POWDER PROCESSING, DENSIFICATION BEHAVIOUR, MICROSTRUCTURE AND MECHANICAL PROPERTIES OF AL₂O₃- 50 Vol% ZrO₂ COMPOSITES

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NOVEMBER, 2009
This is to certify that the thesis entitled “Powder Processing, Densification Behaviour, Microstructure and Mechanical Properties of Al₂O₃- 50 vol% ZrO₂ Composites” being submitted by Mr. Raghunath Prasad Rana for the degree of Doctor of Philosophy in Engineering, is a record of bonafied research work carried out by him under our supervision at Department of Ceramic Engineering. To the best of our knowledge, the work has not been submitted to any other University or Institute for the award of any degree or diploma.

(S Bhattacharyya)                                    (S K Pratihar)
Professor                                           Associate Professor
Department of Ceramic Engineering                    Department of Ceramic Engineering
Dedicated to my parents
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Abstract

Al₂O₃-ZrO₂ composites containing nominally equal volume fraction of Al₂O₃ and ZrO₂ were prepared through solution chemistry route using inorganic precursors of AlCl₃ and ZrOCl₂. It was expected that the solution chemistry route will yield highly reactive fine powders which could be sintered into a dense composite with a small grain size. Such a microstructure is expected to retain t-ZrO₂ without the use of stabilizers. Three different processing routes, viz gelation (ROUTE 1), precipitation (ROUTE 2) and precipitation followed by washing (ROUTE 3) (consisting of hot water and alcohol washing) were employed. However, the ROUTE 1 powders could be sintered only up to 72% relative density and the highest density was 88% for ROUTE 3. FTIR and DSC/TG studies revealed that the washing process not only removed soluble salts but also helped to reduce the extent of agglomeration and produced softly agglomerated powders. However, the washing process could not completely remove chlorides and the presence of the residual chlorine hindered densification by creating residual pores during the final densification stage. The sintered samples had nearly equal grain sizes (1.9 µm and 1.5 µm for Al₂O₃ and ZrO₂ respectively). However, extensive microcracking resulted during spontaneous t→m transformation of ZrO₂ during cooling from the sintering temperature. The combined effect of microcracking and low sintered density resulted in poor mechanical properties (σ₇ = 64 MPa, KIC = 1.74 MPam¹/², HV = 4.1 GPa). The partial substitution of chloride precursor by nitrate precursor (Al(NO₃)₃ for AlCl₃) (ROUTE 4) resulted in improved sintered density (95% relative density) but grain size was more than the critical size for prevention of spontaneous t→m transformation during cooling of sintered sample and once again microcracking resulted in lowering of strength and toughness (σ₇ = 88.7 MPa, KIC = 1.9 MPam¹/², HV = 7.9 GPa). The initial stage densification mechanism of these composites was studied from non-isothermal and isothermal sintering behavior. The densification was controlled by volume diffusion with the activation energy for densification being 236-258 KJmol⁻¹.

Retention of metastable t-ZrO₂ at room temperature is an important factor for achieving higher strength and toughness of the composites. Since, only a small fraction of t-ZrO₂ (10-15 vol%) could be retained in Al₂O₃-undoped ZrO₂, it was decided to use Y₂O₃ as a
stabilizer for t-ZrO$_2$. Four different mole percent of Y$_2$O$_3$ (1.0, 2.0, 2.5 and 3.0 mol%) were added to separate batches of Al(NO$_3$)$_3$-ZrOCl$_2$ mixed solution, followed by precipitation and washing of the precipitated powder using modified ROUTE 4. The t-ZrO$_2$ retention (measured on the sintered surface) was 100% at 3 mol% Y$_2$O$_3$ addition, 97% for 2.5 mol% Y$_2$O$_3$ and only 14% for 2 mol% Y$_2$O$_3$ which further decreased at 1.0 mol% Y$_2$O$_3$. The sintered density was also high (>94%) at 2, 2.5 and 3.0 mol% Y$_2$O$_3$ doped Al$_2$O$_3$-ZrO$_2$ composition while it was low for 1 mol% Y$_2$O$_3$ doped Al$_2$O$_3$-ZrO$_2$. Nearly 100% relative density could be attained in Al$_2$O$_3$-3Y-ZrO$_2$ sintered composites. The positive effect of high sintered density and high t-ZrO$_2$ retention reflected in the improved mechanical properties of the composites. The highest fracture strength was 650 MPa (in 3 point bending) and 350 MPa (in bi axial flexure) for Al$_2$O$_3$-3Y-ZrO$_2$ composites. The fracture toughness was 8.5, 9 and 13.04 MPam$^{1/2}$ respectively for Al$_2$O$_3$-2Y-ZrO$_2$, Al$_2$O$_3$-2.5Y-ZrO$_2$ and Al$_2$O$_3$-3Y-ZrO$_2$ composites sintered at 1600$^\circ$C. The zone depths (measured from ground surface XRD pattern) for Al$_2$O$_3$-2.5Y-ZrO$_2$ and Al$_2$O$_3$-3Y-ZrO$_2$ composites were 2.99 and 4.69 µm respectively. The contribution of transformation toughening ($\Delta$K$_{ICTT}$) for the above two composites were calculated using Mc Meeking and Evans model and was found to be 7.36 and 9.21 MPam$^{1/2}$ respectively. These findings suggested that some additional toughening mechanism was also operative in these composites. FE-SEM images show the presence of both intergranular and transgranular cracks in Al$_2$O$_3$-3Y-ZrO$_2$ samples. HR-TEM image suggests that YAG (Y$_2$Al$_5$O$_{12}$) has formed at the Al$_2$O$_3$-ZrO$_2$ grain interface. The presence of YAG increases the grain boundary fracture energy thereby modifying the crack propagation path from intergranular to transgranular. The indent surface image shows significant deviation of main crack from its original path, crack bowing around an obstacles, and crack branching. All these effects probably combined to give high strength and toughness of Al$_2$O$_3$-Y-ZrO$_2$ composites. Thermal shock resistance of Al$_2$O$_3$-3Y-ZrO$_2$ composites was also studied by air quenching method. For $\Delta$T up to 1000$^\circ$C, significant fracture toughness ($K_{IC} = 7.28$ MPam$^{1/2}$) and strength ($\sigma_f = 547$ MPa) could be retained in the quenched composites. This hints at good thermal shock resistance of the composites. The evaluated properties of Al$_2$O$_3$-3Y-ZrO$_2$ composites suggest that it may be used as a cutting tool material.
Key words:

$\text{Al}_2\text{O}_3$, 50 vol\% $\text{ZrO}_2$ Composites, Powder processing, Solution chemistry route, Powder characterization, Sintering kinetics, Grain growth, $\text{Al}_2\text{O}_3$-$\text{Y}$-$\text{ZrO}_2$ composite, Hardness, Fracture strength, Fracture toughness, Microstructure, Thermal shock resistance, Cutting tool.
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Chapter I

Introduction
Introduction

Ceramics have been known to mankind since the earliest civilization and have played an important role in the evolution and development of human civilization. Generally ceramics are defined as solid crystalline materials composed of oxides, carbides, nitrides, borides having important structural, mechanical, thermal and electronic properties. Most of the ceramic materials have significant fraction of covalent bonding which ensures improved high temperature properties like high melting point, strength at high temperature etc. The improved high temperature mechanical properties, coupled with high wear, oxidation and chemical resistance makes it suitable for many advanced and strategic applications such as ceramic bearings and grinding media, automobile parts, turbine plates, radomes, space shuttle tiles, ceramic armors etc. [1.1]. However, brittle fracture along with low Weibull modulus makes ceramics vulnerable for many advanced applications. There have been numerous efforts to reduce the brittleness and to improve the Weibull modulus of ceramics. Among these, composites have been found to be most successful in overcoming many of these shortcomings. Both metals and nonmetals have been successfully used as reinforcing materials either as particles, platelets, whiskers or fibers. The strengthening and toughening arises due to load transfer or various crack deflection mechanisms. The difference between the matrix and the reinforcement modulus as well as the nature of interfacial bonding becomes the deciding factor for determining the extent of strength and toughness improvement [1.2]. However, another class of composites exists where the toughness is achieved through controlled phase transformations of the reinforcement. These phase transformations are usually stress and/or temperature assisted and involve volume, shape or coordination change and usually occur by a combination of shear and rotation mechanism [1.3]. Ceramic composites utilizing these phase transformation are known as Transformation Toughened Ceramics. Table 1.1 lists some of these materials exhibiting shear type phase transformation involving large volume changes and some of these materials have been used for toughening of the host ceramic matrix.

As seen from Table 1.1 the reverse phase transformation of the ZrO$_2$ ($t$-ZrO$_2$ to $m$-ZrO$_2$) involves a volume expansion of 4-6 % and shear strain of 7-10%. Thus $t$-ZrO$_2$ has been used to toughen many ceramic matrices like Al$_2$O$_3$, SiC, mullite etc. These ZrO$_2$
containing composites are known as zirconia dispersed ceramics (ZDC) or zirconia toughened ceramics (ZTC) [1.3]. Since, the improvement in strength and toughness in these ZDC or ZTC results from the volume expansion and shear strain arising from $t \rightarrow m$ ZrO$_2$ transformation, it is important that $t$-ZrO$_2$ is retained at room temperature as a metastable phase. The retention of $t$-ZrO$_2$ at room temperature depends on many other factors namely the size of ZrO$_2$ particles, the matrix elastic modulus etc. [1.4]. A smaller particle size of ZrO$_2$ along with high matrix modulus provides the activation energy barrier against spontaneous $t \rightarrow m$ ZrO$_2$ transformation [1.5, 1.6]. Thus ideally, the elastic modulus of the matrix material should be much higher than that of ZrO$_2$ for utilizing the transformation toughening phenomenon.

Table 1.1 Shear transformations in nonmetallic substances [1.3]

<table>
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<th>Inorganic Compound</th>
<th>Transformation</th>
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<tr>
<td>Alkali Halides (MX)</td>
<td>(NaCl$<em>{\text{cubic}} \rightleftharpoons$ CsCl$</em>{\text{cubic}}$)</td>
</tr>
<tr>
<td>Ammonium Halides (NH$_4$X)</td>
<td></td>
</tr>
<tr>
<td>Nitrates</td>
<td>(NaCl$<em>{\text{cubic}} \rightleftharpoons$ CsCl$</em>{\text{cubic}}$)</td>
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<tr>
<td>RbNO$_3$</td>
<td>(NaCl$<em>{\text{cubic}} \rightleftharpoons$ CsCl$</em>{\text{cubic}}$)</td>
</tr>
<tr>
<td>TiNO$_3$, AgNO$_3$, KNO$_3$</td>
<td>(Orthorhombic $\rightleftharpoons$ rhombohedral)</td>
</tr>
<tr>
<td>Sulfides</td>
<td>(Zinc blende-type $\rightleftharpoons$ NaCl$_{\text{cubic}}$)</td>
</tr>
<tr>
<td>MnS</td>
<td>(NaCl$<em>{\text{cubic}} \rightleftharpoons$ CsCl$</em>{\text{cubic}}$)</td>
</tr>
<tr>
<td>BaS</td>
<td>(Orthorhombic $\rightleftharpoons$ monoclinic)</td>
</tr>
<tr>
<td>Dicalcium silicate (2CaO.SiO$_2$)</td>
<td></td>
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Minerals

Pyroxene silicates

| Enstatite (MgSiO$_3$)   | (Orthorhombic $\rightleftharpoons$ monoclinic) |
| Wollastonite (CaSiO$_3$) | (monoclinic $\rightleftharpoons$ triclinic) |
| Ferrosilicate (FeSiO$_3$) |                                       |
| Olivine $\rightleftharpoons$ spinel ([Mg,Fe]$_2$SiO$_3$) | (Orthorhombic $\rightleftharpoons$ monoclinic) |
| Quartz (SiO$_2$)        | (Orthorhombic $\rightleftharpoons$ cubic) |

Ceramics

| Boron nitride          | (Wurtzite-type $\rightleftharpoons$ graphite-type) |
| Carbon                 | (Wurtzite-type $\rightleftharpoons$ graphite) |
| Zirconia (ZrO$_2$), HfO$_2$ | (Tetragonal $\rightleftharpoons$ monoclinic) |

Alumina is an important structural ceramic material having many desirable properties like high melting point (2046 ±5°C), hardness (18 GPa), elastic modulus (380 GPa) and excellent resistance to acids and alkalis. It is being widely used as grinding media, textile thread guides, in paper manufacturing industry, cutting tools etc [1.7]. However, it is brittle and has very low resistance to crack propagation i.e. low fracture toughness which
results in catastrophic failure of the components. Among the several approaches that have been used to inhibit the catastrophic failure of alumina ceramics, toughening by incorporating $\varepsilon$-ZrO$_2$ in the alumina matrix has been very successful.

