, alumina-SiC and alumina-TiN/TiC composites are some of the successful ceramic composites processed by this technique (Washburn and Coblenz 1988 and Pivkina et al 1996).

1.4.5 Plasma Sintering

Plasma sintering is a process that uses high-energy plasma produced by microwaves, RF induction, or hollow cathode discharge (HCD). One of the remarkable advantages of this method is a shorter processing time. It has been reported that, Al$_2$O$_3$-10 vol% ZrO$_2$ composites can be sintered to 97% TD at 1300°C by the HCD plasma sintering in 5 minutes, and similar densities were obtained by conventional sintering in air at 1700°C in 20 minutes. This method is applied to many ceramics including Al$_2$O$_3$, HfO$_2$, UO$_2$, ZrO$_2$ and Y-PSZ materials because of rapid sintering. In all the cases uniform and fine-grained microstructures with better mechanical properties were achieved (Kim and Johnson 1985 and Upadya 1988).

1.4.6 Self Propagating High Temperature Synthesis

A ceramic solid-solid exothermic precursor mixture (e.g Ti+C, Zr+2B) is ignited from one end by a heat source (e.g laser beam, resistive wire etc). Once part of the mixture reacts, combustion wave forms and proceeds through the whole mixture, initiating the solid-state reactions between the reactants. The wave motion may be planar, oscillatory, or spiral, depending on the chemical system. The most important advantages of this process are energy savings associated with self sustaining reactions, simplicity, purity provided by volatilization of most impurities at very high temperature. It is also possible for simultaneous synthesis and densification of the products. Problems associated with this method are the presence of a liquid phase and violent ejection of gases that can break the die (Munir 1988 and Rice and Mcdonough 1985).
Although the dry forming processes are simple, they are only partly successful. The powder agglomeration and impurities that are possibly present in the raw materials are not being eliminated in the initial stage itself. The microstructural heterogeneities arise out of the agglomerated particles and result in defective final products.

Viscous processing is considered as an alternate approach because it offers a highly uniform particle packing and defect free green products. In the following sections brief description of the viscous processing methods that are reported in the literatures is presented.

1.5 VISCOUS PROCESSING

Viscous processing can be broadly classified into two major groups with respect to the solids loading of the systems. One is the ‘colloidal processing’, in which a stable colloidal suspension containing 50 vol.% solids loading is required and the product formation is achieved by casting. The other is ‘plastic forming’ where more than 80 vol.% solids loading are necessary and the shaping is achieved by means of mechanical shear.

1.5.1 Colloidal Methods

A colloid is a suspension in which the particle size in the dispersed phase is below 100 nm. In a typical colloid, gravitational force is negligible and short-range forces, such as van der Waals attraction and surface charges, dominate the interactions. The inertia of the dispersed phase is small enough that it exhibits Brownian motion, a random walk driven by momentum imparted by collisions with molecules of the suspending medium. Compared to powder consolidation in the dry or semi dry state, colloidal methods can lead to better packing uniformity in the green body, which in turn leads to better microstructure control during sintering (Aksay 1984).
Colloidal processing finds advantages like production of simple to complex ceramic shapes, porous to dense body, high green density and strength of the unfired component, low sintering temperatures, tailored microstructures and simple operating procedures (Lange 1989 and Wolfgang Sigmund 2000).

The following sections describe the major colloidal techniques, their principle and limitations.

1.5.2 Slip Casting

A ‘slip’ is a suspension of colloidal powders prepared in an immiscible liquid generally water. In slip casting a slip is cast into a porous mould, usually made of plaster (Gypsum). Capillary suction draws the liquid into the mould and leaves a layer of particles deposited against the walls of the mould. Hollow objects can be made by allowing a certain layer thickness to form before draining the rest of the slip from the mould. Solid objects are made by allowing the whole volume to solidify (Cowan 1976). Slip casting is an economical process. Crucibles and chinaware are the common objects fabricated by this method. The advantages of this method are affordability, smooth surface and increased production rate. Since water is the commonly used liquid phase, ceramics such as MgO and CaO could not be used because they quickly hydrate in water. Similarly Si₃N₄ and AlN react with water and liberate ammonia. Non-aqueous solvents such as alcohols, methyl ethyl ketone, trichloroethylene are used for such systems. The capillary force is a driving force for assembling the particles in a mould. Two important practical problems usually encountered in slip casting are, preferential settling and complex interacting parameters. The interacting factors such as solid fractions, its size and distribution, slip pH and viscosity, mold character, time, temperature and drying rate should be carefully controlled for achieving the products reproducibility. The green body with two distinct regions, a high concentration of smaller particles near the mould surface and relatively large particles in the upper region is also reported.
(Schilling and Aksay 1991). The problems in traditional slip casting are slowly removed and modern slip casting techniques are evolved.

