CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

The discovery of new materials results in dramatic change in the life style of mankind that has come a long way from using crude rocks and wood carved into various shapes. The tremendous technological developments dictate the importance and relevance of materials to the well being of mankind and decide his economic development. Among the existing materials which are broadly classified into three major groups, viz. metals, ceramics and polymers, ceramics may well be the probable choice because of its wide applications in as structural materials, electronic materials, functional materials, bio-compatible materials etc. Although ceramics have several excellent properties that make their use as structural materials, they are also known to be brittle, unreliable and do not yield before fracture. “Catastrophic” is the characteristic property of ceramics that has prevented their use in structural applications in the past. Research in structural ceramics thus is rapidly developing and the results of which have already penetrated into commercial markets and large scale industrial applications.

The key to the development of structural ceramics is to improve the reliability and toughness while retaining other desirable properties such as light weight, strength and hardness. The difficulty is overcome by synthesizing powders with optimum particle sizes of less than a micron to achieve consolidation of powders into desired shape and high density at lower
sintering temperature. To achieve the expected comminution, the grinding media used should have high density and high fracture toughness in addition to uniformity in shape and size to perform the effective fracture of particle. Fabrication of fine grinding media (minispheres) through novel processing route with elevated properties is thus the prime objective of this work. The present chapter discusses the various processing methods that are employed in ceramic processing, the characteristic behavior of zirconia and also the specifications of comminution and grinding media required for practical use.

1.2 CERAMIC PROCESSING METHODS

The increasing interest and high demand for advanced ceramics has led to substantial development in processing. Several powder preparation techniques are being used for both laboratory and large scale (industrial) production, though the preparation technique depends on the application of a particular material.

The powder processing techniques are generally classified as
1. Conventional techniques
2. Non-conventional techniques

The success of a preparation method depends largely on achieving and maintaining the necessary fine particle size during processing and controlling their chemical composition and microstructure. Quality of the starting powders and the powder characteristics like size, size distribution, shape and state of agglomeration and chemical and phase composition are also important.
Ceramic preparation can be divided into two categories: mechanical method and chemical method. Mechanical method is used to prepare powders of traditional ceramics from naturally occurring raw materials, while chemical method is generally used to prepare advanced ceramics from synthetic raw materials or naturally occurring raw materials that have undergone a considerable degree of chemical refinement. A summary of the common powder preparation method for ceramics is tabulated in Table 1.1.

1.2.1 Conventional Techniques

In conventional method, the required compositions of individual powders are mixed together into any one of the desired compound. The conventional ceramic processing involves four basic steps:

1. Powder manufacturing
2. Powder preparation
3. Consolidation to an engineering shape
4. Densification to obtain a microstructure with optimal properties.

Each step has the potential for introducing a detrimental heterogeneity which will either persist while processing further or will develop a new heterogeneity during densification and microstructural development (Lange 1989).

1.2.2 Non-conventional Techniques

Non-conventional method helps to prepare powders with the required submicron size and uniformity in microstructural properties.
The powders obtained by this technique

- are highly homogeneous
- have desired composition and purity
- possess desired polymorphic form
- have required chemical and physical structure of surfaces

### Table 1.1 Common powder preparation methods for ceramics

<table>
<thead>
<tr>
<th>Powder preparation method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mechanical Comminution</strong></td>
<td>Inexpensive wide applicability</td>
<td>Limited purity and homogeneity, large particles</td>
</tr>
<tr>
<td><strong>Mechanochemical synthesis</strong></td>
<td>Fine particle size, good for non-oxides, low temperature route</td>
<td>Limited purity and homogeneity</td>
</tr>
<tr>
<td><strong>Chemical</strong></td>
<td>Simple apparatus, inexpensive</td>
<td>Agglomerated powder, limited homogeneity</td>
</tr>
<tr>
<td><strong>Liquid solution</strong></td>
<td>High purity, small particles, composition control, chemical homogeneity</td>
<td>Expensive, poor for non-oxides, powder agglomeration usually a problem</td>
</tr>
<tr>
<td><strong>Non-aqueous liquid reaction</strong></td>
<td>High purity, small particles</td>
<td>Limited to non oxides</td>
</tr>
<tr>
<td><strong>Vapor phase reaction</strong></td>
<td>Inexpensive</td>
<td>Low purity, limited to non-oxides</td>
</tr>
<tr>
<td><strong>Gas-solid reaction</strong></td>
<td>High purity, small particles</td>
<td>Expensive, limited to non-oxides</td>
</tr>
</tbody>
</table>
Based on the various processing steps involved, the following are the classification of the non-conventional preparation routes (Richerson 1992)

- sol-gel method
- Precipitation technique
- Liquid mixing route
- Spray roasting and decomposition
- Freeze drying route
- Hot Kerosene drying technique
- Hydrothermal method
- Plasma route
- Laser method

Among the non-conventional methods, hydrothermal, coprecipitation, spray drying and sol-gel are the most popular techniques for the preparation of powder with desired properties. Although various processing techniques are available for the production of ceramic powders, the best one is the technique which adds up (results) with relatively soft agglomeration, open porosity, less heterogeneity, better phase purity and better control of structure.

1.2.2.1 Sol-Gel Method

The sol-gel processing has been investigated extensively as an alternate to conventional ceramic processing, because of the opportunity for atomic/molecular scale mixing, lower densification temperatures and ultimately improved properties. Sol-gel method is widely used to prepare highly interactive ceramic powders. The sol-gel process favours to room temperature solution route for preparing oxide and non-oxide materials.
The concept behind the sol-gel process is a combination of chemical reaction that turns a homogeneous solution of reactants into an infinite molecular weight polymer. The formed polymer is isotropic, homogeneous and uniform in structure. Sol may be defined as the dispersed colloidal particles in a liquid. According to Flory (1986), a gel is an elastic solid with low modulus of elasticity.

1.2.3 Comparison between Powder Compaction Method and Chemical Method

Non-conventional chemical method has many advantages over conventional powder compaction method. In chemical method, the milling procedure is not required, hence powder contamination is avoided. In spite of its operational simplicity, the chemical method involves a number of variables that should be controlled for processing reproducibility which can influence the microstructure and micro-structure-related properties of the sintered ceramic.