![Classification of zirconia based ceramic composites](image)

Fig.1.1 Classification of zirconia based ceramic composites [1.9]

These reinforcements make use of different energy absorbing mechanism (such as crack deflection, crack branching or crack bowing) which becomes operative in the stress field of an advancing crack tip. The mechanisms result in a process zone surrounding the main crack in which the crack tip stress intensity reduces, thereby arresting the propagation of the main crack. Moreover, the volume expansion due to the phase transition in the frontal zone exerts a back stress to the crack tip and it may also provide the crack closure forces in the fully developed wake region thereby obstructing the propagation of the advancing crack front by applying crack closer forces. The study of Al$_2$O$_3$ - ZrO$_2$ system is also of interest as both pure oxide systems contain a multitude of metastable phases that can be beneficial in many applications [1.8]. The commercially
available Al$_2$O$_3$ - ZrO$_2$ composite are either known as Alumina Toughened Zirconia (ATZ) or Zirconia Toughened Alumina (ZTA) depending on whether ZrO$_2$ or Al$_2$O$_3$ is the matrix phase. Figure 1.1 gives a classification of the different types of zirconia toughened ceramics [1.9].

Recently, Nihara [1.10] has classified the ceramic matrix composites into four different categories (Fig. 1.2) on the basis of the matrix and reinforcement particle size. These are intra-type, inter-type, intra/inter-type and nano/nano-type. These nanocomposites show improved properties both at room temperature and at high temperature. The hybridization of both micro-nano composites is expected to give further improvement. However the synthesis of nanomaterials for bulk production is difficult due to grain growth of initial fine particles, introduction of processing related process flaws during initial sample preparation and handling of materials on its original dimension till the final microstructure development. The different type of ZrO$_2$ based composites which have been discussed above can also be grouped into these four categories as outlined by Nihara depending on their grain size, position (inter or intra granular) and uniformity of dispersion etc. The localized residual tensile strain around the particles induces transgranular fracture and the toughening occurs by the crack tip deflection. Thus, if the composite can be made into a nano/nano or a nano/micro type, additional improvement in strength and toughness can be expected because of the change of fracture mode of the composite which act to deflect or stop the crack propagation.

![Fig. 1.2 Schematic representation of microstructural features of various nanocomposites as well as nano/nanocomposites [1.10]](image-url)
In ATZ, usually low volume/weight fraction of ZrO$_2$ is incorporated in Al$_2$O$_3$ matrix. The increase in strength and toughness can be either due to transformation toughening or due to microcrack toughening [1.6, 1.9]. In the former case, high elastic modulus of Al$_2$O$_3$ helps to retain metastable $t$-$ZrO_2$ phase. Subsequently these metastable $t$-$ZrO_2$ particles undergo stress induced $t \rightarrow m$ ZrO$_2$ transformation in the stress field of an advancing crack tip. The transformation toughening - considered as a crack-shielding mechanism is related to the process zone development. When the process zone is only ahead of the propagating crack, the toughness increment will be zero due to the absence of a fully developed wake region [1.11-1.13]. The maximum toughness increment occurs when the transformation zone fully extends over the crack surface. The contribution of toughness increment resulting from the stress induced toughening depends on toughening mechanism [1.11]. The general expression for the toughness increment is given by

$$\Delta K_{IC} = \frac{\eta E^* e^T V_f \sqrt{h}}{(1-\nu)}$$

where, $\Delta K_{IC}$ is the toughening increment, $V_f$ is the volume fraction of transformable ZrO$_2$ particles, $e^T$ is the dilatational strain, $E^*$ is effective modulus of the composite, $h$ is the width of the transformed zone, $\nu$ is Poisson's ratio and $\eta$ is a numerical constant which depends on the zone shape at the crack tip and the nature of the stress field in that zone (this particular point has been further elaborated in Chapter II during the discussion of transformation toughening models). The factors which controls the relative toughness of the precipitate and particulate-toughened systems are $V_f$, $e^T$ and $E^*$ because $\nu$ is about the same for both classes of material. Higher matrix modulus constrains the transformation, thereby decreasing the extent of the transformation zone depth $h$. The decrease in $h$ is due to the lower fraction of $t$-$ZrO_2$ available for transformation. This restricted transformation situation arises either in very high modulus matrix or due to the presence of stabilizers. The elastic modulus of the composite will increase with increasing alumina content as the Young's modulus of alumina (380 GPa) is almost twice than that of zirconia (210 GPa). The high matrix modulus also causes a lowering of $M_s$ temperature which further helps in $t$-$ZrO_2$ retention [1.14, 1.15]. Elaborate discussion
on this mechanism can be obtained in the classical works of Claussen [1.9], Becher et al. [1.16] Evans et al. [1.17] Rühle et al. [1.18], Lange [1.19] and others.

In the second method, unstabilized ZrO$_2$ ($m$-ZrO$_2$) is introduced in Al$_2$O$_3$ matrix. As the composite is cooled down from the sintering temperature, the reverse $t\rightarrow m$ transformation takes place spontaneously which cause microcracking of the matrix. These microcracks either dilate by absorbing the crack tip stress or can deflect the propagating crack thereby dissipating the crack energy. This toughening mechanism is known as microcrack toughening. However, this toughening mechanism may not always cause a synergetic increase in strength [1.20].

Stabilization of the tetragonal ZrO$_2$ using dopants like MgO, Y$_2$O$_3$, and CeO$_2$ helps to retain $t$-ZrO$_2$ at room temperature even when the particle size is large, i.e. the dopants increase the critical particle size range for spontaneous transformation. Thus it becomes easy to tailor the toughness by controlling the extent of stress induced $t\rightarrow m$ transformation. The critical volume fraction of ZrO$_2$ required for the peak toughness depend on zirconia particle size. The fracture toughness, strength and hardness of sintered ceramics increase with the transformable tetragonal phase retention and are maximum when the crystallite size reaches the critical value for stress induced transformation. In this respect, care must be taken to optimize the sintering temperature and amount of stabilizer added since the matrix is required to reach the high density in order to provide the necessary matrix constraint to zirconia particles.

The key factors that decide the achievement of optimum fracture toughness and strength of ATZ and ZTA are volume/weight fraction of ZrO$_2$, particle size of ZrO$_2$, amount of stabilizer - which determines the transformability and degree of mixing (this depends on powder synthesis). These factors can be controlled during powder processing and green consolidation of the ATZ/ZTA composites. In the sintered composites the factors are sintered density, grain size of Al$_2$O$_3$ and ZrO$_2$, position of ZrO$_2$ grains (intergranular or intragranular), shape of ZrO$_2$ grains, distribution of Al$_2$O$_3$ and ZrO$_2$ grains (homogeneous or agglomerated distribution), variation of stabilizer content within different ZrO$_2$ grains [1.21,1.22].
Homogeneous distribution of ZrO$_2$ grains in Al$_2$O$_3$ is the most desirable microstructural feature of an Al$_2$O$_3$-ZrO$_2$ composite. However, in reality, processing difficulties do cause clustering/agglomeration of ZrO$_2$ particles. The ZrO$_2$ clusters grow to large grains during sintering which not only cause densification problems but also reduces $t$-ZrO$_2$ retention as the agglomerated ZrO$_2$ causes spontaneous $t \rightarrow m$ transformation thereby lowering the strength and toughness of the composite. The above problem becomes more pronounced at higher ZrO$_2$ content. This may be one reason why Al$_2$O$_3$-ZrO$_2$ composites have not been studied extensively 35-40 vol% ZrO$_2$ addition. Secondly, due to lower elastic modulus of ZrO$_2$ ($E = 210$ GPa) with regard to that of Al$_2$O$_3$ ($E = 380$ GPa), the overall elastic modulus is lowered quite significantly at higher ZrO$_2$ content. This factor also adversely affects the retention of $t$-ZrO$_2$ in the alumina matrix and thus the overall toughness increment.

Depending on the volume fraction of zirconia added to Al$_2$O$_3$, the composites that has been studied till now can be classified into two broad categories viz. (i) ZTA with ZrO$_2$ fraction typically up to 20-30 vol% ZrO$_2$ dispersed in Al$_2$O$_3$ and (ii) ADZ with low fraction of Al$_2$O$_3$ (10-20 vol %) distributed in ZrO$_2$ matrix. However, research have been rather limited on the composites having higher volume fraction of ZrO$_2$ (>30 vol %) in Al$_2$O$_3$ or more typically containing equal volume fraction of both phases. One school of thought opined that the toughness and strength increment will not be significant due to possibly low amount of retained $t$-ZrO$_2$. It is predicted that the microstructure of such a composite will be heavily microcracked leading to low fracture toughness. People who disagreed with this theory were of opinion that retention of $t$-ZrO$_2$ may be possible if densification can be lowered to below that of the critical transformation temperature. It is further suggested that $M_s$ temperature can be considerably reduced by controlling the dopant type and amount. The combined effect of smaller grain size and stabilizing oxide may act to retain $t$-ZrO$_2$ even in high or equal volume fraction of Al$_2$O$_3$-ZrO$_2$ composites. The other possible objection for Al$_2$O$_3$-high ZrO$_2$ composites is the increased softness (ZrO$_2$ is softer) of the composites due to the higher amount of ZrO$_2$ and this factor may limit its use as a structural ceramics. However, while accepting the fact that the overall hardness of the composites will be lowered due to higher ZrO$_2$, the situation is expected to change once the ZrO$_2$ undergoes stress induced $t \rightarrow m$ transformation and the matrix may be
became hard. Thus, in the light of the above discussion, it may be summarized that the study of Al$_2$O$_3$-ZrO$_2$ containing equal volume fraction of Al$_2$O$_3$ and ZrO$_2$ (with ZrO$_2$ in both unstabilized and stabilized form) may prove interesting both from understanding the transformation behavior as well as from property upgradation viewpoint. One more obstacle which may become critical is the microstructural coarsening or clustering of ZrO$_2$ at high ZrO$_2$ loading which may change the ZrO$_2$ grain size. But at this stage, it is presumed that if solution chemistry routes are adopted for the processing these composites, many of the above mentioned difficulties may be tackled.

The processing routes adopted for fabricating the Al$_2$O$_3$-ZrO$_2$ composites do play a vital role in deciding the final properties of the sintered composites. It has been reported that the addition of ZrO$_2$ in Al$_2$O$_3$ reduces the grain growth tendency of Al$_2$O$_3$ but it also affects the compact sinterability. Lange [1.23] observed that the densification behavior of the Al$_2$O$_3$-ZrO$_2$ composite depend on the pore coordination number which in turn depends on the volume fraction of ZrO$_2$ and its packing behavior. It has been reported that the uniform distribution of Al$_2$O$_3$ and ZrO$_2$ can be achieved if the starting particle size of both Al$_2$O$_3$ and ZrO$_2$ is very small (nano range). Fine starting particle sizes can also give rise to several other advantages: (i) it can cause high packing density if agglomeration tendency can be controlled, (ii) finer particle size can considerably reduce the sintering temperature and increase the sintered density, (iii) dense fine grained microstructure can give rise to super plastic effect in the composites. However, all the above advantages could be realized if the agglomeration behaviour could be controlled and high density of the composite could be achieved. Extensive research has been carried out on the agglomeration tendency of fine powder of Al$_2$O$_3$ and ZrO$_2$ [1.24] which cites the importance of processing routes, nature of the solvents on the agglomeration behavior etc.

Presently, submicron or nano size Al$_2$O$_3$-ZrO$_2$ composites are mainly processed through solution chemistry routes like sol-gel [1.25], combustion synthesis [1.26-1.27], coprecipitation [1.28], gel-precipitaion [1.29], slurry compaction [1.30] etc.

Although these individual routes have subtle variations as dictated by their precursors, mixing techniques, processing conditions etc, all of them use solution based precursors
for intimate mixing and aim to produce a homogeneous mixture of sub-micron or nano size materials. In many cases, the initial mixture is found be amorphous or partially crystallized. The use of solution precursors not only ensures homogeneous mixing at the molecular level but it also ensures crystallization of fine particles. Such powder due to its extremely high surface area have high reactivity and if properly densified can give rise to a nano structured composites provided post processing problems can be successfully tackled. Further, it is also observed that because of intimate mixing of precursors in the solution stage, powder prepared through these routes show many metastable phases which are absent in the powder prepared through conventional solid state routes and these metastable phases play crucial role in determining the final microstructure and hence the final properties of the sintered composites [1.31].

On the negative side of the solution chemistry route, it is often noted that the residual anions affect the phase evolution, agglomeration behaviour and sinterability of the powder. Residual chloride ions reduce the crystallization temperature of the powder. However, they go off at very high temperature leaving behind large voids which reduces the final sintered density. For this reason, chloride precursors need some extra post precipitation processing steps for overcoming the densification problem [1.32]. Nitrates, sulphates, and citrates precursors similarly have their characteristic problems.

Summarizing the above discussion, it can be said that the optimization of the microstructure – mechanical properties of Al₂O₃-ZrO₂ composites depends both on the characteristics of the starting powder, the fabrication and densification route that will be adopted for shaping and densification of the composites as well as on the type of precursors that are being used for powder processing.

Therefore, the present work proposes to study the processing and characterization of Al₂O₃-ZrO₂ (50:50 v/v) composites. The effect of precursors and post precipitation processing (washing) on the phase evolution, tetragonal ZrO₂ retention and densification behavior will be studied along with mechanical properties like strength, toughness and hardness. Optimization of microstructure and properties will be carried out through controlled processing, optimized sintering schedule and the use of Y₂O₃ as stabilizer for
ZrO₂ for fine tuning the mechanical properties. In the light of the above discussion, the entire problem has been elaborated in five different chapters besides this chapter.