1.5.3 Pressure Casting

This process is similar to pressure filtration. Here, the slip is pressed into a porous mould. Due to good strength and wear resistant, polymeric moulds are acts as a filter. Complex shapes can be formed by pressure casting with high production rates than slip casting (Grazzini and Wilkinson 1992 and Lyckfeldt et al 1994). Highly stabilized slips with fine particles pose an important risk of filling up the very large pores of polymeric molds during pressure casting. Therefore, slip properties should be optimized by suitable size fraction of the particles and degree of stability. The slip that has pseudoplastic rheology is found suitable for pressure casting. The earlier studies indicate the formation of cracks due to a large elastic strain during release of pressures. However, increase in green toughness by adding small amounts of polymeric additives, up to 2 wt.%, solve the problems of forming cracks. This process was successfully applied to develop Al₂O₃ and Al₂O₃ - SiC composites (Blanchard 1988).

1.5.4 Electrophoretic Casting

The electrophoresis phenomenon is utilized for producing ceramic parts with limited thickness. Electrophoresis is simply the motion of solid particles in a suspension electrically charged by an applied electric field (Heavens 1990). The principle is different from electroplating, where the anions and cations move, whereas in electrophoresis particles move as a whole. Two important applications are continuous clay strip forming and production of β-alumina tubes for the sodium and sulphur battery. Green forming of alumina radoms, electronic thin and thick film coatings, and corrosion - wear - heat resistant coatings is also achieved by this method. The main disadvantages are gas evolution at electrodes at high field strengths and Joule heating of the suspension due to high current densities. The advantages are short
forming times, less than 5 minutes, excellent dimensional control of electrophoretically cast articles, and a fine distribution of micro pores that makes sintering easier (Freidrich Harbach and Nienburg 1988).

1.5.5 Tape Casting

Tape casting is a proven technique for thin ceramic plates and sheets. The process-involved ceramic slurry based on powders, solvents, dispersants, binders and plasticizers. The degassed, well-dispersed slurry is fed onto a moving carrier and is flattened by thin blade. After a sheet structure is formed, the solvent is evaporated and dry tape strong enough to be cut is obtained and fired (Rodrigo Moreno 1992a and b). The technique is highly useful to produce multilayer composites, and functionally gradient materials for special applications (Young 1986). Composite materials with specific orientation of whiskers, platelets are reported by this technique (Plucknett et al 1994). Since the high forming pressures do not need in tape casting, full de-agglomeration is essential to obtain defect free product. Recently, sol gel assisted tape casting in which nanometer scale powder slurry is used for forming a thin sheet is reported (Junhui Xiang et al 2002).

1.5.6 Centrifugal Casting

There are two approaches reported for centrifugal casting. In the first method, a hollow cylindrical plaster mold is rotated about its axis with the slip in the interior. This approach results in tubular and also axis-symmetrical green shapes. In the second approach, a mold is placed at the bottom of a centrifugal bucket, and while rotation it produces the centrifugal action and in the action direction of mold leaving the object (Steinlage et al 1996). Centrifugal casting has the advantage of much shorter casting times compared to slip casting, adaptability to both small and large complex shapes and reduced the risk of stress gradients in the green compact. One draw back of this process is the segregation due to differential settling rates of suspension constituents by density and size (Huisman et al 1995).
1.5.7 Vacuum and Freeze Casting

The driving force for suction in permeable mold can be increased up to five times by applying reverse pressure, i.e. vacuum created around the mold. This can increase the casting rate and uniformity (Haunton et al 1990).

Freeze casting a recently reported novel method, employs an impermeable mold filled with slurry. After freezing the slip at suitable temperature, liquid is removed by freeze-drying. This method allows casting thick slips and faster rate of freezing is required to prevent settling of the particles.