X-ray diffraction patterns for sintered specimens prepared from powder compaction and sol-gel method are compared in Figure 1.1. These figures are the results obtained by Muccillo (1999) with same concentration. Lattice parameters determined using Si as internal standard are also shown in Table 1.2. The calculated theoretical density (TD) value is 6.29 g/cm³. For specimens prepared with mixed powders, a maximum value of 92% TD has been obtained. Specimens prepared with sol-gel powders reaches 98% TD without using any comminution process or other special step during processing. This result is ascribed to the optimization of the synthesis parameters.
Table 1.2  Comparative analysis of processing techniques used for synthesis of zirconia

<table>
<thead>
<tr>
<th>Technique</th>
<th>Tetragonal phase fraction (%)</th>
<th>Lattice parameters (in nm)</th>
<th>Density (% TD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder compaction</td>
<td>100</td>
<td>0.513(0)</td>
<td>0.523(0)</td>
</tr>
<tr>
<td>Sol-gel</td>
<td>100</td>
<td>0.513(1)</td>
<td>0.525(8)</td>
</tr>
</tbody>
</table>

Figure 1.1. XRD patterns of sintered specimens prepared by: (a) powder compaction method (mixing of oxides) (b) chemical method (sol-gel technique) (Muccillo 1999)

For specimens prepared with sol-gel powders, relative low porosity and uniform grain size are the main microstructural features. The most important fact is that this synthesis technique is carried out in its simplest way, that is, without any further comminution or other special step. The main results show that this solution technique can be greatly improved whenever the influences of the processing variables are taken into account.
1.3 LIQUID PRECURSOR METHODS

Methods in which a solution of metal compounds is converted into a solid body are sometimes referred to as liquid precursor methods. A liquid precursor route that has attracted intense interest since the mid-1970s is the sol-gel process. Chemical compositions consisting of simple or complex oxides are produced by this route. Another route that has attracted a fair degree of interest in the past 20 years is the polymer pyrolysis, in which nonoxides (mainly Si$_3$N$_4$ and SiC) are produced by pyrolysis of suitable polymers.

1.3.1 Sol-Gel Processing

Sol-gel processes developed during the mid-1960s for nuclear fuel processing has in recent years, become attractive for the applications outside of the nuclear fuel industry and has been generally devoted to preparing for metallic oxides. The prime requirement of sol-gel process is that the oxide component should be capable of forming a concentrated colloidal sol of the metallic oxides or hydroxides and converting this sol (a solution of metal compounds or a suspension of very fine particles in a liquid) to a gel (semirigid mass). The shape and size of the final oxide product is determined at the gelation stage which is therefore crucial to the whole process.

A broad classification of the sol-gel process is given in Figure 1.2, which is based on the availability of starting material and characteristics of the sol and gel. The classification of the sol-gel process is based on the nature of formation of the sol and gel (Johnson 1985). The sol-gel method is a promising processing technique because of its inherent advantages such as controlled particle size, shape and distribution, desired composition, relatively
low-temperature sinterability, etc., and because of its recent advancement for industrial applications.

![Figure 1.2 Classification of sol-gel process (Johnson 1985)](image)

### 1.3.1.1 Polymerized Alkoxide Route

To prepare a single component oxide material using its corresponding alkoxide, initially the alkoxide is partially hydrolysed as given below:

\[
M(OR)_x + yH_2O \rightarrow M(OR)_{x-y} (OH)_y + yROH
\]  

(1.1)

Where, ‘R’ represents an alcoholic group and ‘M’ a cation. The partially hydrolyzed species are then allowed to form M-O-M linkage by a polymerization or condensation reaction. This type of continuous condensation leads to the formation of polymerized sol. Depending on the availability, cost and convenience the polymerized alkoxide method is further subdivided into ‘all alkoxide’ and ‘alkoxide with metal salts’.
1.3.1.2 Colloidal Sols

Sol-gels processed from colloidal sols best fit the common definition of a sol, a stable dispersion of colloidal particles in a liquid. The inter-particle surface forces force a three-dimensional network to form in the whole span of the sol, which finally forms a semi rigid mass called a gel. This type of gelation is known as physical gelation. The category of sol-gel processing can be further classified as (i) the colloidal sols formed by a precipitation peptization and (ii) Colloidal sols formed by dispersion of very fine particles.

1.3.1.3 Hydrolysis

The mechanism of hydrolysis of metal alkoxide is fairly complex and depends on the experimental conditions. The rate of hydrolysis of metal alkoxide depends on the characteristic of the metal and loses of the alkyl group. However, in the initial step, one water molecule interacts with the alkoxide and one molecule of alcohol is expelled. The alkoxide – water reacting in which the hydroxyl ion is attached to the metal atom is termed as hydrolysis.

\[
M \text{(OR)}_z + H_2O \rightarrow M\text{(OR)}_{z-1} \text{OH} + ROH
\]  

The amount of water and catalyst added to the system control the reaction critically and on completion of hydrolysis the metal alkoxide transforms into metal hydroxide.
1.3.1.4 **Effect of Catalyst**

The sol-gel transition depends on the catalyst used to promote the rate of hydrolysis. Acid catalysts such as HCl and HNO₃ promote the hydrolysis through electrophilic reaction. The rate of hydrolysis increases when the pH of the starting mixture decreases from 7. However, the condensation reaction has a local minimum at around pH equal to 2. Thus a sol prepared with acid catalyst requires very long gelling time and the resulting gel undergoes large shrinkage during drying.

1.3.1.5 **Sol-gel Transformation**

Transformation from the sol to gel state can be achieved in three different ways, namely,

1. Growth of polymeric molecules which cross-link randomly to form a three dimensional network.
2. Growth of individual particles, which grow together as they become larger.
3. Stabilization of colloids by surface changes due to the change of zeta potential and inter particle condensation process.

1.3.1.6 **Polycondensation**

The linking of smaller and partially hydrolysed molecules into larger molecules is termed as ‘condensation’ or ‘polycondensation’ where monomeric chains condense to form polymeric network.

\[
\text{M(OR)}_{Z-1} \text{OH} + \text{M(OR)}_Z \rightarrow (\text{RO})_{Z-1} \text{-M-O-M (OR)}_{Z-1} + \text{ROH} \\
\text{(Polymer)}
\]  

(1.3)
Polycondensation results in the formation of the semi-solid phase i.e., the gel that evidently contains water in structural cavities. The step proceeds with a sharp increase in the viscosity. The small amount of water or alcohol molecules held in the structure is eliminated when the sol is subjected to heat treatment. The condensation of gel will have a critical effect on the structural and phase transformation occurring during the heat treatment of gel and in turn, on the characteristics of the prepared products.