The literature on ZTA and related materials is discussed in Chapter II. The chapter begins with a general review on the different transformation mechanism involving zirconia (ZDC, ATZ and ZTA) and the different transformation models available, followed by the different powder processing routes that are adopted for processing of ZDC, ATZ and ZTA, their relative advantages and disadvantages, the importance of post precipitation washing on the densification behavior during sintering. This is followed by the literature on sintering behavior, sintering models, the role of Al₂O₃, residual ions and pore coordination number etc on the densification mechanism of ZDC, ATZ and ZTA ceramics. The chapter ends with a detailed literature review discussing the mechanical properties-microstructure relationships in different of ZDC, ATZ and ZTA ceramics.

Chapter III elaborates the work plan and methodology for carrying out the proposed study.

Chapter IV discusses the experimental procedure and the different experimental parameters involved during powder processing, densification of the composites as well as mechanical property evaluation (strength, toughness, hardness, thermal shock resistance) of Al₂O₃-ZrO₂ composites and microstructural studies.

Chapter V discusses the results and the related discussions involving the processing of Al₂O₃-ZrO₂ composites (with undoped ZrO₂). The chapter clearly demonstrates why precipitation route for powder preparation is better than gelation route, the adverse effects of chloride ions and the advantages of water/alcohol washing on the agglomeration behavior and sintered density. The chapter also discusses the advantages of using nitrate precursors and the reasons for not retaining higher amount of t-ZrO₂ in the sintered composites. The isothermal and non isothermal densification behavior and the mass transport mechanism of Al₂O₃-ZrO₂ composites (with undoped ZrO₂) during the initial stage of sintering have been discussed. The effects of Y₂O₃ doping on the sintering mechanism, density and t-ZrO₂ retention have also been separately discussed.
Chapter VI discusses the effect of $\text{Y}_2\text{O}_3$ doping on the strength, toughness and hardness of ZTA composites. The correlation between microstructure and properties is also elaborated and the effect of grain boundary phase on the crack propagation behavior is also discussed. At the end, the thermal shock resistance behavior of some selected ZTA compositions has also been discussed.

Chapter VII summaries the results of the present investigations with the possible directions for future work.
References


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Chapter II

Literature Review
Ever since the classical paper by Claussen [2.1] discussed the effectiveness of ZrO$_2$ in increasing the fracture strength of Al$_2$O$_3$, Al$_2$O$_3$-ZrO$_2$ compositions have been widely used for the last three decades. Immediately after Claussen, Lange [2.2-2.5] published a series of four papers which discussed the thermodynamics of constrained phase transformation with reference to critical size of ZrO$_2$ required for $t$-ZrO$_2$ retention, physics of transformation toughening leading to the increased fracture toughness of stabilized ZrO$_2$ containing composites as well as the validation of the theory with the experimental observation in Al$_2$O$_3$-ZrO$_2$ system. For the next three and half decades, numerous researches have been conducted on the different aspects of Al$_2$O$_3$-ZrO$_2$ composites. Owing to the density difference between Al$_2$O$_3$ and ZrO$_2$, the processing of Al$_2$O$_3$ and ZrO$_2$ has been of concern and extensive literatures are available on the different aspects of powder processing. The need for uniform dispersion of Al$_2$O$_3$-ZrO$_2$ composites have also been addressed by many researchers along with the different processing techniques adopted for achieving uniform dispersion. The mechanical properties, viz, strength, toughness and hardness, thermal shock resistance as well as aging behavior are controlled by microstructure and therefore many literatures are also available on this aspect. In view of the large numbers of available literature, in the present study, the available literature has been discussed under four different headings. These are transformation toughening mechanism, processing of Al$_2$O$_3$-ZrO$_2$ composites, densification behavior of Al$_2$O$_3$-ZrO$_2$ composites and finally microstructure and mechanical properties.

2.1 Transformation Toughening Mechanism

The basic idea behind the development of any transformation toughened ceramics is the retention of $t$-ZrO$_2$ in a metastable state and to ensure that this $t$-ZrO$_2$ undergo stress induced $t \rightarrow m$ ZrO$_2$ transformation in the stress field of an advancing crack tip at stress level not exceeding the material fracture strength. Thus this transformation acts as a crack shielding mechanism. These prerequisites are met through composition control, use of stabilizer for ZrO$_2$ (which shifts the critical particle size for $t$-ZrO$_2$ retention to higher value) as well as by controlling $M_S$ temperature closer to room temperature (this helps to prevent spontaneous $t \rightarrow m$ ZrO$_2$ transformation during cooling from the sintering
temperature. For a single or a multiphase brittle ceramic material/composite, [2.6, 2.7] the fracture toughness is given by

$$K_{ic} = K_o + \Delta K_C$$

(2.1)

where, $K_o$ is the matrix toughness and $\Delta K_C$ is the contribution to the toughness from various crack shielding mechanism [2.8]. In the case of zirconia dispersed ceramics (ZDC), the stress induced $t \rightarrow m$ ZrO$_2$ transformation may increase the toughness through a change in the transformation zone shape. The volume change (4-6%) and the strain energy associated with the above transformation generate a compressive strain field around the crack tip which acts to stop or retard the crack tip propagation. Further increase in toughness can be realized from the microcracking associated with the $t \rightarrow m$ ZrO$_2$ transformation, the associated strain energy and the crack deflection by microcracks [2.9].

The three principal crack shielding mechanisms operative in the ZDC or other tough ceramics are transformation toughening ($\Delta K_{CT}$), transformation induced microcrack toughening ($\Delta K_{CM}$) and crack deflection toughening ($\Delta K_{CD}$) [2.10, 2.11]. The extent of contribution by each of the above mechanisms is controlled by the morphology, size, shape, volume fraction and distribution of ZrO$_2$.

Either the energetic or the mechanistic approach is used to understand and develop the transformation toughening behavior and the resultant change in overall toughness. Both the approaches assume that the starting material is isotropic and the transformation effect diminishes from the crack tip to the surface or bulk [2.12-2.14]. The contribution of stress induced phase transformation to the overall toughness is given

$$\Delta K_{CT} = \frac{\eta E^* e^T V_f \sqrt{h}}{(1 - \nu)}$$

(1.1)

where, $\eta$ depends on the zone shape at the crack tip as well as on the nature of stress field, $E^*$ is the effective modulus of the material, $e^T$ is the dilation strain, $V_f$ is the volume fraction of $t$-ZrO$_2$ actually transformed, $h$ is the zone depth and $\nu$ is the Poisson ratio.
The effective matrix modulus $E^*$ controls the extent of dilatational strain [2.12]. Matrix materials having a high elastic modulus (Al$_2$O$_3$) ($E^* \approx 380$ GPa, $\nu = 0.2$) is more effective in constraining the transformation ($E_{ZrO2} = 210$ GPa, $\nu = 0.3$). This factor although helps to retain ZrO$_2$ in tetragonal form but also opposes the stress induced $t \rightarrow m$ ZrO$_2$ transformation because the volume change has to work against a greater constraining force. In ZDC materials, although the room temperature toughness may be high, it decreases at high temperature due to the increased stability of $t$-ZrO$_2$ at high temperature. However, there are reports that some ZDC materials may retain high toughness at elevated temperature through additional toughening mechanism [2.15].

In most of the transformation toughened ceramics, strength is inversely related to toughness. Swain [2.16] observed that for achieving toughness $> 8$ MPa$\sqrt{m}$, the strength need to be sacrificed. It was noted that for $K_{IC} < 8$ MPa$\sqrt{m}$, the strength value is flaw controlled while for $K_{IC} > 8$ MPa$\sqrt{m}$, it is controlled by the extent of transformation toughening.

2.2 Transformation Toughening Models

The two widely accepted models are either based on linear elastic fracture mechanics proposed by Evans [2.10] and McMeeking [2.12] or based on energy changes or work of fracture model proposed by Budiansky et al. [2.13]. Evans [2.10] and McMeeking [2.12] considered that only the dilatational strain was effective during the transformation and within the transformation zone and that the transformation was uniform. However, the model proposed by Budiansky et al. [2.13] computed the energy balance analysis for the transformation with a dilatational strain as well as considering that the transformation strain is not uniform throughout the transformation zone. Budiansky et al. further suggested that both the models were equivalent once steady state cracking condition is reached. This assumption was later corroborated by Rose [2.17].

The other factor that can affect the toughness calculation using the two existing models is the degree and nature of transformation (i.e. whether supercritical or subcritical toughening). The supercritical transformation implies complete transformation taking place within the process zone and zero transformation outside the process zone. This
kind of step function type transformation is probably unrealistic and a gradient in the volume fraction of transformed material across the process zone provides a more realistic picture of the actual transformation i.e. transformation is more likely to be subcritical [2.13]. Marshall et al. [2.18] and Yu et al. [2.19] have experimentally observed this type of transformation behavior in Mg-PSZ and Ce-TZP-Al$_2$O$_3$ system. From the toughness prediction view point, supercritical transformation overestimates the toughening and subcritical transformation (a more realistic assumption) results in reduction of predicted toughness by a factor of two. Budiansky et al. [2.13] also introduced a parameter “intensity of the transformation” defined as

$$\omega = \frac{1 + \nu EV_t e^T}{1 - \nu \sigma_T}$$  \hspace{1cm} (2.2)

where, $E$ is the elastic modulus, $\nu$ is Poisson’s ratio, $V_t$ is the volume fraction of transformed material, $e^T$ is the transformation strain and $\sigma_T$ is the critical stress required to initiate the transformation process. A large value of $\omega$ ($>> 1$) denotes intense or strong transformation which can be realized if the $M_s$ temperature is close to the test temperature and only a small stress is required to initiate the transformation ($\sigma_T$ is small).

Still another important factor which can affect the toughness prediction is the nature of transformation, i.e. whether it is pure dilatational, pure shear or a mixture of shear and dilatational. Table 2.1 provides the different values of $\eta$ considering different strain couplings when dilatation model is considered. $\eta$ is $0.214/(1-\nu)$ for supercritical transformation and it is $0.107/(1-\nu)$ for subcritical transformation. However, this type of strain conditions could not account for the experimentally observed toughness, which in many cases was higher by a factor two. Evans [2.20] proposed that both dilatational and shear transformation need to be operative to account for the experimental value of toughness and using this proposal Lambropoulos [2.21] suggested $\eta = 0.55$ [i.e., $0.385/(1-\nu)]$. Comparable values were obtained by other workers, a comprehensive list of which is provided in Table 2.1. The shape and size of the process zone also affects the toughness enhancement. Usually, three types of process zone are observed – underdeveloped, fully developed and partially developed. When the process zone
remains only in front of the crack tip of the propagating crack, the main crack lies in the untransformed material. Under this condition, the application of load changes the zone shape similar to that of dilatational strain, which interacts only with the crack tip.

Table 2.1 Comparison of toughening model predictions with the value of \( \eta \)

<table>
<thead>
<tr>
<th>Model</th>
<th>Transformation initiation stress</th>
<th>Transformation Strain ((e^\eta))</th>
<th>Constant ((\eta))</th>
</tr>
</thead>
<tbody>
<tr>
<td>McMeeking and Evans</td>
<td>Hydrostatic</td>
<td>Volume change</td>
<td>0.214</td>
</tr>
<tr>
<td>Budiansky et al.</td>
<td>Hydrostatic</td>
<td>Volume change</td>
<td>0.214</td>
</tr>
<tr>
<td>Evans and Cannon</td>
<td>Shear bands</td>
<td>Volume change</td>
<td>0.38</td>
</tr>
<tr>
<td>Lambropoulos</td>
<td>Maximum principal stress</td>
<td>Uniaxial dilatation</td>
<td>~0.37</td>
</tr>
<tr>
<td>Lambropoulos</td>
<td>Volume change and reduced shear</td>
<td>Volume change and reduced shear</td>
<td>~0.22</td>
</tr>
<tr>
<td>Chen and Reyes-Morel</td>
<td>Shear and volume change</td>
<td>Volume change</td>
<td>0.48</td>
</tr>
<tr>
<td>Swain</td>
<td>Experimental</td>
<td>Volume change</td>
<td>0.45</td>
</tr>
<tr>
<td>Chen and Reyes-Morel</td>
<td>Experimental</td>
<td>Volume change</td>
<td>0.22-0.32</td>
</tr>
</tbody>
</table>

For such a case, integration of the tractions along the transformation zone boundary shows that \( \Delta K_{CT} \) is zero and no toughening is observed due to the transformation effect (Fig. 2.1 a, b) [2.21, 2.22]. When the transformation process zone fully encompasses the main crack (and not the crack tip only), it exerts closer tractions on both the crack surface and the zone boundary (Fig. 2.1c, d). Integration of these tractions over the transformation zone gives the maximum toughness increment same that as Eqn. (2.1). However, when the transformation zone partially covers the crack, R-curve behavior is observed and \( \Delta K_C \) increases with the increase in crack length \((\Delta a)\), and the approximated \( \Delta K_C \) is given by

\[
\Delta K_C \approx \left[ \frac{0.44}{\pi(1-v)} \right] \frac{E e^\eta V f}{\tan^{-1} \left( \frac{\Delta a}{h} \right)}
\]

(2.3)
In the end, it can be said that nature of transformation is dependent on material properties like grain size, dopant concentration, and volume fraction of ZrO₂ etc. and the theoretical prediction of toughness increment varies from model to model. However, closer matching of the theoretical and experimental toughness could be obtained for
cases where the transformation was assumed to be subcritical and both shear and
dilatant transformation strain was considered in the model.