1.6 SPECIAL FORMING TECHNIQUES

1.6.1 Solid Free Form Fabrication of Ceramics

The continuous efforts on improvement of the existing ceramic fabrication techniques led to few innovative processing techniques, and gaining more attention because of their accurate control over intricate designs. A new class of computer controlled fabrication method referred to as “solid free form fabrication (SFF)”, has been developed and is being transferred gradually to the industries (Klosterman et al 1988 and Halloran 1999). It is a tool-less manufacturing method in which functional components are produced directly from a computer model. The most popular SFF process that is studied by many researchers is three-dimensional printing (3DP™) (Griffith and Halloran 1996). In this process, dry powders are spread in a thin layer followed by a selective printing of binder to bond powders is the working principle. The unbound powder is removed to reveal a three dimensional green body after some repeated sequential operations. 3DP is being used to produce porous ceramic hot gas filters, investment casting shells/cores, rapid metal tooling and drug delivery devices. The stereolithography also has similar principle and belong to this category of processing techniques (Cawley et al 1996).
1.6.2 Gel Casting

Gel casting is a relatively new process for the fabrication of ceramic parts originally developed at Oak Ridge National Laboratory USA (Omatete et al 1991). A slurry is made consisting primarily of ceramic powder, a monomer and a solvent. The slurry is cast into a mold and the monomer is polymerized to form a green part in which the ceramic particles are embedded in the polymer network. The solvent occupies the pore spaces in the green part. Advantages of gel casting include the relatively low fraction of binder, which makes burnout and sintering faster and easier. The good mechanical strength of the green parts allows the green part to be handled without too much risk of damage and makes them well suited to green machining (Prabhakaran et al 2000a and b and Nunn and Kirby 1996). Gel cast parts also exhibit isotropic sintering shrinkage, which makes it easier to achieve the desired sintered shape. Gel casting has been reported to produce alumina, silicon nitride, SiAlON, silicon carbide, zirconia and fused silica ceramic parts (Young et al 1991).

Temperature induced gelation (TIG) and thermo reversible gelation are recently proposed in gel-casting techniques (John Montgomery et al 2002). In TIG, the principle is the collapse of an adsorbed polymer layer on cooling to eliminate steric repulsion between ceramic particles. TRG involves a rapid, reversible, cross-linking process to form a polymer network rather than a monomer reaction, as in the case of traditional gel casting. The reversible polymer gel is a tri-block copolymer whose mid block is selectively solvated by an alcohol solvent. Below 60°C, the tri-block co-polymer end-blocks dissociate, creating a freely flowing liquid. The thermo reversible gel can be filled with high loadings of ceramic powder and still maintain its thermo reversibility. After casting, the solid can be reheated to form a liquid and then recast, thus minimizing ceramic and polymer use.
1.6.3 **Sol-gel Processing**

Sol gel processing has been one of the well recognized techniques for synthesizing nano scale ceramic powders and structured surfaces (Klein 1988 and Carl Turner 1991). The advantages such as chemical homogeneity, well defined particle size, increased surface area and low sintering temperatures have been realized over a period of time and therefore many attempts have been made to produce range of (porous to dense) ceramics and ceramic matrix composites (Burggraaf et al 1991). In sol gel technique, the chemical precursors (mostly inorganic metal salts, metal alkoxide and polymers) are hydrolyzed under controlled chemical conditions and converted to form a gel either by aging or evaporation. The gel is further peptized to form a stable colloidal sol. Figure 1.3 shows different processing steps involved in sol gel processing and its products diversification. Hench and Ulrich (1986) has reviewed the applications of sol gel process, advantages and disadvantages. The technique has been found very successful for the fabrication of nano-structured materials rather than three-dimensional objects. Some of the dense ceramics that are developed through the sol gel method are the nuclear fuel pellets, cubic zirconia and piezo electric ceramic components and oxide glasses. The sol gel process is presently used for making aerogels (Alain Pierre and Pajonk 2002), organic-inorganic hybrid objects (Barry Arkles 2001), ceramic micro spheres (Chatterjee et al 1998) and ceramic nano composites (Warrier and Anilkumar 2001). Shingo Katayama and his co-workers (2002) have reported the formation of flexible hybrid ceramic zirconia sheets using sol gel process. The common problems in sol gel process are the cracking and large volume of shrinkage during drying. However, the addition of drying control chemical additives minimizes the drying defects. The sol gel process is also one of the efficient techniques for producing electronano ceramics, for using in the field of microelectronics (Marie Paule 2001).
Figure 1.3  Sol gel process flow sheet and products diversification (Klein 1988)
1.7 PLASTIC FORMING TECHNIQUES

Injection moulding and extrusion are the two conventional plastic forming methods followed for producing ceramic objects. The ceramic powder phase is mixed with suitable binders and processing aids to behave as a plastic mass with suitable flow properties, is allowed to either fill a cavity, which is mostly the shape of the required product or through a die, is the fundamental principle in plastic forming. The most attractive features of these techniques are ability to form a product that has varying dimensions like thin and thick sections, extended objects and near net-shape production possibilities.