1.3.2 Advantages and Disadvantages of Sol-Gel Method

Although various liquid precursor routes are available for the preparation of fine ceramic powders, a sol-gel method is very advantageous. Some of the advantages of sol-gel method are:

- molecular or atomic level mixing and hence homogeneity
- extreme purity
- perfect stoichiometry and thus the desired composition
- selective doping
- narrow particle size and distribution
- fine spherical particles, which can hardly be produced by milling
- high surface area and hence high surface reactivity
- low processing temperature requirements

Though the sol-gel method has many advantages, it also has a number of disadvantages like, high cost of the starting materials and long processing times. There are some serious disadvantages like; very large shrinkages associated with the gelation process and drying of gels, presence of large concentrations of pores and undesirable residuals like hydroxyls and
organics. The greatest disadvantage of them all is the lack of scientific understanding of the many complexities involved in the process.

1.4 ZIRCONIA

The development of zirconia-based ceramic materials is of prime interest because of their superior properties such as toughness, oxidation, corrosion resistance and tolerance to severe environments, which enable numerous industrial applications. Zirconia based ceramics are well known for their excellent mechanical, electronic, thermal and optical properties and are successfully employed in several industrial and commercial fields.

The pioneering work of Garvie et al (1975) and Gupta (1978) and co-workers stimulated considerable attention; particularly after the discovery of ‘stress induced transformation toughening of zirconia’ that has stimulated intensive research on this particular material. By proper utilization of this property, the fracture toughness could be increased considerably. Typical properties of zirconia are listed in Table 1.3.

The high temperature cubic crystalline form, called 'cubic zirconia', is rare, if ever found in nature, but is synthesized in various colours for use as a gemstone. The cubic crystal structured variety is the best-known diamond simulant. This material is also used in the manufacture of subframes for the construction of dental restorations such as crowns and bridges which are then veneered with a conventional feldspathic porcelain. Zirconium dioxide can occur as a white powder and possess both acidic and basic properties. Zirconia is also an important dielectric material that is being investigated for potential applications as an insulator in transistors in future nanoelectronic devices.
<table>
<thead>
<tr>
<th>General Properties</th>
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<tbody>
<tr>
<td>Systematic name</td>
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<tr>
<td>Other names</td>
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<td>Molecular formula</td>
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<td>Appearance</td>
</tr>
<tr>
<td>CAS number</td>
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<tr>
<td>Density and phase</td>
</tr>
<tr>
<td>Solubility in water</td>
</tr>
<tr>
<td>Melting point</td>
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<tr>
<td>Poisson’s Ratio</td>
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<td>Refractive Index</td>
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<table>
<thead>
<tr>
<th>Thermodynamic / Mechanical data</th>
</tr>
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<tbody>
<tr>
<td>Standard enthalpy of formation ΔfH°solid</td>
</tr>
<tr>
<td>Standard molar entropy</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
</tr>
<tr>
<td>Specific Heat</td>
</tr>
<tr>
<td>Thermal Expansion Coefft.</td>
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<tr>
<td>Bend Strength</td>
</tr>
<tr>
<td>Hardness</td>
</tr>
<tr>
<td>Elastic Modulus</td>
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<td>Shear Modulus</td>
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<td>Compressive Strength</td>
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<tr>
<td>Flexural Strength</td>
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<tr>
<td>Fracture Toughness</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
</tr>
</tbody>
</table>

1.4.1 Nature of Pure Zirconia

Zirconium dioxide (ZrO₂), known as zirconia, is a white crystalline oxide of zirconium. It is the most naturally occurring form the rare mineral
baddeleyite with a monoclinic crystalline structure and is one of the most studied ceramic materials. Pure ZrO$_2$ is monoclinic (m) at low temperatures and transforms to tetragonal (t) at temperatures higher than 1443K. The m to t transformation is accompanied by a volume change of 4.6%; cracks are then formed throughout the material when cooled from the phase transition temperature.

High temperature X-ray investigation illustrates the behavior of pure zirconia (Burger et al 1997). As is demonstrated in Figure 1.3, the sample possesses the monoclinic phase up to a transition temperature 1175°C at which the phase transformation from monoclinic to tetragonal takes place. As is evident from the figure, further cooling results in the expected retransformation from tetragonal to monoclinic phase.

Figure 1.3  Phase transformation in pure zirconia (Burger et al 1997)
1.4.1.1 Polymorphs of Zirconia

Pure zirconia is a white powder with a melting point of 2710°C ±35°C and exists in three well defined polymorphs, namely,

- Cubic (c) above 2370°C
- Tetragonal (t) between 2370 and 1150°C
- Monoclinic (m) below 1150°C

Heuer and Lenz (1982) have shown that a high pressure orthorhombic form also exists. The schematic representation of the zirconia polymorphs is shown in Figures 1.4 (a, b and c). The monoclinic cell (Figure 1.4a) shows the four zirconia molecules per unit cell. Zirconia or zirconium dioxide is the most important and stable oxide of zirconium.

1.4.1.2 Crystalline Structure of Zirconia

Polymorphs of the pure zirconia can be easily distinguished by X-ray diffraction and the quantitative analysis of the amounts of the monoclinic phase has been done by Evans et al (1984) and Toraya et al (1984). A high angle (2θ = 74-76) X-ray trace is required to distinguish between the tetragonal and cubic phases because of the superposition of the relevant peaks. The crystallographic data of the zirconia polymorphs are given in the Table 1.4.

The structure of zirconia is depicted in Figures 1.5 (a and b). The Zr⁴⁺ ion has seven-fold co-ordination with the oxygen ions with the O¹⁻ co-ordination nearly tetragonal and one angle in the structure differing significantly from the tetrahedral value. The monoclinic polymorph is frequently twinned, a phenomenon directly related to the amount of shape
change resulting from the tetragonal to monoclinic transformation. In its
tetragonal form $\text{Zr}^{4+}$ ions have eight fold co-ordinations again with a
distortion due to four of the oxygen ions being at a distance of 2.065 Å in the
form of a flattened tetrahedron and four at 2.455 Å in an elongated
tetrahedron rotated through 90° as shown in Figure 1.6a. Hence tetragonal
structure zirconia can simply be a described CaF$_2$ structure. Figure 1.6b shows
the high-temperature cubic phase, which has a face centred CaF$_2$ structure
with each Zr$^{4+}$ ions having eightfold symmetry with the oxygen ions that are
arranged in two equal tetrahedral.

1.4.2 Stabilization of Zirconia Ceramics

Zirconia is very useful in its 'stabilized' state. The zirconia can be
stabilized at room temperature by doping with oxides of di, tri- and tetravalent
metals such as calcium, magnesium, yttrium, lanthanum, ytterbium and
cerium.