2.3 Other Toughening Mechanisms for ZTA Ceramics

Besides transformation toughening two other toughening mechanisms are also effective
for ZTA ceramics. They are toughening by crack deflection toughening through the
generation of compressive surface layer, and other energy dissipating mechanisms.

2.3.1 Toughening by Crack Deflection

Localized residual stress fields are generated during any type of phase transformation
involving volume change or due to thermal expansion mismatch between the two phases
or arising from the fracture of a second phase. This residual stress field can deflect the
main propagating crack thereby causing toughening of the composite. The extent of
toughening depends on the reduction in the force on the deflected portion of the
propagating crack. However, for crack deflection involving second phases particulates,
the extent of deflection and thereby the toughness increment is dependent on the
volume fraction of second phase particles, its morphology and aspect ratio [2.21-2.26].

2.3.2 Toughening by the Generation of Compressive Surface Stress

The compressive strains are generated during the volume expansion and shear strain
developed during controlled $t\rightarrow m$ ZrO$_2$ transformation. The presence of these surface
compressive stress (500 to 1000 MPa and concentrated in a depth of about 20 µm) acts
to toughen and strengthen the ZTA ceramics because the crack has to overcome these
compressive stresses before it can propagate. The compressive stress can be generated
through various processes like grinding [2.25], impact [2.26] and low temperature
quenching [2.27].

2.3.3 Toughening by other Energy Dissipating Mechanisms

The transformation twins due to $t\rightarrow m$ transformation and the associated coherency loss
are energetic process and results in the lowering of crack tip stress intensity. This also
can result in a toughness increment [2.9]. Usually, the stress induced transformation are
irreversible in nature but under certain conditions the transformation becomes reversible
on removal of the applied stress or in the wake zone. Rice [2.28] and Marshall [2.29] have noted that this transformation due to change of stress state can affect the extent of toughening in ZTA ceramics. Crack branching by secondary phase present in the matrix by the localized stress fields can also cause toughening effect. Wang [2.24] has noted crack branching effect in ZTA duplex structures, containing large PSZ or TZP agglomerates.

2.4 Toughening in Zirconia Toughened Al₂O₃ system

The two previous sections summarized the generalized toughening mechanisms in ZrO₂ and ZrO₂ based ceramics. In this section, the different toughening mechanisms operative in ZTA system has been briefly discussed. The main idea of introducing ZrO₂ in Al₂O₃ matrix is to increase the resistance to crack propagation or in the other words to increase the fracture toughness ($K_{IC}$). ZTA systems have been mostly used as grinding media, cutting tool inserts. The ZrO₂ has been introduced either as unstabilized ZrO₂ or as TZP. The toughening mechanisms that are operative in ZTA are stress induced transformation toughening, microcrack toughening as well as crack deflection. While the effect of stress induced transformation toughening and crack deflection on the toughness and strength are additive in the increase in toughness due to the combined effect of transformation, microcrack toughening may not cause a concurrent increase in strength. The decrease in strength in heavily microcracked ZTA is caused by a lowering of matrix elastic modulus. Evans [2.30] has discussed the characteristic features of crack shielding mechanisms exhibited by the nonlinearity in the stress – strain curve above a critical transformation stress ($p_i$). At the transformation condition and within the transformation zone, the strain becomes discontinuous, which lowers stress state at the crack tip provided that the transformation strain has the same sign as that of crack tip. The lowering of crack tip stress causes crack shielding and helps to increase the fracture toughness.

2.5 ZTA Powder Processing

In the previous section, it has been elaborated that a uniform dispersion of ZrO₂ in Al₂O₃ matrix is required for significant improvement in strength and toughness of ZTA ceramics. An optimized processing route of sufficient quality ensures minimum density
variation and small scale of the residual flaw population and absence of large scale porosity/flaws. These two factors result in a ZTA microstructure in which stress induced $t \rightarrow m$ transformation takes place during the crack propagation. Ideally, this calls for sufficient microstructural integrity for sustaining the stress level which is required for activating the $t \rightarrow m$ ZrO$_2$ transformation and necessitates a close control of processing parameters for achieving uniform dispersion of both the phases (Al$_2$O$_3$ and ZrO$_2$). The processing route also affects the morphology and size of ZrO$_2$ grains. Solid state route has been traditionally used to prepare the ZTA powder mix but the mixing is nonuniform (particularly at higher ZrO$_2$ loading) and may also cause segregation of Al$_2$O$_3$ and ZrO$_2$ due to wide difference in density. Chemical precipitation routes mostly ensure uniform mixing of Al$_2$O$_3$ and ZrO$_2$ at any concentration level, but it usually gives spherical and smaller particles which are usually difficult to transform. The other negative aspect of these routes is the tendency for hard agglomerate formation during powder processing and drying (due to the formation of Zr-O-Zr or Al-O-Al bonds). This hampers densification, which in turn affects the end properties. Other processes like alkoxide sol-gel, CVD or reactive processing has also been used and each of them has their specific advantages and disadvantages and depending on the desired properties or applications one or the other type of powder processing route are adopted by researchers. Besides powder processing, consolidation or shape forming method may also affect the microstructural integrity and the end properties. The function of the powder processing finishes at the powder stage itself, but even a homogeneous powder may not yield good properties due to problems in shape forming operations. Besides uniaxial dry pressing, the other major shape forming operations are cold isostatic pressing, slurry compaction, centrifugal casting, reactive hot pressing, hot isostatic pressing, spark plasma sintering etc. All of these different shape forming operations also aim to reduce the processing flaws as well as enhance the microstructural homogeneity and structural integrity. In this section, a summary of the literature on the different ZTA powder processing route as well as their shape forming results have been summarized.

The initial papers on Al$_2$O$_3$ – ZrO$_2$ composites were based on mixing of Al$_2$O$_3$ and ZrO$_2$ powders (solid state mixing). Usually two mixing methods – dry and wet mixing was being used. The wet mixing method generally produced a better dispersion and
compositional homogeneity in comparison to dry mixing but the chances of segregation or agglomerate formation was higher in the latter case. However, due to ease of operation, till date, this method has been preferred by many researchers. Claussen [2.1] prepared Al$_2$O$_3$ – unstabilized ZrO$_2$ composite powder mix by wet mixing of Al$_2$O$_3$ and ZrO$_2$ in planetary mill. The wet slurry was dried and hot pressed in graphite die under vacuum at 1400°C.

Lange [2.5] also prepared Al$_2$O$_3$-Y$_2$O$_3$(ZrO$_2$) composite containing different volume fractions of ZrO$_2$ by dry mixing of Al$_2$O$_3$ and ZrO$_2$ while yttrium nitrate was used for Y$_2$O$_3$. The powder mix was wet milled, dried and cold isopressed. The bars were sintered in air at 1400, 1500 and 1600°C depending on the composition.

Liu et. al. [2.31] prepared Al$_2$O$_3$ - 2YTZP composites by ball milling a mixture of Al$_2$O$_3$ powder and hydrothermally prepared 2Y-TZP. The milled powder was calcined at 600°C for 3 hours and sintered in air at 1450, 1550 and 1600°C. Basu et al. [2.32] studied ZrO$_2$-Al$_2$O$_3$ (72:28 volume ratio) composites, where ZrO$_2$ was introduced either as Y-TZP or as a mixture of unstabilized ZrO$_2$ and Y$_2$O$_3$. The ZrO$_2$-Al$_2$O$_3$ powder mix was mixed in propanol medium. The composites were cold compacted and hot pressed at 1450°C. Huang et al. [2.33] used solid state mixing to prepare Ce - TZP/Al$_2$O$_3$ composites.

Chemical synthesis routes like co-precipitation, chemical polymerization, destabilization of mixed sols, ammonolysis have been widely used for preparation of different single and bi-phasic composites. Debsikdar [2.34] prepared 80 Al$_2$O$_3$ – 20 ZrO$_2$(wt %) powders using three different processes like chemical polymerization, destabilization of mixed sols and co-precipitation. The primary particles were amorphous with sizes between 1.5 - 3 nm. The decomposition and crystallization behavior, surface area, pore size as well as tetragonal ZrO$_2$ retention was reported to be dependent on the synthesis chemistry. All the powders could be densified at 1200°C. Chan et al. [2.35] prepared ZTA powder (15 ZrO$_2$/85 Al$_2$O$_3$ vol%) by co-precipitation route using Al(NO$_3$)$_3$ ·9H$_2$O and ZrO(NO$_3$)$_2$·2H$_2$O. The precipitated gels were aged at room temperature for different time periods varying from 0.5 to 40 hours followed by washing with distilled water and ethyl alcohol. The desired composite powder was uniaxially compacted and sintered in air at 1550°C. Large number of intragranular ZrO$_2$ was observed in the as precipitated powder.
due to high grain growth of $\alpha$-Al$_2$O$_3$. The aging treatment reduces the surface area and the grain growth rate was less. Thus most of the intragranular ZrO$_2$ was converted to intergranular ZrO$_2$ along with less number of entrapped pores.

Shi et al. [2.36] reported the processing of nano Y-TZP/Al$_2$O$_3$ composites obtained by co-precipitation from a mixed salt solution of Y$^{3+}$, Zr$^{4+}$ and Al$^{3+}$. It was proposed that in the precipitated powder alumina existed as an amorphous phase within the Y-TZP lattice and later it crystallized as $\alpha$-Al$_2$O$_3$. The presence of Al$_2$O$_3$ in the Y-TZP caused its lattice distortion due to which the crystallite growth of Y-TZP was slow.

Hong et al. [2.37] studied the crystallization behavior of Al$_2$O$_3$-ZrO$_2$ (20 mol %) solid solution powder prepared by co-precipitation method. AlCl$_3$ and ZrOCl$_2$ were used as the precursors. In the calcined gel powder, alumina crystallization followed the sequence bayerite $\rightarrow$ $\gamma$-Al$_2$O$_3$ $\rightarrow$ c-ZrO$_2$ + $\gamma$-Al$_2$O$_3$ $\rightarrow$ c-ZrO$_2$ + $\delta$-Al$_2$O$_3$ $\rightarrow$ t-ZrO$_2$ + $\theta$-Al$_2$O$_3$ $\rightarrow$ t-ZrO$_2$ + $\alpha$-Al$_2$O$_3$. They concluded that the presence of ZrO$_2$ shifted the $\theta$ to $\alpha$-Al$_2$O$_3$ transformation from 1100°C to 1300°C. It was also observed that the crystallization of c-ZrO$_2$ was influenced by the presence of Al$^{3+}$ in ZrO$_2$ lattice.

Upadhyay et al. [2.38] studied the crystallization behavior of 3Y-TZP/Al$_2$O$_3$ (0-20 vol %) composite powder which were prepared by co-precipitation method using ZrOCl$_2$, Y(NO$_3$)$_3$ and AlCl$_3$ as the precursor. They observed that the presence of Al$_2$O$_3$ inhibited the crystallization of ZrO$_2$ and the shifting of the crystallization temperature was directly proportional to the Al$_2$O$_3$ concentration. It was further observed that the nucleation and growth of crystallites in the low temperature region (< 900°C), was interface controlled (inter agglomerate growth) involving short range migration of ions. At higher temperature (>900°C), the growth was intra-agglomerate type causing rapid densification of primary particles.

Enomoto et al. [2.39] made a process study of Al$_2$O$_3$-ZrO$_2$ (10 mol %) nano composite prepared by ammonolysis route. The mixed sol of Al$_2$O$_3$-ZrO$_2$ was prepared by adding Al(NO$_3$)$_3$ aqueous solution to a hydrolyzed ZrO$_2$ sol. Al$_2$O$_3$-ZrO$_2$ composite powder was precipitated (at pH 7) from the mixed sol via four different process (gaseous NH$_3$, concentrated NH$_3$ water (25%), diluted NH$_3$ water at 50°C and diluted NH$_3$ water at 70°C.
under N₂ atmosphere). It was observed that the gradual precipitation process using NH₃ gas (at 70°C) was preferable for avoiding the crystalline bayerite formation and for uniform dispersion of nano ZrO₂ particles in Al₂O₃ precursors.

Besides solid state mixing or precipitation, several investigators have also used aqueous solutions or sols of Al and Zr followed by either gelation or precipitation or by spray pyrolysis. These chemical routes often offer closer control over particle morphology and composition even in multicomponent oxide systems. A series of porous structure (meso & micro) can developed during the sintering process.

Low et al. [2.40] studied the crystallization behavior of gel derived alumina zirconia ceramics prepared from zirconium oxychloride and aluminium isopropoxide. The in situ gelation process allowed highly homogeneous structure. Zirconia accelerated the crystallization of transition alumina to corundum (α-Al₂O₃) through the formation of intermediate solid solution (γ-Al₂O₃ – 4 mol% ZrO₂). The microstructure was very fine and uniform which could be related to the microporous texture of gel structure.

Bala Gopal et al. [2.41] prepared Al₂O₃ – 10 wt% ZrO₂ and Al₂O₃- 5 wt% ZrO₂ powders using aqueous sols obtained through hydrolysis and peptization. The mixed sol was spray dried at a fixed inlet temperature of 175°C. The powders had spherical particles with narrow size distribution. The linear compaction response implied homogeneous powder and similar packing arrangement. Ceria addition was found to favor the densification of alumina.