1.7.1 Ceramic Injection Moulding

Injection moulding process was initially used for making the spark plugs (Mangels 1982) and now it is considered as a potential method for producing turbine rotor blades which has a complex design, wire drawing dies, combustion pre-chamber inserts, and nozzles (Mutsudy and Ford 1982 and Edirisinghe 1990). In this process, three major steps are involved. In blending and compounding, the ceramic powder is mixed with suitable binders and additives, and rheology is adjusted to yield an injectable blend. In molding, the mix is pressed by ram or plunger with hydraulic, pneumatic, or screw mechanisms, into a cold die cavity with the desired net shape. The final step is the removal of binder phase from the green shape. The factors that have to be controlled for an un-defected ceramic objects are, injection speed, pressure, barrel and mould temperature and hold time (Edirisinghe and Evans 1986a, 1986b). The factors that are related to plastic mass preparation are the solids loading, binder quantity, and particle shape and size distribution. Injection moulding is used for various ceramic systems like alumina, zirconia, alumina-SiC and SiC-Si$_3$N$_4$ composites (Storm et al 1982 and Quackenbush et al 1982). The disadvantages of this technique are, inability to mold large components without macroscopic internal defects, and the high volume fraction of binders that need to be burned before sintering.
1.7.2 Ceramic Extrusion

Extrusion is the process of forcing the plastic mass through an orifice to produce green parts with the desired cross section. The main difference from injection moulding is that there is no cavity in extrusion, which allows forming parts with unlimited length (Blackburn 1992). Refractory tubes, honeycomb supports for catalytic converters (Keizer and Burggraaf 1988 and Graczyk et al 1993), ceramic heat exchanger tubes, transparent Al$_2$O$_3$ tubes for sodium lamps (Pett et al 1982), small electronic and magnetic parts, as well as graphite electrodes are the current applications of extrusion technique. The various processing steps that are involved in an extrusion process are, blending, pugging, extrusion, cutting and drying. The blending process is similar to injection moulding. In pugging the plastic mix is placed in an evacuated cylinder and kneaded to remove the entrapped air. In extrusion step, the paste is ejected through a die by the application of pressure or by the screw movement for the desired product profile.

During extrusion, differential shear flow under compression occurs as the material flows through the barrel or the die. The flow mechanisms of ceramic pastes are studied by many researchers and reported that the flow is governed by plastic deformation at the die entry and plug flow along the die land where no cross sectional change occurs (Benbow et al 1987 and Huan-ting Wang et al 1998). The flow behaviour of a perfect plastic body is expressed by the Bingham relation and is stated in Equation 1.1.

$$\tau - \tau_y = \eta_p \dot{\gamma}$$  \hspace{1cm} (1.1)

where $\tau$ is the applied shear stress, $\tau_y$ is the yield stress to initiate flow, $\dot{\gamma}$ is shear rate and $\eta_p$ is the plastic viscosity. The flow analysis is one of the most important aspects in any plastic forming method (Parks and Hill 1959).
1.7.3 Rheology

Rheology is the study on flow and deformation patterns of ceramic mass and it is essential to determine the plastic character and workability of the ceramic mass. The rheological factors are the development of torque, viscosity and the yield stress offered by the ceramic paste. In plastic forming techniques, the rheology of the ceramic paste is characterized by the capillary rheometer (Carter 2001). The plastic character or ‘plasticity’ of the ceramic paste is defined as the ability of the ceramic body to permanently change its shape in a continuous manner without change in its volume. A good plastic mix does not form structural discontinuity and rupture. The plasticity of a ceramic mass is designed in such a way that, the extruded product will have a defect free microstructure, and does not leave excessive particle orientations and draining of liquid. The deformability of the ceramic mass is stable and must elastically retain its new shape. It must have a yield stress capable of supporting its weight and the forces introduced during product handling (John Wight Jr and Reed 2001). The term ‘workability or working range’ is defined with respect to the plastic behaviour of the mass. When a ceramic mass responds very sensitively and changes even for a low plastic strain, it can be said to have a good workability. When the body exhibits a satisfactory workability, over a wide range of liquid phase, it will have a larger working range. High plasticity is indicative of a greater working range (Schilling et al 1999a). The ceramic mass with respect to their plastic character exhibits different shear flow behaviour (Terpstra et al 1995 and Goodwin 1976) and typical of flow curves are presented in Figure 1.4.