Partially stabilized zirconia (PSZ), which is typically a two-phase
cubic and tetragonal or single-phase tetragonal, is of importance for
mechanical and structural applications. The fully stabilized zirconia (FSZ) is
normally a single-phase cubic. It is of interest for applications in heating
elements, oxygen sensors, fuel cell, electrolytes, coating, structural and wear
components and toughening agents (Howard et al 1988).

Zirconia could be either fully stabilized zirconia (FSZ) or partially
stabilized zirconia (PSZ) by proper additions of dopants. The resulting form
will either be in single phase or multiphase. Typically two phases coexist in
PSZ with the dopant ratio deciding the predominant phase in it, which in turn
decides the structural and mechanical properties. To produce a high strength
zirconia minisphere small grain structure is required, which can be obtained
by the addition of dopants like magnesia, yttria, calcia & ceria in the (5-13) mol % range, that also sets the crystal structure in partially stabilized tetragonal phase (Koji Tsukuma 1985).

![Figure 1.4 Polymorphs of zirconia](image)

**Figure 1.4** Polymorphs of zirconia  
(a) Monoclinic  
(b) Tetragonal  
(c) Cubic

**Table 1.4** Crystallographic data of the zirconia polymorphs

<table>
<thead>
<tr>
<th></th>
<th>Monoclinic</th>
<th>Tetragonal</th>
<th>Cubic</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Space Group</strong></td>
<td>P21/C</td>
<td>P42 / nmc</td>
<td>Fm3m</td>
</tr>
</tbody>
</table>
| **Lattice Parameter** | $a_m = 5.1698 \text{ Å}$  
$b_m = 5.2328 \text{ Å}$  
$c_m = 5.3418 \text{ Å}$  
$\beta = 98.9^\circ$ | $a_t = 5.094 \text{ Å}$  
$c_t = 5.177 \text{ Å}$ | $a_c = 5.08 \text{ Å}$ |
| **Density**    | 5.83 g/cc  | 6.1 g/cc   | 6.09 g/cc |

- Zirconia
- Oxygen
A special case of zirconia is that of tetragonal zirconia polycrystalline (TZP), which is indicative of polycrystalline zirconia composed of only the metastable tetragonal phase and which can be made stable by carefully selecting the initial particle size of the powder and the
sintering conditions. Ingel and Lewis (1986) systematically investigated the yttria-zirconia system and explained the change in lattice parameter in terms of the Y$^{3+}$ substitution of Zr$^{4+}$ in the unit cell with a corresponding change in the anion vacancy concentration.

1.4.2.1 Role of Stabilizer

To use zirconia to its full potential, the properties of the oxide have been modified extensively by the addition of stabilizing agents. Depending on the nature and quantity of the stabilizer used, different types of stabilized zirconia can be prepared.

In general, among the aliovalent additives, CaO leads to a fully stabilized zirconia (FSZ) which is completely of cubic phase; yttria (above 3 mol %) and magnesia lead to a partially stabilized zirconia (PSZ) containing t phase particles as precipitates in a cubic matrix; yttria (<3mol%) and ceria (<20mol%) can lead to tetragonal zirconia polycrystals (TZP) consisting of complete t phase structure (Hannink 1988). The stabilizers strongly affect the unit cell volume of the tetragonal and cubic phases, leading to larger unit-cell volumes than the idealized structure (French et al 1994).

1.4.3 Phase Transformation

The transformation in zirconia powders is believed to occur by diffusionless shear process at near sonic velocities, with a thermal hysteresis between the cooling and heating cycles. Garvie (1978) based on unconstrained crystals has concluded that the monoclinic - tetragonal transformation ($T_c= 1174\pm6^\circ$C) in zirconia is thermodynamically reversible.
1.4.3.1 Crystallography of Transformation

Generally, any martensitic transformation is characterized by

- a fixed orientation of planes between the parent and product phases
- the orientation of the habit plane between the parent and product phases and
- the existence of a lattice correspondence between the parent and product phases

Experimental results (Ruhle and Evans 1989) show that the c axis of the t grain is parallel to the c axis of the m grain. The crystallography of transformation of 12 mol% of Ce-TZP has been investigated by means of selected area electron diffraction (SAED) technique. They have reported that the single phase t samples were partially transformed to m due to indentation stresses. These are then heated by an electron beam and also by heat induced due to grinding. The forward (t to m) transformation is found to have any one of the following orientation relationships:

a. \((001)_m \parallel (010)_t\) and \([100]_m \parallel [100]_t\)

b. \((100)_m \parallel (010)_t\) and \([001]_m \parallel [100]_t\)

For reverse (m to t) transformation, the orientations for electron beam heating and for heat induced by machine grinding are quite different. In the case of electron beam heating, the m to t has the same correspondence as that of the t to m transformation and there was only a single t variant. For the grinding induced heating, the lattice correspondence of m to t need not be the same as that of the t to m. Crystallography of the transformation can be examined by optical and electron microscopy in single crystal zirconia. There
are two orientation relationships above and below 1000°C. The orientation relationship if the temperature is above 1000°C is

\[(100)_m \parallel \sim(100)_t \text{ and } [010]_m \parallel [001]_t\]

and if the temperature is less than 1000°C, then it is

\[(100)_m \parallel \sim(100)_t \text{ and } [001]_m \parallel \sim[001]_t\]

The martensitic crystallography of the t to m transformation has been analysed by Kriven et al. (1981), reporting in shape strains ranging from 5-17%. Masaki and Murata (1987) have also reported the orientational relationship between tetragonal and monoclinic crystal for 2.5 mol% of Y₂O₃-ZrO₂ system after ageing at 1200°C for 1000 hours as

\[(100)_m \parallel (100)_t \text{ and } [010]_m \parallel [001]_t\]

1.4.4 Transformation Toughening

The potentiality for obtaining very high toughness materials by careful control of the zirconia ceramics microstructure relies on the metastable retention of the tetragonal phase at ambient temperature. Upon the action of external stresses, such as in the surrounding zones of a propagating crack, tetragonal grains may transform to their stable monoclinic structure. Since the transformation is accompanied by a large shear (0.16) and volume expansion (0.04), the stresses and strains induced by the transformation lead to the formation of a zone with large compressive stresses that can partially close the crack and slow down its propagation, increasing the material toughness. This phenomenon has been the object of numerous studies over the last 30 years.
The room temperature stabilized t phase is in a metastable condition and needs energy to transform to a monoclinic (m) stable phase. If a passing crack front meets the t-phase particle, it will absorb energy from the passing crack and transform to m-phase with an associated volume expansion of about 5% which serves to retard the passage of the crack in two ways:

1. by absorbing energy, thereby depriving the crackfront of that energy by virtue of which it could have propagated further, and
2. by exerting compressive stresses, which is generated by the \( t \rightarrow m \) transformation and the associated volume expansion against the passing crack, thereby preventing the crack from further propagation.