Jayaseelam [2.42] used sol gel process to prepare three different series of alumina-zirconia compositions: (i) composites with unstabilized zirconia, (ii) composites with 12 mol% CeO₂ - stabilized zirconia and (iii) composites with 3 mol% Y₂O₃-stabilized zirconia of varying amount (5,10,15, 20 and 25 vol% ZrO₂). All the gel compositions were prepared using stable boehmite sol and oxalate of Zr, Ce and Y. It was noted that substantial amount of ZrO₂ remain dissolved in transition alumina lattice and during the transformation process of transition alumina to α-Al₂O₃ the zirconia comes out of the alumina lattice and enters the interstitial and vacant lattice sites causing expansion of the lattice along the a-axis. The Zr⁴⁺ exerts dragging force on Al³⁺ thereby shifting the α-
Al₂O₃ transition to higher temperature. Similarly, the presence of alumina grains provides a constraining force to the grain growth of ZrO₂ and it also helps to retain τ-ZrO₂.

Chatterjee et al. [2.43] prepared Al₂O₃-ZrO₂ microspheres with Al₂O₃:ZrO₂ molar ratios as 87:13, 78:22, 74:26 and 64:36 by sol emulsion gel synthesis method. It was observed that the surfactant concentration and sol viscosity controlled the characteristics of derived microspheres. The gel crystallized at 900°C and retained some τ-ZrO₂ even after sintering at 1600°C. The retention was related to the smaller grain growth of ZrO₂.

Lee et al. [2.44] studied the TEM microstructure of sol-gel synthesized Al₂O₃-50 wt% ZrO₂ (Y₂O₃) nano-composites. The composites were prepared through a sol-gel process using Al - sec butoxide and Zr-butoxide. The as prepared amorphous powder showed the normal c→t ZrO₂ transformation at 1200°C. However, due to the nano size powder, alumina remained in the amorphous state till 1050°C and converted to α-Al₂O₃ at 1200°C.

Chandradass et al. [2.45] prepared Al₂O₃- (5, 10 15 wt%) ZrO₂ composite microspheres by sol gel method using Al-tri-isopropoxide and ZrOCl₂. α-Al₂O₃ crystallization was shifted to 1290°C and the shift was attributed to the pinning effect of Zr⁴⁺ ions which came out of amorphous alumina during heating. While only α-Al₂O₃ and ZrO₂ was observed for Al₂O₃ – 5 wt% ZrO₂ composition, it was a mixture of α-Al₂O₃, τ-ZrO₂ and m-ZrO₂ for 10 and 15 wt% ZrO₂ compositions. The appearance of m-ZrO₂ at higher ZrO₂ content was due to growth of ZrO₂ particles beyond the critical size.

Recently, Palmero et al. [2.46] has prepared Al₂O₃-ZrO₂ and Al₂O₃-YAG composite material by post doping of α-Al₂O₃ powder either with Zr-alkoxide or with yttrium methoxide respectively. The Al₂O₃-ZrO₂ composite had 95 vol% Al₂O₃ and 5 vol% ZrO₂. The synthesized powder was very fine and could be sintered at 1500°C for 3 hours.

Gilan et al. [2.47] prepared Al₂O₃-ZrO₂ (Y₂O₃) nano powders containing 5, 10, 15 wt% ZrO₂ by aqueous sol-gel method using Al—sec-butoxide and Zr-butoxide as precursors. An increase in ZrO₂ content reduced the powder surface area and it also shifted the transition alumina to α-Al₂O₃ temperature to a higher temperature.
Bhattacharyya et al. [2.49] have used a simple gel-precipitation method to prepare Al₂O₃-ZrO₂ (50 vol %) composites starting with inorganic precursors of AlCl₃ and ZrOCl₂. In this process, the concentration of the starting solution is increased to such an extent that during gelation process, when the gel becomes fully viscous, a substantial portion of the starting solute (or metal ions) are in solution. During the drying of gel, the solute precipitates out in the pores of the hydroxide network. In this process, the two cations may be precipitating at different rates between the hydroxide network and the liquid phase.

Colloidal processing is another important processing route which helps to achieve uniform dispersion of particles in single and multicomponent oxide systems. The particle dispersion is achieved by controlling the electrosttic/electrosteric repulsion by changing the suspension pH. A homogeneous particle dispersion in suspension helps to improve the microstructure as well as the sintered density. In the following section, a summary of the available literatures on the colloidal processing of Al₂O₃-ZrO₂ is presented.

Novak et al. [2.50] correlated the electrokinetic properties of ZrO₂ to the rheology and microstructure of Al₂O₃-ZrO₂ suspensions. They observed that the adsorbed ions (CO₃⁻, Cl⁻) do affect the isoelectric point of both Al₂O₃ and ZrO₂ as well as of their mixed suspension. Washing/ageing of the ceramic particles prior to suspension making is expected to improve the dispersion and densification as well as the sintered microstructure.

Ramakrishnan et al. [2.51] noticed that due to the difference in pH range of stability of Al₂O₃ and ZrO₂, their mixed suspension exhibited heterocoagulation. Experimental results indicated while the suspension is stable either below pH 6; zirconia is stable either below pH 6 or above pH 8. For mixed suspension of Al₂O₃-ZrO₂, the suspension is unstable between pH 7 and 9. They concluded that at pH level where the surface charge is high enough to counter the vander waal attraction, the suspensions are stable and the reverse is true at pH level close to isoelectric point.

Suzuki et al. [2.52] studied the dispersion behavior of Al₂O₃-ZrO₂ suspension and observed that additional redispersion treatment like ultrasonication helps to produce
dispersed suspension by preventing the agglomeration tendency of fine particles. Compacts prepared from ultrasonicated suspension (ultrasonication power 160 w) exhibited more that 55% elongation as a result of extremely fine and uniform microstructure resulting from colloidal processing.

Working with aqueous or nonaquous colloidal suspension allows one to go for complicated shaping. This particular aspect was studied by Daskobler et al. [2.53] who prepared ZTA composites with corrugated microstructure. They used non-polar suspension of alumina and zirconia of high solid loading for making thick Al₂O₃ and ZrO₂ tapes by tape casting. Corrugated composite structure was prepared by repeated rolling and folding of the stacked tapes.

Sarraf et al. [2.54] studied the fabrication of fine grained Al₂O₃-ZrO₂ composites through optimized colloidal processing. Highly dense and uniform sintered microstructure was obtained on sintering at 1510°C. The results suggested that the optimized rheological behavior of Al₂O₃-ZrO₂ suspension is likely to influence the microstructure of sintered Al₂O₃-ZrO₂ composites.

Combustion technique or solution combustion synthesis method uses the combustion of a redox mixture. The process is advantageous because (i) it is simple and can be up scaled easily, (ii) easier and faster (iii) with proper choice of fuel, α-Al₂O₃ can be obtained at a low temperature, and (iv) yields homogeneous powder mixture of high purity. An excellent review of different combustion processing and their applicability have been carried out by K. C. Patil et al. [2.55]. Following are the summary of the literatures on ZTA processing by combustion synthesis.

Wu et al. [2.56] reported the processing of nano powders of alumina and zirconia using sucrose as a chelating agent and using the corresponding metal nitrates as the precursors. The prepared powder was in the nano size range and had good sintered density. The authors commented that the sucrose template method could be applied to multicomponent nano oxide systems.

Biamino et al. [2.57] prepared nanostructured ZTA composites (Al₂O₃-20 vol% 3Y-TZP) by solution combustion route using urea as fuel. The authors tried a two step process in
which firstly 3Y-TZP was obtained through the combustion reaction followed by dispersion of 3Y-TZP in a solution of Al(NO₃)₃ and urea which was then combusted for the second time. On the other hand, in single stage process, all the metal nitrates (Zr, Y, Al) were simultaneously added to prepare a mixed nitrate solution followed by the combustion in single step. They observed that in the single step processing a superior homogeneity of zirconia and alumina was achieved and it also allowed a higher retention of t-ZrO₂ at room temperature.

Kingsley et al. [2.58] developed a novel combustion process for the synthesis of α-Al₂O₃ and oxide materials including Al₂O₃-ZrO₂ composites. The authors used metal nitrates as the oxidizers and urea as fuel to produce ultrafine powders of Al₂O₃-t-ZrO₂ composites.

S.T. Aruna et al. [2.59] prepared nanocomposites through a modified solution combustion approach using a mixture of fuels. ZTA-1 was prepared from the corresponding metal nitrates and urea and had an average particle size of ~37 nm. ZTA – 2 was prepared from metal nitrates and a mixture of fuel (ammonium acetate, urea and glycine) with an average particle size of < 10 nm. It was observed that the above fuel mixtures changed the energetic of combustion reaction and the final properties of the composite.

Zhao et al. [2.60] prepared Al₂O₃-ZrO₂ (Y₂O₃) self growing composites prepared by combustion synthesis under high gravity condition (> 200g). The prepared ceramics had triangular dispersion of orderly nano-submicrometer t-ZrO₂ fibres, surrounded by either inter colony regions containing micrometer size –ZrO₂ spherical grains.

Kikkawa et al. [2.61] used two types of solution synthesis method for processing of (Y₂O₃) ZrO₂–Al₂O₃ binary system. In the first route, the precursors were yttrium chloride, zirconyl chloride, aluminium chloride with citric acid as fuel and the powder was prepared by combustion synthesis. In the second method, composites were prepared by coprecipitation of metal chlorides by freezing the mixed aqueous solution under microgravity. Microgravity was found to be effective in obtaining both good crystallinity and good mixing of metal salts precipitated from aqueous precursors.
Beitollahi et al. [2.62] studied the synthesis of Al₂O₃-ZrO₂ nanocomposite through a modified sol-gel route using sucrose, poly vinyl alcohol and metal nitrates. α-Al₂O₃ crystallized at 1200°C or above and ε-ZrO₂ at lower temperature.

The available literature shows that ZTA are mostly prepared by one of the above discussed routes. Among them, sol-gel and co-precipitation have been commercially up scaled to prepare many ZTA components. Combustion synthesis has also become popular because of its certain distinct advantages in comparison to other solution based routes. However, two more routes (viz. hybrid route and hydrothermal route) have also been (and is being) used to process ZTA composites with properties comparable to those obtained by other routes and this review may remain incomplete without referring to those literatures.

Rao et al. [2.63] precipitated hydrous zirconia (from zirconyl chloride) on a suspension of Al₂O₃ for preparing ZTA composites. Subsequently, the composite powder was either slip casted (in the as prepared state) or it was calcined at 500°C followed by dry pressing. The compact from the as prepared powder did not undergo required coarsening and had lower strength after sintering.

Saha et al. [2.64] used the hybrid route to prepare Al₂O₃- Ce-TZP (10 vol%) composite. Ce-TZP was prepared from a sol containing Zr – n-propoxide and Ce(NO₃)₃.6H₂O. Al₂O₃ powder was coated by the zirconia sol and it was gelled, calcined compacted sintered at 1400°C. Fine intergranular zirconia was observed in the Al₂O₃ matrix.

Rao et al. [2.65] processed Al₂O₃–ZrO₂ powders containing 15, 50 and 85 wt% Al₂O₃ via mixing of α-Al₂O₃ powder with Zr(OH)₄ gel. Their objective was to investigate the effect of Al₂O₃ content and the calcination temperature on the ZrO₂ phase composition. They observed that the crystallization temperature of ZrO₂ increased with Al₂O₃ content probably hinting that alumina distorts the ZrO₂ lattice and thereby delays the nucleation and growth of ZrO₂ crystallites.

Mills et al. [2.66] carried out the low temperature synthesis and zirconia doped alumina (5-20 wt% ZrO₂) nanopowder by hydrothermal process at a reaction temperature of
190°C and pressure 4 Kgf/cm². In the as synthesized powder, alumina was present as bayerite and boehmite while in the calcined samples it was $\alpha$-Al₂O₃ and $t$-ZrO₂.

Chandradass et al. [2.67] reported the synthesis of zirconia doped alumina nanopowder by hydrothermal process. Al₂O₃-ZrO₂ composite precursor powder containing 5-20 wt% ZrO₂ had been prepared at 190°C and pressure 4 kgf/cm². Bayerite and boehmite was found in the as synthesized powder. The phases present in the powder calcined at 500 and 800°C are $\alpha$-Al₂O₃ and $t$-ZrO₂. The particle size of alumina was found to be 60-70 nm whereas zirconia was 10-15 nm in the 800°C calcined powder.

2.6 General Literatures on Sintering

In ceramic manufacturing, sintering is a high temperature process which converts loosely bound particle compact in to a dense and cohesive body with a fine grained microstructure. This is usually achieved only when pores are uniformly distributed on grain boundaries which facilitate pore annihilation during final stage of sintering and avoids rapid grain growth [2.68, 2.69]. Usually a green compact made from an initial small particle size and narrow pore size distribution [2.70-2.75] usually sinters to a uniformly dense body.

Agglomerated powders, [2.74-2.76] on the other hand, disrupts the particle packing and produce a spatially heterogeneous green microstructure – a situation usually observed with nanopowder compaction. Such an inhomogeneous microstructure affects densification kinetics as well as the final sintered density achievable [2.76-2.78].