The Newtonian type flow is present once the shear stress is directly proportional to the shear rate, giving a straight line passing through the origin. By definition, the slope of this line is the shear viscosity of the mass. When the shear rate increases, a progressively smaller increase in shear stress is developed to maintain the shear rate. It is characterized as ‘shear thinning or pseudoplastic’ behaviour. Ceramic pastes that have irregularly shaped filler particles, or additives that may have sticking nature at high shear rates, form a ‘dilatant’ or ‘shear thickening’ behaviour. In non
Newtonian flow, the logarithmic relationship of shear stress against shear rate is straight line with characteristic slope and intercept. For such a non-Newtonian material, viscosity is not constant, but is a function of shear rate. When a ceramic mass does not flow until a certain yield point is reached, after that a flow occurred linearly is classified as ‘Bingham’ bodies. If the same has non-linear flow, it is said to have Herschel-Bulkley fluids. The mathematical relationship between shear stress and applied shear rate is given in Table 1.6 for different flow behaviour (Mewis and spaull 1976).

![Figure 1.4 Typical flow curves for ceramic paste](image)

**Table 1.6** Relationship of shear stress with applied shear rate for different paste flow curves (Terpstra et al 1995)

<table>
<thead>
<tr>
<th>Types of Flow</th>
<th>Mathematical relationship</th>
<th>Parameter Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Newtonian</td>
<td>$\tau = \eta \left(\frac{dv}{dr}\right)$</td>
<td>$\tau$ = Shear stress</td>
</tr>
<tr>
<td></td>
<td>$\eta$= Viscosity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$v$ = Velocity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$r$ = Distance from the radial wall</td>
<td></td>
</tr>
<tr>
<td>Pseudoplastic</td>
<td>$\tau = K(\dot{\gamma})^n$</td>
<td>$K$ = Consistency index</td>
</tr>
<tr>
<td></td>
<td>When $n &lt; 1^*$</td>
<td>$\dot{\gamma}$ = Shear rate</td>
</tr>
<tr>
<td>Bingham plastic</td>
<td>$\tau - \tau_y = \eta_p \dot{\gamma}$</td>
<td>$n$ = shear thinning constant</td>
</tr>
</tbody>
</table>

* when $n > 1$, the flow is dilatant
1.8 PROCESSING AIDS FOR CERAMIC FORMING

In both colloidal as well as plastic forming methods, use of processing aids and additives are essential without which a ceramic product is impossible to be manufactured. The addition of binders, solvents, lubricants, surfactants, and antifoaming agents, flocculating and coagulating agents are treated as processing aids. All processing aids play their own role and function in a unique manner. Even in the case of simple dry pressing, plasticizers are employed for making the powder granulation (Bast 1990 and Dale Niesz et al 2002). The binders are necessary to adhere ceramic particles to each other and impart appropriate elastic properties and green strength for handling or shaping. The binder phase is very critical and they not only assemble the particles but also have considerable influence in the final sintered microstructures. The maximum limit for using the binder phase in dry pressing is less than 2 wt% and in the case of plastic forming up to 20 wt% is used. In general, polymer is preferred as a binder. Polyvinyl alcohol (PVA) is widely employed. PVA has a tendency to stick to the mold and mostly used with a releasing agent. Polyvinyl butyral (PVB) is another type of binder, which gives medium strength compared to PVA. But PVB is soluble only in organic solvents, where as PVA is soluble in water (Hendry 1988).

The plastic forming methods generally require different types of binders. The thermal based polyethylene polymer was used earlier (Randall German and Hens 1991). However, due to a long binder burn out process, it was superseded by water-soluble binder systems, mostly based on cellulose ethers (Schuetz 1986). The binders can also serve as lubricants to impart high plasticity. The cellulose binders such as hydroxy propyl methylcellulose and hydroxy ethyl methylcellulose have a characteristic of thermal gelation (Nitis Sarkar and George Greninger 1983). Thermal gelation is primarily caused by hydrophobic reaction between molecules containing methoxyl substitution. At low temperatures, molecules are hydrated, and there are little polymer-polymer interactions except chain entanglement. At high temperatures,
molecules dehydrate and once it is sufficient, an infinite gel network forms, increasing the viscosity of the binder. Recent literatures indicate the use of various kinds of binders (Satapathy 2000). Examples are, starch, agar-agarose (Zhang et al 1994) and carbohydrates (Chen et al 1997). In general, the temperature required for removing the binders from the green product is at least 400°C.