Since, this \( t \rightarrow m \) transformation absorbs energy, and the ability of a material to absorb energy is defined as toughness, this \( t \rightarrow m \) transformation leads to an increase in the toughness of the material. Hence the material is said to be toughened and this phenomenon is termed as transformation toughening. Transformation toughening depends directly on the t phase content and therefore materials which contain 100% t phase are capable of possessing very high toughness. Ceria and yttria are the two materials that can lead to TZP.

Several oxides are well known to retain zirconia in its tetragonal structure at ambient temperature, totally or partially, i.e. yttria (\( Y_2O_3 \)), ceria (\( CeO_2 \)) or magnesia (\( MgO \)). The potentiality to observe autoclave ageing induced martensitic relief in yttria stabilized zirconia (Deville and Cevalier 2003), Ceria stabilized zirconia (Deville et al 2005) with great precision has been demonstrated recently. It is found that the critical stress intensity factor can be described by the combination of the matrix intrinsic toughness and the
addition of crack-shielding mechanisms, among which transformation toughening and crack bridging arise in the particular case of ceria-doped zirconia.

The important characteristics of martensitic transformation are:

1. Transformation is diffusionless and there is no change in chemical composition.
2. The transformation proceeds only during cooling and stops if cooling is interrupted. Therefore, the transformation depends only upon the temperature and is independent of time at a given temperature. The start temperature of martensitic formation is known as $M_s$ and the end of martensitic formation as $M_f$.
3. The martensitic transformation of a given alloy cannot be suppressed, nor can the $M_s$ temperature be changed by changing the cooling rate.

**1.4.4.1 Stress Induced Transformation Toughening**

The tetragonal to monoclinic transformation can be avoided and the metastable tetragonal phase can be retained, if the zirconia is finely divided or the matrix exerts a constraining pressure on it. If a crack is made to extend under stress, large tensile stresses are generated around the crack, and if sufficient, could result in a net tensile stress on the tetragonal zirconia particles that can, under the new conditions, transform to the monoclinic symmetry. Due to this a 3% volume expansion and a shear strain of 1-7% develop in the transformed particle, with a resultant compressive strain in the vicinity of the crack. This requires extra work to move the crack through the ceramic, thus accounting for the increase in toughness and hence the strength.
Metastable inclusions of tetragonal ZrO$_2$, dispersed in a ceramic matrix will transform to the thermodynamically stable monoclinic form on application of an external tensile stress. When t-ZrO$_2$ particles transform in the tensile stress field of a crack tip, the crack tip tensile stress is decreased and the external tensile stress must be increased to generate sufficient tensile stress for the propagation of the crack.

When a transformation zone extends fully over the crack surface, the increment in the toughness is

\[
\Delta K_c = \frac{0.21}{(1-\gamma)} E \exp(T) V_f h^{1/2}
\]  

(1.4)

When a transformation zone extends partially over the crack, R-curve behaviour occurs, and the resistance for crack propagation increases as the crack advances. Now the increase in toughness is

\[
\Delta K_c = \left[ \frac{0.21}{\pi(1-\gamma)} \right] E \exp(T) V_f h^{1/2} \tan^{-1} \left( \frac{\Delta a}{h} \right)
\]  

(1.5)

where, ‘E’ is Young’s modulus of the composite, ‘\(\gamma\)’ is the Poisson ratio, ‘h’ is the transformation width, ‘\(V_f\)’ is the volume fraction of the material susceptible to transformation, \(\exp(T)\) is the dilation strain associated with the transformation and ‘\(a\)’ is the increment in crack length. The t to m transition in yttria-containing zirconia might be controlled by short-range diffusion of oxygen vacancies produced due to replacement of zirconium ions by yttrium ions to keep neutrality, and in this sense the concept of bainite-like transformation (Nakanishi and Shigematsu 1991).

1.4.5 Previous Reports on the Preparation of Zirconia by Sol-Gel Method

Though zirconia was found in the year 1789 from the Srilankan beach sand, extensive research has been started only after the seminal publication of Garvie et al (1975) on the stress induced phase transformation.
Following this many researchers have intensively studied the various aspects of zirconia such as preparation by different routes, crystallization behaviour, stabilization of metastable to tetragonal phase at room temperature, sintering studies under various conditions, toughening mechanism, etc. In the subsequent text, the work carried out by various authors on the preparation and powder characterization of zirconia using sol-gel method is discussed.

1.4.5.1 Alkoxide Routes

Many reports are available on the preparation of zirconia and zirconia based ceramic powders by using alkoxides. Mazdiyasni et al (1965) have reported the preparation of pure and yttria doped cubic zirconia by decomposition of metal alkoxide and they have analyzed the decomposition and crystallization behaviour. Yoldas (1986) has studied various factors which affect the condensation reaction such as type of alkyl group in the alkoxide, water/alkoxide ratio, molecular separation of species and the reaction temperature. These factors also affect the m to t transformation structure. Mono dispersed powders of (3 mol%) yttria-zirconia have been prepared (Bagley et al 1993) by hydrolysing the metal alkoxides. Effect of synthesis conditions such as ageing, water concentration and refluxing of the alkoxide solutions on powder preparation has been analyzed.

Preparation of spray quality yttria-stabilized zirconia powders of high purity has been reported by Sheyif and Shyu (1991) from the emulsion hydrolysis of metal alkoxides, acetates and also from their mixtures. By varying the experimental conditions, spherical or granular powders with particle sizes ranging from submicron to hundred micron have been obtained. Hydrolysis of zirconia tetra-n-butoxide in 2-propanol yields mono dispersed sol containing 4nm sized particles (Okubo and Nagamoto 1995) and their subsequent sintering results only a few tens of nanometer sized grains.
1.4.5.2 Colloidal Preparation

Pure monoclinic zirconia has been prepared by mixing the chloride salt of zirconium and oxalic acid which results in the formation of zirconyl oxalate gel and decomposing it at 850°C (Etienne et al. 1990). Gongyi and Yuli (1992) have prepared Y-TZP powder by oxalate precipitation in ethanol solution with various pH values. Gangadevi et al. (1980) have also reported the preparation of zirconyl oxalate precipitates and they have studied the thermal decomposition behaviour of oxalates. Oleg Vasylkiv and Yoshio Sakka (2000) obtained powder with a composition of 3 mol% Y2O3-97 mol% ZrO2, a process of Y-Zr oxalate powder production has been optimized, to produce an oxalate with minimal particle size. Fine oxalate powders with surface area 196 m²/g (~6 nm primary particles size) have been obtained.