Sinterability could also be improved by controlling the agglomeration tendency during powder processing. The elimination of agglomerates by colloidal processing produces homogeneously packed green microstructure which could be sintered to high density at lower sintering temperature [2.70-2.75, 2.79]. Besides colloidal processing, two step sintering process can also produce a high density, fine grain size sintered body [2.82, 2.83].

The production of dense ceramics from nanocrystalline powders require clear understanding of the fundamental sintering theory as well as sintering models.
Densification and microstructure evolution are interdependent and the densification process is influenced by the mechanism, material transport paths, material flux and mass transport distance [2.68-2.87]. An excellent review by Exner [2.88] discusses the initial stage of sintering kinetics and the controlling parameters. The particle – particle contact during sintering require simple geometrical assumptions for neck area, volume, radius of curvature and diffusion distance. The early models assumed several simple geometric approximations and ignored the possibility of multiple or parallel material transport paths. These simplified assumptions were less accurate when compared with the rigorous mathematical treatments obtained with exact neck shape. However, numerical analysis of the geometrical changes during sintering has been subject to criticism [2.89-2.96].

In the past, isothermal study was the major source of sintering data many of which did not agree well with the theoretical predictions. The discrepancy was partially due to the finite time required for reaching the isothermal sintering temperature and various corrections incorporated in the sintering result to account for the transient events during heating [2.97]. Two key decisions were made in an effort to minimize the experimental errors. Firstly, the use of constant heating rate measurements for establishing the initial events which did not require time or temperature corrections during the heating cycles [2.98-2.102] and secondly, both shrinkage and surface area were measured to monitor the geometric changes and sintering mechanisms. On the other hand, constant rate heating (CRH) method required lesser experimental work. In a single experiment involving slower heating rates, the temperature variation was less across a wide range and steady state could be reached at every temperature [2.103, 2.104].

Several methods had been used for the kinetic parameter calculation from the sintering curves obtained at different linear heating rates. The initial stage sintering activation energy had been obtained from the Arrhenius plots of the shrinkage rate (or densification rate) at equal values of the shrinkage (or density) [2.97, 2.98, and 2.105].

Several integer and differential methods had been applied for the kinetic analysis of a single sintering curve for Y-TZP [2.106-2.110] and result was the product of activation
energy and kinetic law exponent and either of these two parameters needed to be known for evaluating the sintering mechanism. However, both the parameters could not be simultaneously determined from a single nonisothermal experiment. [2.107, 2.108]

2.7 Sintering of Al₂O₃ –ZrO₂ Composites:

Young and Cutler studied the kinetic analysis of the initial stage of sintering in CRH experiment [2.97] for YSZ which permitted simultaneous determination of activation energy as well as the kinetic model from a single CRH dilatometric curve. The results suggested that grain boundary (GB) diffusion dominated the initial stage sintering.

CRH sintering experiments had also been carried out for estimation of the sintering activation energy for sintering of Al₂O₃, Al₂O₃ - 5 vol% ZrO₂ or Al₂O₃ - 5 vol% TiO₂ [2.105]. The kinetic analysis was complicated by grain growth and the later was restricted by controlling powder characteristics by adopting improved colloidal processing. GB diffusion was the dominant densification mechanism. The sintering activation energies were 440 ± 40 kJ/mol for pure Al₂O₃, 585 ± 40 kJ/mol for Al₂O₃ - 5 vol% TiO₂, and 730 ± 60 kJ/mol for Al₂O₃ - 5 vol% ZrO₂.

Wang and Raj [2.109] had investigated the sintering activation energy in two phase Al₂O₃ –5 vol% ZrO₂ ceramics using both CRH and isothermal densification experiments. The activation energy was 700 ± 100 kJ/mol for ZrO₂ content 5 to 95 vol%. In contrast, the activation energy 615 ± 80 kJ/mol for pure ZrO₂ and 440 ± 45 kJ/mol for pure Al₂O₃. The addition of 2.8 mol% Y₂O₃ (as dopant) did not have any measurable influence on activation energy.

High density ultrafine Al₂O₃ - 5 vol% ZrO₂ ceramics had been processed by two-step sintering process [2.110]. First step was CRH experiment (1400-1450°C) and the second step was isothermal sintering (1350-1400°C) for varying time periods, the first step ensured high initial density and the second step increased the density further with a concurrent grain growth. It appeared that ZrO₂ acted to pin down the Al₂O₃ grain growth. The resultant Al₂O₃-ZrO₂ had high density (> 99%) and fine grain size (0.62-0.88 μm) of Al₂O₃.
Green sheets of YSZ/Al₂O₃ nanocomposite ceramics made from coprecipitated powder were densified by pressureless sintering [2.111]. The sintered YSZ/Al₂O₃ sheets were characterized for relative density, grain size, phase, and microstructure. The relative density >95% were obtained for 20-85 mol% YSZ composition. The average grain size of both ZrO₂ and Al₂O₃ decreased at higher YSZ content. YSZ also restricted the rapid grain growth of Al₂O₃.

Al₂O₃-ZrO₂ (1, 3, 5 vol %) nanocomposites prepared from commercial Al₂O₃ and YSZ powder [2.112] were sintered in microwave hybrid sintering. Microwave hybrid fast firing helped in arresting the grain growth of the composite. The resultant microstructure was uniform with small grains, the average grain to particle ratio being 2:1.

The isothermal shrinkage behavior of 2.9 mol% Y₂O₃-ZrO₂/Al₂O₃ (0-1 mol %) was investigated to ascertain the role of Al₂O₃ addition during initial stage of sintering (950-1050°C) [2.113]. Al₂O₃ addition increased the densification rate and mass transport mechanism changed from GB diffusion to volume diffusion.

Huang et al. [2.114] studied the densification behavior of gel precipitated and heterogeneous azeotropically distilled ZrO₂-Al₂O₃ composite powder. High elastic modulus alumina caused pinning effect, blocks Zr⁴⁺(Y³⁺) mass transfer process as well as grain boundary movement. An increase in Al₂O₃ content inhibited ZrO₂ grain growth caused delayed crystallization of ZrO₂ and resulted in high dense and strong composite.

Grain growth behavior in Al₂O₃-ZrO₂ (≤ 5 vol %) had been studied by Nagashima et al. [2.115]. It was observed that even a small amount of ZrO₂ could retard Al₂O₃ grain growth. At lower ZrO₂ percent, majority of ZrO₂ was at intragranular position and this tendency was reduced at higher sintering temperature. The grain growth inhibition of ZrO₂ was in agreement with modified Zener’s pinning model.

Matsui et. al. [2.116] added small amount of Al₂O₃ to fine ZrO₂ powder either by direct powder mixing or alkoxide hydrolysis or homogeneous precipitation and observed the densification behavior by CRH method. Al₂O₃ addition slightly raised the densification onset temperature and simulated the densification above 1100°C. In the isothermal
densification analysis, Al₂O₃ addition retarded the densification rate (in comparison to Al₂O₃ free samples) just after the onset of sintering followed by a significant increase in the densification rate. These results implied that during the initial stage, Al₂O₃ particles pin ZrO₂ particles causing a reduction of densification and in the later stage, Al₂O₃ diffuses to the ZrO₂ surface and enhance the sintering rate.

The influence of Al₂O₃ on sintering and static grain growth behavior of high purity commercial 8YCSZ-Al₂O₃ (1-10 wt %) were investigated. The powders were made by colloidal processing which ensured uniform and homogeneous distribution of both phases. Till 0.5 wt% Al₂O₃ addition, sintering 8YCSZ-Al₂O₃ for 1hr between 1250-1400°C resulted in density increase. At higher addition, the density decreased. Rearrangement of Al₂O₃ particles (at low addition) resulted in density increase. Higher (>0.5%) Al₂O₃ content reduced grain boundary diffusivity and grain mobility thereby reducing sintering.

2.8 Mechanical Properties

Chaim [2.120] studied the processing and mechanical properties of Alumina-20 wt% Zirconia and Zirconia- 20 wt% Alumina (ZTA) which had been prepared by pressureless sintering between 1400°C to 1600°C. They observed that due to the change in particle packing, higher green densities were obtained for powders having large particle size. The final sintered density was higher for finer particle size. The volume fraction of retained t-ZrO₂ was dependent on final density and t-ZrO₂ grain size. Many ZrO₂ had twinned feature characterizing m-ZrO₂. An increase in density resulted in an increase in Vickers hardness. Although the bending strength of ATZ composites was lower (250-500 MPa), the fracture toughness was significantly higher (9 MPa √m) in the sample containing about 96% retained t-ZrO₂ of critical size and the toughness resulted from transformation toughening effect. Due to presence of Al₂O₃, ZTA samples also showed improvement in hardness over that of pure ZrO₂ but at the same time had lower bending strength (due to porosity) but higher fracture toughness (due to higher t-ZrO₂ fraction and its transformability).

Krell et al. [2.121] studied the influence of microcrack density as well as dispersion homogeneity on the mechanical properties of Al₂O₃- ZrO₂ composites. The composites were prepared by two different routes. In the first route (Route-A), commercial Al₂O₃ and
milled ZrO$_2$ (5-20 vol %) were mixed and the mixture was remilled in planetary milled, dried and granulated. In the second method (Route-B), aqueous ZrOCl$_2$.8H$_2$O solution was added to Al$_2$O$_3$ and mixture was homogenized in planetary mill for 4 to 10 hours followed by freeze drying and calcination (950°C/2 hours). In all the specimens (prepared by both routes), 1400 ppm MgO (as MgCl$_2$.6H$_2$O) was added. The green compacts were sintered between 1560°C and 1625°C for 1 hour. Microcrack toughening was the dominant toughening mechanism and the maximum toughness was 8 MPa $\sqrt{m}$ at 11.5 vol% ZrO$_2$ addition for Route-A samples. However, in Route-B, the highest toughness was 11.8 MPa $\sqrt{m}$ which was attributed to finer and more homogeneous distribution of ZrO$_2$ in Al$_2$O$_3$ matrix.

Hirano et al. [2.122] studied the fracture toughness, strength and Vickers hardness of Y$_2$O$_3$-CeO$_2$ codoped ZTA composites. Dense composites were prepared by hot pressing. The ZTA composites were 75 wt% (Y-Ce) TZP and 25 wt% Al$_2$O$_3$. Three different compositions of (Y, Ce) TZP viz. (4 mol% YO$_{1.5}$ – 4 mole% CeO$_2$) TZP, (2.5 mol% YO$_{1.5}$ – 4 mole% CeO$_2$) TZP, (2.5 mol% YO$_{1.5}$ – 5.5 mole% CeO$_2$) TZP were studied. The HIPing operation was carried out 1400°C. CeO$_2$ $\rightarrow$ Ce$_2$O$_3$ phase transformation took place in the reducing gas atmosphere during HIPing which resulted in lower amount of retained $t$-ZrO$_2$ for zero Al$_2$O$_3$ addition. However, Al$_2$O$_3$ addition suppressed the $t\rightarrow m$ phase transformation. It was further noted that the fracture toughness, strength and hardness of (Y, Ce) TZP/ Al$_2$O$_3$ composite were dependent on the hot pressing temperature. The strength and toughness decreased when the composites were hot pressed at 1600°C.

Grigoryev et al. [2.123] studied the effect of different volume fraction of 3Y-TZP addition Al$_2$O$_3$ on the strength, toughness, hardness and microstructure after hot pressing. They noted that in the hot pressed composite a non transformable $t$-ZrO$_2$ ($t$-ZrO$_2$) was also present besides $t$ and $m$-ZrO$_2$. While the fracture toughness remained essentially unchanged (~7 MPa $\sqrt{m}$) at different 3Y-TZP volume fraction, the hardness decreased and the strength increased with 3Y-TZP volume fraction. The results were explained with reference to the fraction of $t$-ZrO$_2$, change in crack propagation path, microstructure refinement and change in the matrix hardness resulting at higher 3YTZP addition.
Srdic et al. [2.124] studied the effect of fine and homogeneous microstructure on the transformation toughening behaviour of Al₂O₃ – 20 wt% unstabilized ZrO₂. The composites were prepared through sol-gel method by mixing α-Al₂O₃ seeded alumina sol (containing 20 wt% boehmite) with three different concentration zirconia sols (hydrolyzed alcoholic solution of Zr-n-P). The composites had high sintered density (>90 %) at all sintering schedules (1400°C, 1500°C and 1600°C). The average size of zirconia grains increased with sintering temperature. Uniformly dispersed ZrO₂ grains (0.45 µm) restricted the grain growth of Al₂O₃. However, at 1600°C, most of the ZrO₂ converted to m-ZrO₂. Although transformation toughening was dominant toughening mechanism, the rather low toughness (\( K_{IC} < 6 \text{ MPa}\sqrt{\text{m}} \)) suggests that in these composites addition of a small fraction of unstabilized ZrO₂ are not effective for a significant improvement of fracture toughness.