The paraffin wax, stearates, stearic acid, oleic acid, polyglycols, talc and hexagonal boron nitride are commonly employed as lubricants. Silicon provides a water repellant coating and reduces the tendency for sticking. Lubricants facilitate movement under pressure and reduce die friction.

The dispersants are playing the role of preventing agglomeration, and keeping the powder dispersion in stable state, and it is one of the important ingredients for casting technique (Ortega et al 2002). Organic polyelectrolytes like sodium poly acrylate, ammonium polyacrylate, sodium and ammonium citrate are commonly used. Sodium carbonate, sodium silicate, sodium borate and tetrasodium phosphate are some of the inorganic polyelectrolytes used as dispersants (Sheppard 1991 and Robinson 1992). The surfactants are added if there is immiscibility between the solvent and the lubricants. Silicone is one of the surfactants, and it reduces the surface tension of the water and allows the oil to form an emulsion. The other additive are antifoaming agents and plasticizers.

Plasticizers are required to modify the visco-elastic properties of the binder layer on powder surface and impose formability on the system. Water is a common plasticizer for clay systems. The addition of plasticizer also modifies the viscosity of the liquid phase and increases the plastic strength and formability.

1.9 GREEN MACHINING

The mechanical machining is normally preferred for a green ceramic blank just after it is formed. The blank is machined to shape using milling, turning, drilling
or other machining processes. The blank might be simply a block from which the part will be cut, or it might be a shape produced by another forming process. For example, green machining may be used to drill holes in an extruded part. CNC machining is well employed for green machining. Since ceramic materials are very hard, abrasive tool life becomes very short, even if diamond-cutting tools are used.

1.10 SCOPE OF THE PRESENT WORK

There has been increased interest on different processing methods for the fabrication of ceramics and ceramic matrix composites using simple and efficient techniques. As discussed earlier, many processing techniques have been evolved over the years. However, each process has its own advantages and industrial limitations. The scope of the present thesis work is to use a nano particulate precursor gel as a reactive binder for the fabrication of alumina ceramics. The study is conducted on two major emerging fields such as extrusion and gel casting. There have been many binder systems proposed for ceramic processing but mostly they are based on polymers. Since the problems in polymer binders are well realized, there is a need at present to search for new matrix-friendly binder systems, for making more reliable ceramic components. The present investigation is oriented in this direction and an inorganic gel (Boehmite gel) is considered as binder for the fabrication of ceramic shapes. Since the wet processing routes have many advantages in green body microstructure, the combination of sol-gel assisted colloidal processing has been adopted. Although the processing factors related to ceramic extrusion have been systematically conducted on ceramic pastes involving polymeric binder systems, such studies have not been carried out systematically for boehmite incorporated ceramic slurries and pastes. Hence, the present work is designed for studying various processing parameters such as rheology, pressure and flow characteristics, fluidity, packing and green strength, machining characteristics, sintering, and associated microstructures on alumina-boehmite ceramic pastes and dispersions. In addition to
this, alumina and alumina base ceramic composite has been fabricated through paste extrusion and gel casting.

1.11 STATEMENT OF THE PRESENT PROBLEM

"To investigate the gel assisted ceramic fabrication processes for the development of advanced ceramic and ceramic matrix composites and evaluation of the composite properties"

The tasks involved are,

i. Colloidal processing of alumina and alumina matrix composites involving nano particulate boehmite sol as a dispersing medium.

ii. Gel assisted extrusion of alumina, alumina-aluminium titanate ceramics involving boehmite gel as a reactive binder.
   ➢ Preparation and characterization of alumina-boehmite pastes
   ➢ Fabrication of alumina shapes
   ➢ Sol gel synthesis of aluminium titanate
   ➢ Fabrication of alumina –aluminium titanate composites
   ➢ Properties evaluation, sintering and microstructural studies

iii. Colloidal processing of mullite-aluminium titanate ceramic nano composites
   ➢ Sol gel synthesis of mullite, aluminium titanate
   ➢ Characterisation and thermal behaviour of the nano composites
   ➢ Gel assisted extrusion of the composites
   ➢ Sintering and microstructural features
   ➢ Strength and creep properties of the nano composites

iv. Gel casting of alumina monoliths using boehmite gel binder

v. Development of alumina -silicon carbide nano composites

vi. Summary and suggestions for future work.