1.4.6 Role of Binder Addition

Binders, when used in small concentrations serve primarily to provide bridges between the particles. In this way they aid the granulation of a powder and serve to provide strength in the green body. In fairly high concentration, they serve to provide plasticity in the feed material during deformation.

In most of the forming methods, binders are the first additive selected. A large number of organic substances can be used as binder. Some are soluble in water, whereas others are soluble in organic liquids. When the binder is incorporated as a solution, the solubility of the binder in the chosen solvent (water or organic liquid) must be considered.

The use of organic binders in the forming of ceramics has been reviewed by Onoda (1978). Most soluble organic binders are long-chain
polymer molecules with side groups located at frequent intervals along the length of the molecule. The chemical nature of the side groups determines, in part, what liquids will dissolve the binder. If the side groups are polar, solubility in water is promoted, whereas if they are nonpolar, solubility in nonpolar solvents is promoted. Binders soluble in polar organic liquids have side groups of intermediate polarity.

Once the type of liquid (i.e., water or organic liquid) and the class of binder (i.e., water-soluble or soluble in organic liquids) are chosen, the effect of binder on the rheology of the liquid must be considered. Organic binders increase the viscosity and change the flow characteristics of the liquid. Some can even lead to the development of a gel. The behaviour of the suspension produced by adding the powder to the binder solution is influenced significantly by the rheology of the solution. The increase in viscosity of the solution produced by the binder forms one of the primary considerations in the selection of a binder for a specific forming process.

Binders are often arbitrarily classified according to how effectively they increase the viscosity of the solution. The terms low, medium and high viscosity grades are normally used for specific binders that are available in different molecular weights. From the point of view of comparing different binders, the scheme shown in figure 1.7 has been proposed by Onoda (1978) to establish definitions of viscosity grades. Among varies binders, PVA shows the viscosity grade variation from very low to medium, which is suitable for the minisphere processing due to which PVA is chosen as binder in the present work.
1.5 COMMINUTION

The desired particle size and size distribution usually cannot be achieved simply by screening, classifying or electricating the raw material. More typically a particle size reduction step is required. The particle size and distribution have large impact on the rheology, fabrication behaviour, sintering behaviour and ultimate microstructure of the product. The process in which small particles are produced by reducing the size of larger ones by mechanical forces is usually referred to as comminution.

Comminution involves operations such as crushing, grinding and milling, with the most common way is by milling. One or more of variety of mills may be used, including high-compression roller mills, jet mills (fluid energy mills), and ball mills. Ball mills are categorized into various types, depending on the method used to impart motion to the balls (e.g., tumbling, vibration and agitation).

Figure 1.8 shows the range of particle sizes achieved from different types of mills. In the milling process, the particles experience mechanical stresses at their contact points due to compression, impact, or shear with the mill medium or with other particles. The mechanical stresses lead to elastic and inelastic deformation and if the stress exceeds the ultimate strength of the particle, to fracture the particles.

Changes in the chemical properties (especially the surface properties) can also occur, especially after prolonged milling or under very vigorous milling conditions. Figure 1.8 summarizes the stress mechanisms and the range of particle sizes achieved with various types of mills for the production of fine powders. Primary crushers such as jaw crushers and cone crushers, crushing rolls and hammer mills reduce the feed from a coarse
nature to below 1mm. One or more of a variety of mills may then be used to further reduce the average particle size, as indicated in Figure 1.9. Common mills used for grinding ceramic materials are ball mills, vibratory mills, attrition mills, fluid energy mills and roller mills.

![Figure 1.7 Criterion for viscosity grades based on viscosity-concentration relationship (Onoda 1978)](image_url)

**Figure 1.7** Criterion for viscosity grades based on viscosity-concentration relationship (Onoda 1978)

1.5.1 **Hammer Milling**

It involves a rapidly rotating rigid bar or plate. The particles are dropped in the path of this bar and fragmented by the impact. Further, fragmentation occurs as the particles strike the walls of the mill. In a hammer mill, rotating hammers pulverize particles of a brittle but relatively soft material and force the fines through the opening in a circular wear-resistant
screen. A hammer mill is capable of producing a large reduction in size down about 0.1mm.

1.5.2 **Roller Milling**

It provides a course crushing alternative to hammer milling. The ceramic particles are directed between two hard fused rollers that rotate in opposite direction such that the ceramic are pinched between them. Although the process is unsuitable for the production of particle size below 10μm, it has two significant advantages. a) The energy utilization is fairly good for the production of the same size of particles from a stock of coarse particles b) Only small amount of material makes contact with the roller, the wear can be fairly low.

1.5.3 **Jet Milling**

The operation consists of the interaction of one or more streams of high-speed gas bearing the stock of coarse particle with another high-speed stream. Comminution occurs by particle-particle collisions. In some designs, comminution is achieved by collisions between the particles in the high speed stream and a wall (fixed or movable) within the mill. The milled particles leave the mill in the emergent fluid stream and are usually collected in a cyclone chamber outside the mill.

1.5.4 **Ball Milling**

In ball milling, the particle to be grounded is placed in a closed cylindrical container with balls or rods as grinding media and rotating the cylinder horizontally on its axis so that the media is cascaded.
Figure 1.8  Range of particle sizes reached with different types of mills (Polke and Stadler 1991)

Figure 1.9  Nominal feed and product mean size capabilities of industrial equipment
Ball milling is suitable for wet or dry milling. Wet ball milling has an advantage over dry milling in that its energy utilization is higher (~10-20%). It also has the ability to produce a high fraction of finer particles. Disadvantages of wet milling are the increased wear of the grinding media, the need for grinding the powder after milling, and contamination of the powder by the adsorbed vehicle.

The rate of grinding depends on number of factors, including the mill parameters (diameter, speed, amount of media), the properties of grinding media (size, hardness, shape) and the properties of the particles to be ground (Beddow 1980).