Konsztowicz et al. [2.125] studied the effect of heteroflocculation on the mechanical properties of zirconia toughened alumina composite (ZrO₂ 5-30 vol %). The composites were colloidally processed from dense aqueous suspensions (>50 vol% of solids). Three different type of ZrO₂ were used viz. unstabilized ZrO₂, partially stabilized with 2mol% Y₂O₃ and nontransformable t-ZrO₂ (t') with 3 mole% Y₂O₃. The microstructural changes of sintered composites indicated an increasing degree of hetero flocculation of ZrO₂ - Al₂O₃ at higher ZrO₂ content. For ZrO₂ content ≤ 10 vol%, the grains were well dispersed and at 30 vol% ZrO₂, large clusters were observed. At lower ZrO₂ content (≤ 10 vol %), the dispersed ZrO₂ phase primarily acts as grain growth inhibitor for Al₂O₃. With undoped ZrO₂, both peak strength (1000 MPa) and toughness (8 MPa\sqrt{\text{m}}) was obtained at 10 vol% ZrO₂ additions. For ZTA with 2 mole% YSZ, the peak strength (1500 MPa) was obtained at 20 vol% ZrO₂ addition and peak toughness (9 MPa\sqrt{\text{m}}) was at 30 vol% ZrO₂ addition. While stress induced microcracking was responsible for the property enhancement for the first case, both transformation toughening and microcracking accounted for the strength and toughness increment in the second case. In the third case, use of 3 mole% TZP for preparing ZTA resulted in nontransformable t-ZrO₂ in Al₂O₃ matrix and the strength , toughness were mainly governed by dispersion strengthening mechanism.
Balasubramanium et al. [2.126] used sol-gel method to prepare $\text{Al}_2\text{O}_3$-12.5 wt% $\text{ZrO}_2$ composites using different combinations of precursors, viz. (i) aluminium sulfate and zirconium oxychloride and (ii) aluminium sec butoxide and zirconium isopropoxide. While the mixed ZTA powders from the first route were spherical (average particle size 3 $\mu$m), the powders from the second and third route were irregular shape (average particle size 10 $\mu$m). Due to the smaller particle size, the first route powders had higher sintered density (92%) than the other two (75 and 78% respectively).

Casellas et al. [2.127] studied the effect of thermally induced microstructural coarsening on the fracture toughness of zirconia-alumina composites containing 5, 15 and 30 vol% 3YTZP. The composites were cold isopressed at 200 MPa and sintered at 1600°C for 2 hours. It was observed that microstructural coarsening of this dual phase ZTA was dependent on the volume fraction of the second phase. At low volume fraction (5 vol%) of 3YTZP, the grain growth of the matrix ($\text{Al}_2\text{O}_3$) is pinned by the dragging force of 3YTZP. However, at 10 vol% 3YTZP, zirconia clusters are formed which becomes more effective pinning the grain boundaries. When 3YTZP addition > 30 vol%, microstructural coarsening became difficult and $\text{Al}_2\text{O}_3$ grain growth was absent due to large volume of $\text{ZrO}_2$ which prevent grain to grain contact of $\text{Al}_2\text{O}_3$. The increase in fracture toughness with 3YTZP addition was correlated to transformation toughening effect.

Vleugels et al. [2.128] studied the mechanical properties of $\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3$ coated YTZP ceramics. The mixed nanopowder was prepared from a suspension of aluminium nitrate, yttrium nitrate and $\text{ZrO}_2$ powder in an alcohol water mixture. Fully dense YTZP ceramic were obtained by hot pressing at 1400, 1450 or 1500°C. It was also noted that the fracture toughness of the $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3$ coated powder based YTZP ceramics could be tailored by optimum selection of overall $\text{Y}_2\text{O}_3$ content. The maximum toughness of $\text{Y}$-TZP with 2 wt% $\text{Al}_2\text{O}_3$ was obtained at 1.75 mole% $\text{Y}_2\text{O}_3$ content and at a hot pressing temperature at 1450°C. The yttria-coated $\text{ZrO}_2$ starting powder could result in $\text{Y}$-TZP ceramics having both wide distribution of yttria content (containing both c and transformable $t$-$\text{ZrO}_2$ grains) as well as grain size. The superior fracture toughness resulted from the presence of $\text{Y}$-TZP grains having wide variation in $\text{Y}_2\text{O}_3$ content thereby making some grains more transformable.
Adachi et al. [2.129] studied the effect of nano SiC dispersed (5 vol %) on the crack propagation behaviour of Al₂O₃ /3Y-TZP hybrid composites. The multilayer composite was prepared by doctor blade process through alternate stacking of 99.99 % pure α-Al₂O₃, 3Y-TZP and SiC. The microstructural analyses of the layer boundaries were smooth with no visible reaction between the phases. The magnitude of residual stress was dependent on the mismatch of CTE between the layer components and residual stress could be controlled by changing SiC dispersion. The study of crack propagation suggested that the crack deflection was influenced by the nature and magnitude of residual stress within the composites.

Celli et al. [2.130] utilized fractal geometry concept to analyze the Vickers indented path in alumina-zirconia composites. The fractal dimension parameter (ηₙ) for each crack referred to a corresponding three dimensional geometry of fracture surface. The study suggested that samples with high percentage of alumina as well as pure zirconia were characterized by intergranular of fracture surface. This class of composites had a correlation between microstructure, crack path and toughness. A higher population of larger alumina grains, rough and irregular crack geometry as well as fracture surface geometry leads to higher toughness on account of crack deflection mechanism. However, in composites containing high zirconia content, transgranular fracture was predominant.

Han et al. [2.131] studied the microstructure of Al₂O₃-50 wt% ZrO₂ composites using insitu synthesized Al₂O₃-ZrO₂ composite powder. The composite powders were prepared via sol-gel process with aluminium iso-propoxide and zirconium butoxide as the precursors. The as received amorphous composite powder on being calcined between 900°C and 1100°C, crystallized to t-ZrO₂ and finally to m-ZrO₂ through the intermediate phase of c-ZrO₂. However, they claimed that alumina particles remained in an amorphous stage till 1100°C. The different pore sizes (400-1100 nm) of the sintered porous composites were uniformly distributed.

Cesari et al. [2.132] simulated the toughening effect in alumina-zirconia using a simple model based on two concentric spheres and a crack in the matrix near the interface of the inclusion. The model had taken into consideration the $t\rightarrow m$ phase transformation.
effect and the thermal stress developed during cooling of the composite from the sintering temperature. The authors had simulated the toughening effect by imposing a uniform temperature field both to the matrix and the inclusion and the effect was studied at different temperatures. The simulated fracture toughness results (at room temperature) correlated well with the experimentally data obtained fracture toughness for different volume fraction of zirconia.

Vasylkiv et. al. [2.133] prepared zirconia / alumina nano composite using Y-TZP (0.75 to 3 mol% $\gamma_2O_3$) with $\gamma$-alumina (0.2 to 0.7%) through a colloidal processing route (powder loading 18-20 vol %). The slip cast composites were sintered in air at 1150 °C for 2 to 30 hours. The authors observed that $\gamma$-alumina helped to enhance the densification rate and the average grain size was 92 nm. The fracture toughness was high (15.7 MPa√m) for 1.5-2 mol% Y-TZP/ 0.35 wt% alumina composites and it was 7.86 MPa√m for 3Y-TZP/0.35 wt% alumina composites.

Basu et al. [2.134] prepared ZrO$_2$–Al$_2$O$_3$ composite with tailored toughness. The composites were prepared from both commercial and precipitated ZrO$_2$ powder as well as a mixture of 3Y-TZP + Y free monoclinic ZrO$_2$ with 28 vol% Al$_2$O$_3$. The densification was via hot pressing in vacuum at 1450°C for 1 hour. Different levels of toughness were obtained for the two composites which were explained in terms of yttria content, the yttria distribution and the residual stress due to the presence of Al$_2$O$_3$ particles in the matrix. Transformation toughening was the major toughening mechanism. They further observed that due to an inhomogeneous distribution of Y$_2$O$_3$ in the mixture Y-TZP + $m$-ZrO$_2$ it gave rise to high toughness probably due to auto catalytic effect.

The effect of residual stresses on the wear and friction behaviour during sliding in water of functionally graded alumina-ZTA composites were studied by Novak et. al. [2.135]. The predominant tribological mechanisms were assessed and analyzed using neutron diffraction, X-ray diffraction and scanning electron microscopy and using homogeneous alumina as base material. The authors observed that an increase in the residual compressive stresses of FGM reduced the wear and friction as well as produced thinner tribomechanical layer of detached debris from the surface.
Bermejo et al. [2.136] optimized the strength and toughness of ZrO$_2$–Al$_2$O$_3$ laminates through designing with external or internal compressive layers. The authors designed two alumina-zirconia laminates - one with external (ECS laminates) and the other with internal laminated (ICS laminates) compressive stress and the stress optimization was investigated using fracture mechanics weight fraction analysis. They observed that in general, ECS laminates had maximum apparent toughness at the first interlayer (A/AZ) for a relatively thin outer compressive layer. However, in the ICS laminates the maximum apparent toughness was realized at the second phase interface (AMZ/ATZ) for a relatively thick tensile (ATZ) layer. The strength optimization was found for a laminate design consisting of 9 layers and total thickness of 3 mm.

Gougalez et al. [2.137] studied the damage and R-curve behavior of alumina-zirconia-niobium multiphase composites by indentation strength method. They prepared different kinds of samples. The first variety had 3Y-TZP matrix which was strengthened by Al$_2$O$_3$ particles (ATZ). In the second variety, alumina matrix was strengthened with 3Y-TZP (ZTA). Both types of composites had further addition of niobium as reinforcement and were hot pressed. The authors studied the crack growth behavior of the composites and observed that both the stress induced transformation effect by ZrO$_2$ as well as crack bridging effect by Nb were the main factors for crack shielding as well as for exerting crack closure forces. The synergistic effect originated due to the interaction between toughening mechanism of Nb grains and zirconia grains in the Al$_2$O$_3$-ZrO$_2$-Nb composites.

Weimin et al. [2.138] studied the densification behavior, microstructure and transformation behavior of Al$_2$O$_3$-2YTZP and Al$_2$O$_3$-3YTZP (TZP 10, 15, 20, 25, 30 vol %). The volume fraction of Y-TZP affected the $t\rightarrow m$ ZrO$_2$ transformation. At 15 vol% TZP addition, the composites sintered to near theoretical density. Energy spectrum analysis confirmed different bonding level of Al$^{3+}$ with 3Y-TZP and 2Y-TZP. High toughness values were obtained at TZP level 15-20 vol% with transformation toughening being the predominant mechanism.

Guimaraes et al. [2.139] worked on the Al$_2$O$_3$-ZrO$_2$ nanocomposites containing 1, 3 and 5 vol% m-ZrO$_2$ nanoparticles. The authors correlated the microstructure, mechanical
properties and wear resistance of these composites. The microstructural analysis showed that zirconia addition helped to retard $\text{Al}_2\text{O}_3$ grain growth and improved the mechanical properties as well. At 5 vol% $\text{ZrO}_2$ addition, the improvement was 8% for microhardness, 11% for flexural strength and 23% for wear resistance in comparison to pure alumina. The results were explained in the light of microstructural refinement due to $\text{ZrO}_2$ addition.

Liu et al. [2.140] studied the effects of $\text{Sr}_2\text{Nb}_2\text{O}_7$ addition on the microstructure and mechanical properties of 3Y-TZP (45 vol %) /$\text{Al}_2\text{O}_3$ (55 vol %) composites. The volume fractions of $\text{Sr}_2\text{Nb}_2\text{O}_7$ were 0.005, 0.01, 0.015 and 0.02. During the sintering of composites (1500°C to 1600°C), the added $\text{Sr}_2\text{Nb}_2\text{O}_7$ reacted with $\text{Al}_2\text{O}_3$ to form elongated $\text{SrAl}_{12}\text{O}_{19}$ platelets which contributed positively towards the composite fracture toughness. The fraction of transformable $\epsilon$-$\text{ZrO}_2$ as well as fracture toughness firstly increased with $\text{Sr}_2\text{Nb}_2\text{O}_7$ addition (up to 0.005) and then decreased with further addition. The maximum toughness was 10.5 MPa$\sqrt{\text{m}}$ and toughness enhancement is due to the combined effect of transformation toughening and elongated grain toughening.

Jin et al. [2.141] prepared ZTA/La$\text{Al}_{11}\text{O}_{18}$ composites by two different methods and studied the effects of powder preparation on the microstructure and mechanical properties of ZTA/La$\text{Al}_{11}\text{O}_{18}$ composites. Both type of composites retained $\epsilon$-$\text{ZrO}_2$ in non transformable form. When aqueous precursors were used for composite preparation, the obtained microstructure was homogeneous with smaller $\text{Al}_2\text{O}_3$ grain. The $\text{Al}_2\text{O}_3$ grains showed a higher tendency for transgranular fracture thereby increasing the fracture strength though the toughness did not improve.

Daguano et al. [2.117] studied the different mechanical properties of ZTA (20 wt %) ceramics as a function of isothermal holding time at 1600°C. The grain growth exponent ($n$) of the composite for $\text{ZrO}_2$ and $\text{Al}_2\text{O}_3$ were 2.8 and 4.1 respectively, indicating different grain growth mechanisms for $\text{ZrO}_2$ and $\text{Al}_2\text{O}_3$. The hardness had a sintering time dependency. The high hardness (1300 to 1500 Hv) and fracture toughness (8 MPa$\sqrt{\text{m}}$) makes it suitable as dental implants.
Yang et al. [2.142] studied the influences of nano particles on the microstructure and the mechanical behavior of Ce-TZP/Al₂O₃ nano composites. The five different compositions were prepared from synthesized Ce-TZP powder and commercial Al₂O₃ powder wherein Ce-TZP was varied from 10 to 50 wt%. The composites were hot pressed at 1450°C at 20 MPa. The addition of 20 wt % nano Ce-TZP to Al₂O₃ improves the densification behavior of the composites. The mechanical properties and microstructure were also optimum at this level of Ce-TZP. TEM revealed dislocation structure formation in Al₂O₃ as well as in grain boundary and these could have helped crack deflection thereby providing strengthening effect.