1.5.5 Attrition Milling

Attrition milling is similar to ball mill as it is cylindrical and also contains balls as grinding media. But rather than rotating the cylinder the very small balls are agitated by a series of stirring arms mounted to an axial shift. It is quicker than ball milling, is more effective in achieving fine particle size with less contamination and can easily be done in dry, wet or with vacuum or inert gas atmosphere. Contamination due to wear of the mill lining and media is considerable and is commonly eliminated by chemical leaching, sedimentation or magnetic separation. Attrition grinding is used for producing sub- micron powders of hard refractory oxides, carbides, nitrides, titania pigments and paper grade kaolin.

1.5.6 Vibratory Milling

Vibrating milling is substantially different from ball milling or attrition milling. The energy for comminution is supplied through vibration rather than tumbling or mechanical stirring. The powder is placed in the
stationary chamber of the mill together with suitable grinding media and a liquid. In the process the vibration is transmitted through the chamber and into the media and powder.

This results in two types of movement

1. Causing a cascading or mixing of the content of the milling chamber.
2. It causes local impact and shear fracturing of powder particles between adjacent grinding media.

Vibrating milling is relatively fast and efficient and yields a finer powder. The chamber is typically lined with polyurethane or rubber to minimize the contamination. Media acceleration produces an impact energy that is continuous in some models. With vibrations, discharge is quick even when the product is a pseudo plastic suspension. The grinding capacity of a large vibrating mill is about 2 tons per hour.

1.5.7 Fluid Energy Milling

Fluid energy mills achieve particle size reduction by particle-particle impact in a high velocity fluid. The fluid can be compressed air, carbon dioxide, super heated stream, water or any other gas (or) liquid compatible with specific equipment design. The powder is added to the compressed fluid and accelerated to sonic (or) near sonic velocity through jets leading into the grinding chamber. The grinding chamber is designed to maximize particle-particle impact and minimized particle-wall impact thus achieving minimum contamination. An advantage of jet mills is that when combined with a particle classification device they provide a rapid method for the production of a powder with a narrow size distribution of particle size down to 1μm.
1.6 GRINDING MEDIA

The size of the grinding medium is an important consideration. Ball mills that run at low speed contain large size balls because most of the mechanical energy supplied to the particle is in the form of potential energy. Those mills that run at high speeds contain small size balls because, in this case, most of the energy supplied to the particle is in the form of kinetic energy. Since the mass is proportional to the density for a given size of grinding media, the grinding media should consist of materials with as high a density as possible.

A disadvantage of ball milling is that wear of the grinding medium can be fairly high. For advanced ceramics, the presence of impurities in the powder is a serious concern. The best solution is to use grinding medium that is chemically inert at the firing temperature of the body (eg. Zirconia balls).

1.6.1 Materials Used as Grinding Media

Media selection criteria and the operation of horizontal media mills have been discussed in several professional publications (Way 1993; Sheppard and Edward 1999).

Grinding medium chosen should possess high level of inertness and wear resistance. A common problem is the use of proclaim balls or low purity alumina balls that wear easily and introduce fair amount of silica into the powder. A list of grinding balls available commercially with approximate density is given in Table 1.6. The harder the media, better will be the grinding efficiency and longer the wear resistance.
Although alumina is the common material applied to all-ceramic mechanical applications, fracture and chipping caused by impingement and stress concentration may cause break down. Yusuke Morita (2003) confirms that the strength and toughness of zirconia are higher than those of alumina and also the wear factor of zirconia is larger than that of alumina. Bending strength of zirconia is two times as high as that of alumina and fracture toughness of zirconia is also higher than that of alumina. Comparative data analysis on mechanical properties of zirconia and alumina is given in Table 1.5.

Recently high wear resistant media material of Ce-TZP has been prepared by conventional powder compaction method and its properties are comparatively high with other types of ceramics currently used as media material.

**Table 1.5 Mechanical properties of ceramics (Zirconia and Alumina)**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Zirconia</th>
<th>Alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>6.06</td>
<td>3.97</td>
</tr>
<tr>
<td>Bending Strength(MPa)</td>
<td>1200</td>
<td>640</td>
</tr>
<tr>
<td>Young’s modulus(GPa)</td>
<td>210</td>
<td>400</td>
</tr>
<tr>
<td>Vickers Hardness(Hv)</td>
<td>1300</td>
<td>1900</td>
</tr>
<tr>
<td>Fracture toughness(MPa m¹/²)</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>Grain size (μm)</td>
<td>0.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Thermal conductivity (293K) (W/(mK))</td>
<td>3.8</td>
<td>25.1</td>
</tr>
</tbody>
</table>
Table 1.6 Commercially available grinding media for ball milling

<table>
<thead>
<tr>
<th>Grinding media</th>
<th>Density (10^3) Kg/m(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Procelain</td>
<td>2.3</td>
</tr>
<tr>
<td>Silicon nitrate</td>
<td>3.1</td>
</tr>
<tr>
<td>Alumina</td>
<td>3.9</td>
</tr>
<tr>
<td>Zirconia</td>
<td>6.0</td>
</tr>
<tr>
<td>Steel</td>
<td>7.7</td>
</tr>
<tr>
<td>Tungsten carbide</td>
<td>14.8</td>
</tr>
</tbody>
</table>

1.6.2 Zirconia as Grinding Media

The grinding materials should satisfy a set of conditions, such as stability during environmental changes, thermal expansion coefficient and hardness close to that of SiO\(_2\) glass, high density, fracture toughness, wear resistance, and good-quality polished surface, etc. Since, stabilized zirconia satisfies the above requirements, it is generally selected for use as a grinding media.

The fundamental properties of zirconia grinding media which are of interest to the engineer or designer are

- high strength, fracture toughness and hardness
- wear resistance and good frictional behaviour
- non-magnetic
- electrical insulation
- low thermal conductivity
- corrosion resistant to acids and alkalis
- modulus of elasticity similar to steel
- coefficient of thermal expansion similar to iron
Stabilized Zirconia grinding media feature high density, excellent toughness and superior hardness, enabling to achieve superior grinding efficiencies comparing with other conventional lower density grinding media. The high wear-resistant TZP grinding media makes it effectively eliminate product contamination and lengthen media life substantially making it suitable for sensitive products and critical applications.

1.6.3 Advantages of Zirconia Grinding Media

The advantages of using Zirconia as a grinding media are:

- Ultra low wear loss as a result of the transformation-toughening mechanism
- Higher grinding efficiency and reduced grinding time due to the higher density of zirconia (compared to alumina and glass)
- Most durable grinding material, reducing operational cost in the long run
- Wear rate substantially lower than Al₂O₃ and other grinding media
- Suitable for high velocity operations and wet grinding operations
- Do not oxidize ("rust") in the presence of aqueous dispersions. As a result, they offer the advantages of the density of metallic media without the oxidation
- Ultimate in high performance dispersion media for horizontal mills. It's density (> 6 g/cc) makes it ideal for high viscosity mill bases
- Most durable and efficient media for ball milling and attrition milling of ceramic materials. Zirconia grinding media provides a virtually contamination-free ball milling solution for a variety of industries
High-density media can accomplish a specified size reduction much more quickly than low-density media since smaller sizes can be used, providing more grinding contacts per batch. For instance, media made from partially stabilized zirconia (density = 5.6-6.1 g/cm$^3$) can mill twice as fast as high-density alumina (density = ~3.6 g/cm$^3$) with about 50% less media wear loss and one-third the mill wear.

1.6.4 Applications of Zirconia Grinding Media

Zirconia is found to be used as a grinding media in various fields such as:

- High strength and high toughness products, such as dielectric materials, piezo electric materials, magnetic materials.
- Wear and corrosion resistance products, such as coating, textile, pigment dispersions, ink and dyestuffs.
- Prevention of product contamination, such as pharmaceutical, foods.
- Ceramics: such as electronics ceramics, refractory ceramics, engineering ceramics, nanometer materials.
- Iron- and chrome-based magnetic materials (for audio/video recording tapes) and other magnetic materials.
- Electronic-grade ceramics (ferroelectric, piezoelectric, dielectric, capacitors, sensors, etc.), advanced structural ceramics, and other ceramic ingredients.
- Nanostructured and superfine powders.
- Toner materials for photocopiers and laser printers.
- Inks, dyes, paint, and other pigments.
- Pharmaceutical, food, chemical, and textile applications.
- Lab milling operations demanding minimized contamination from milling media.
1.7 SCOPE OF THE PROBLEM

From the foregoing discussion, it can be observed that pure zirconia and various stabilized zirconia are prepared mostly by using the precipitation method, sol-gel process (parent material are mostly metal alkoxides), spray pyrolysis route, hydrothermal technique and citrate process. The manufacture of zirconia as a fine grinding media (~ 1mm) is heavily depending on any one of the above said ceramic processing routes. Conventionally ceramic grinding media are prepared by powder compaction method. Fabrication of high quality ceramic grinding media via powder compaction method has certain major limitations in the processing parameter such as variations in size, density, strength and shape, since even a slight change in any of the processing parameter leads to drastical structural changes.

In course of finding an alternative method to improve the quality and cost effectiveness of the final product, a novel sol-gel oxalate drop generation route has been identified. But, the reports available on oxalate gel derived route are limited. Etienne et al (1990) have prepared pure zirconia using oxalate gelation method. They have not prepared the doped zirconia and analyzed sintering and mechanical behavior. Shi and Lin (1989) have studied only the preparation of zirconium dioxide powder by oxalate precipitation method. Gongyi and Yuli (1992) have prepared Y-TZP powders by oxalate precipitation in ethanol solution with various pH values. Few attempts have also been made on oxalate route for zirconium synthesis by Oleg Vasylktiv and Yoshio Sakka (2000), Asuncin Fermnndeze et al (2002), Chandradass and Balasubramanian (2005) and Settu and Gobinathan (1996). Recently, Lakshmi (2001) and Chandradass (2005) made an attempt for preparing alumina and zirconia toughened alumina grinding media with an alternative sol-gel route.
There is no concrete literature evidence on the preparation of a zirconia grinding media using sol-gel drop generation method through the synthesis of zirconium oxalate. A modification of the conventional sol-gel route to produce fine zirconia minispheres would be an attractive alternative approach. Relatively little work has been reported on the properties of technical ceramics plasticized with organic binders. Therefore an attempt is made to study the effect of binder content on the sintered density of the stabilized zirconia minispheres. Effect of solid loading in the synthesis and properties for zirconia minispheres have also been identified as an innovative analysis to enhance the properties of zirconia minispheres.

Hence in this work, detailed studies on the preparation of zirconia minispheres stabilized with ceria (9-15 mol%), yttria (3-8 mol%) and magnesia (5-10 mol%) by sol-gel oxalate drop generation method using metal salts of chlorides, nitrates and oxalic acid. Extensive characterization and property evaluation studies have been performed to reveal the physical, structural and mechanical properties of all stabilized zirconia minispheres.

1.8 OBJECTIVE OF THE WORK

In order to overcome the limitations of powder compaction method, the present investigation is aimed to develop a novel processing technique based on sol-gel drop generation technique to prepare near-net-shape prototype zirconia minispheres. It is well known that the sol-gel synthesis makes it possible to prepare shaped material with out the use of powder processing. This great advantage of sol-gel method has to be exploited in the present work to produce spherical shaped fine grinding media of required size with improved properties.
It is well known that the rate of grinding increases inversely with the radius of the ball. If the grinding media is very small, the milling will be effective. However, the balls should possess sufficient energy to fracture the particle. So, fabrication of high quality fine grinding media (~1mm diameter.) by sol-gel drop generation method through zirconium oxalate is the major objective of the present study.

Focus is made to optimize the processing parameters such as pH, viscosity, extrudability, binder concentration, sintering temperature, heating rate and soaking time for the fabrication of zirconia minispheres.

Stabilization of zirconia minispheres by using various stabilizing agents such as CeO$_2$, Y$_2$O$_3$ and MgO are performed. The role of sintering additives (stabilizers) and sintering temperature on surface area, phase transformation, sintered density, porosity, weight loss, shrinkage, microstructure development, hardness, fracture toughness and wear resistance are studied in detail.

The commercial production of ceramic components must be cost effective. The cost of production can be reduced if the transformation and densification could be achieved at lower temperature. Therefore, an attempt is also made to reduce the shrinkage and to enhance the density by solid loading using t-zirconia powder.

With these objectives, the present work reveals the processing and characterization of zirconia minisphere using the oxalate precursor method. Homogeneous mixing at the atomic level, weakly aggregated particles, narrow size distribution and with elevated physical, structural and mechanical properties are expected.
1.9 CONCLUSION

A brief review has been presented regarding ceramic processing methods, nature of pure and stabilized zirconia, crystallographic modifications, stabilization, role of stabilizer, transformation toughing, effect of binder addition, sol-gel synthesis of zirconia, type of grinding operation, grinding media and its applications.

Scope of the problem and objectives of the present work have also been elaborated.