Balakrishnan et al. [2.143] studied the effect of low thermal expansion MgO-Al₂O₃-SiO₂ glass infiltration at the surface on the mechanical properties of Al₂O₃-10 wt% ZrO₂ (3Y-TZP). The glass infiltration improved both the room temperature as well as high temperature composite strength. The weibull modulus as well as thermal shock resistance increased significantly after glass infiltration. The strength increment could be correlated with surface residual stress generated by the thermo-elastic properties mismatch between the composite and the glass.

Rascon et al. [2.144] studied the influence of pressureless sintering on the Vickers hardness and fracture toughness of ZrO₂ reinforced with Al₂O₃ (ATZ) and Al₂O₃ reinforced with ZrO₂ (ZTA). 3Y-TZ particles situated at the grain boundaries inhibited Al₂O₃ grain growth. ZrO₂ (80 wt %) / Al₂O₃ (20 wt %) composites had high hardness (16.05 GPa) and fracture toughness (7.44 MPa√m). It is interpreted that submicron grain size and low residual porosity causes the hardness and fracture toughness to increase. The composite properties are well suited for use as dental implants.

Ganesh et al. [2.145] prepared ZTA composites of different compositions (containing 30 wt% 3Y-TZ) and ZTA-60 (containing 60 wt%). The composites were shaped by hydrolysis induced aqueous gel casting method. 1.5 wt% Al₂O₃ in the precursor powder were replaced by an equivalent amount of AlN for co-promoting the green consolidation by aqueous gel casting method. The uniform microstructure obtained through gel casting process resulted in higher toughness (7.38 MPa√m) and strength (660 MPa).
Ahmad Azhar et al. [2.146] studied the effect of Al₂O₃/YSZ microstructure on wear and mechanical properties of ZTA cutting inserts. It was observed that composites with 20 wt% YSZ produced minimum wear area. However, Vickers hardness decreased with increasing in YSZ content. Above 60 wt% YSZ, the composite microstructure had microcracks and large grains of YSZ and these effects hindered the transformation toughening mechanism from being effective.
References


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Chapter III

Statement of Problem
Extensive literature review on Al₂O₃–ZrO₂ composites led to conclude that in recent times, solution chemistry routes (sol – gel, gelation, combustion synthesis etc) were mainly used for the composite powder processing, though solid state route of composite preparation was not totally neglected. Most of the investigations involving Al₂O₃–ZrO₂ composites were carried out either in the ZTA zone (ZrO₂= 5-35 vol %) or in ATZ zone (ZrO₂=70 – 95 vol %). In all the investigations on Al₂O₃-ZrO₂, ZrO₂ was added as stabilized ZrO₂ (Y-TZP/Ce – TZP being most common), although some investigators have studied Al₂O₃ – undoped ZrO₂ composites. However, very few literatures were available for Al₂O₃–ZrO₂, prepared from equal volume fraction of Al₂O₃ and ZrO₂. There may be two possible reasons why this particular composition was not investigated. One of them relates to the possible instability of tetragonal ZrO₂ (on account of lowered composite elastic modulus) and the other reason may be the increased softness of the composite which may limit the use of this composite.

But it is quite possible that through controlled processing, Al₂O₃– high ZrO₂ composite may be developed in which as a result of transformation toughening, reasonable strength, toughness and hardness will result. Thus, the present study aims to study these specific aspects from a processing view point:

I Use of different powder processing methods on the powder properties, its optimization and t-ZrO₂ retention. This aspect will be studied using three different powder processing routes, viz. gelation, precipitation and washing of the precipitates prior to calcination.

II Effect of precursor type (or nature of anions) on the metastable phase evolution and densification behaviour as well as properties of similar composites. To study this effect two different precursor combination will be used- all chloride (AlCl₃ and ZrOCl₂) and nitrate- chloride combination (Al(NO₃)₃ and ZrOCl₂)

III Detailed densification mechanism of the composites during initial stage sintering. This particular study is being planned using isothermal and non isothermal sintering behavior.

IV Effect of stabilizer on the composite properties, microstructures, strength, toughness and hardness. This part will be studied in Al₂O₃-Y-ZrO₂ composites where Y₂O₃ of
different concentration (viz 1, 2, 2.5, 3 mol %) will be added during powder preparation stage with a view to stabilize the tetragonal ZrO$_2$.

V Exploring the possible strengthening and toughening mechanism in these composites. To study this part, the observed strength, toughness and hardness values will be correlated with microstructure, density and different toughening and strengthening models. An attempt will also be made to explore the possibility of a second phase on the strength, toughness thermo-mechanical properties of the composites.
Chapter IV
Experimental Work
Alumina-zirconia composites having nominally equal volume of Al$_2$O$_3$ and ZrO$_2$ were prepared by gel-precipitation and precipitation method. The precursors for Al$_2$O$_3$ were AlCl$_3$ (Merck, India), Al(NO$_3$)$_3$ .9H$_2$O (Merck, India) and ZrOCl$_2$.8H$_2$O (Loba, India) for zirconia. Separate stock solution of individual precursors AlCl$_3$, Al(NO$_3$)$_3$ .9H$_2$O and ZrOCl$_2$.8H$_2$O were prepared by dissolving them in double distilled water. Each of the solution was 0.75 mol/Lit. Before proceeding with powder preparation from these precursors, it was necessary for quantitative estimation of these precursor stock solutions.

4.1 Estimation of AlCl$_3$, Al(NO$_3$)$_3$, and ZrOCl$_2$ stock solution

3 ml of respective stock solution was taken in a clean and dried 250 ml volumetric flask. 2-3 drops of methyl-red indicator was added to the solution and the colour changed to pink for ZrOCl$_2$ and light pink for both AlCl$_3$ and Al(NO$_3$)$_3$ solution. The stock solution was titrated with AAC buffer solution (NH$_4$OH & NH$_4$Cl) with continuous stirring. The complete precipitation of Al(OH)$_3$ (or Zr(OH)$_4$) took place between pH of 9 and 10. The end point of the reaction was marked by the change in the solution colour from pink to light pink to pale yellow. The precipitate was warmed and filtered through Whatman 40 filter paper and washed with hot water to make the precipitate free from chloride, nitrates and excess AAC buffer. The washing was continued till the precipitate colour changed to white. The precipitate along with the filter paper was transferred to a preweighed platinum crucible and fired at 1000°C for 1 hr. The weight of the calcined precipitate on firing was equivalent to weight of the oxide per 3 ml of solution. The possible chemical reactions during precipitation are as follows:

\[
\text{AlCl}_3 + \text{NH}_4\text{OH} \rightarrow \text{Al(OH)}_3 + 3\text{NH}_4\text{Cl} \quad (4.1)
\]

\[
\text{Al(NO}_3\text{)}_3 + \text{NH}_4\text{OH} \rightarrow \text{Al(OH)}_3 + 3\text{NH}_4\text{NO}_3 \quad (4.2)
\]

\[
\text{ZrOCl}_2 + \text{NH}_4\text{OH} \rightarrow \text{ZrO(OH)}_2 + 3\text{NH}_4\text{Cl} \quad (4.3)
\]

\[
\text{ZrO(OH)}_2 + \text{NH}_4\text{OH} \rightarrow \text{ZrO(OH)}_2 + 2\text{NH}_4\text{Cl} \quad (4.4)
\]

The precipitated Al(OH)$_3$ and Zr(OH)$_4$ could be correlated to their respective oxides according to the following equations:

\[
\text{Zr(OH)}_4 \rightarrow \text{ZrO}_2 + 2\text{H}_2\text{O} \quad (4.5)
\]

\[
\text{ZrO(OH)}_2 \rightarrow \text{ZrO}_2 + \text{H}_2\text{O} \quad (4.6)
\]

\[
2\text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \quad (4.7)
\]
4.2 Powder Synthesis

\( \text{Al}_2\text{O}_3 - 50 \text{ vol\% ZrO}_2 \) composite powder was prepared from solution chemistry routes using aluminum chloride and zirconium oxychloride as precursors. Three different processing routes, viz gelation (ROUTE 1), precipitation (ROUTE 2) and precipitation followed by washing (consisting of hot water and alcohol washing) (ROUTE 3) were employed for preparing the composite powder. In the later stage, further modification of ROUTE 3 was made by replacing \( \text{AlCl}_3 \) with \( \text{Al(NO}_3)_3 \) (ROUTE 4).

4.2.1 Synthesis of Alumina-Zirconia Powder by Gelation Method (ROUTE 1)

Alumina-zirconia powder, containing 50 vol\% \( \text{Al}_2\text{O}_3 \) and ZrO\(_2\) has been prepared from the pre-estimated precursor solutions of aluminum chloride (\( \text{AlCl}_3 \), AR grade) and zirconium oxychloride (\( \text{ZrOCl}_2 \cdot 8\text{H}_2\text{O} \), AR grade). The two precursor solutions were mixed thoroughly at room temperature; the pH of the mixed solution was found to be less than 2. The mixed precursor solution was subjected to gelation by drop wise addition of \( \text{NH}_4\text{OH} \) (AR grade) while the mixed solution was being vigorously stirred on a magnetic stirrer. The colour of the mixed solution changed from pale yellow to colourless on addition of few initial drops of \( \text{NH}_4\text{OH} \). Further addition of \( \text{NH}_4\text{OH} \) resulted in the formation of few white flocks of precipitates which increased in number finally leading to the complete gelation of the formed precipitates (pH 6.5 - 6.7) [4.1]. Figure 4.1 shows the process flow diagram and the gelation route (ROUTE 1) is step 1-3 and 9.

4.2.2 Synthesis of Alumina-Zirconia Powder by Precipitation from Chloride Precursors (ROUTE 2)

In the precipitation route, \( \text{AlCl}_3 \) and \( \text{ZrOCl}_2 \) precursor solutions were mixed as before (section 4.2.1). With addition of \( \text{NH}_4\text{OH} \), at first gelation of the entire solution took place in the pH range 6 - 6.5. Following this, the gel network was mechanically disturbed by high speed stirring and \( \text{NH}_4\text{OH} \) addition was continued till the precipitation was complete (pH range 8.7 - 9.1) [4.2]. The precipitates were allowed to settle and the clear supernatant liquid contained \( \text{NH}_4\text{OH}, \text{NH}_4\text{Cl} \) and \( \text{NH}_4\text{NO}_3 \) which was removed by decantation. The precipitate was dried and ground to a fine powder and characterized. Figure 4.1 shows the process flow diagram and the precipitation route (ROUTE 2) is steps 1-6 and 8-9.
4.2.3 Preparation of Alumina-Zirconia Composite Powder from Washed Precipitates using Chloride Precursors (ROUTE 3)

The precipitates were prepared following the steps mentioned in section 4.2.2. The precipitates were allowed to settle and the clear supernatant liquid was removed. Following this, the precipitates were washed with hot water for several times. Between each washing step, the precipitate was settled and the clear liquid was removed. The washing was continued till the precipitate was white in colour. This water washed precipitated was further washed with isopropyl alcohol. In order to facilitate better and faster washing by isopropyl alcohol, this stage of washing was carried in a laboratory centrifuge to separate the liquid and precipitates. Figure 4.1 shows the process flow diagram and the washed precipitate route (ROUTE 3) is steps 1-9.

4.2.4 Preparation of Alumina-Zirconia Composite Powder from Washed Precipitates using Chloride-Nitrate combined Precursors (ROUTE 4)

It has been reported that entrapped ions (Cl⁻) as well as water affects the densification process and therefore, it was necessary to remove both of these during the powder preparation steps. In ROUTE 4 this was realized by replacing AlCl₃ by Al(NO₃)₃ and making the precipitate by similar route as in section 4.2.2 and carrying out the post precipitation washing process (water and alcohol washing) as mentioned in section 4.2.3. Later on, a further modification of ROUTE 4 was made when Y(NO₃)₃ was also introduced in the system. The partially modified ROUTE 4 was used to prepare Al₂O₃-Y-ZrO₂ composite powder from co-precipitation of Al(NO₃)₃, ZrOCl₂ and Y(NO₃)₃ solution. Thus, for the preparation of Al₂O₃-Y-ZrO₂ composite powder (Y₂O₃ = 1, 2, 2.5 and 3 mol%), the required amount of Y₂O₃ (Loba India) was added to 1:1 HNO₃ and the mixture was warmed for complete dissolution of Y₂O₃ in HNO₃. The Y(NO₃)₃ solution thus prepared was added to the mixed solution of Al(NO₃)₃ and ZrOCl₂ and the precipitation was carried out following similar method as discussed in the section 4.2.3. Figure 4.1 shows the process flow diagram and the washed precipitate route (ROUTE 4) is steps 1-9 using precursors given in second column.
Fig. 4.1. Generalized flow diagram for processing of Al₂O₃-50 vol% ZrO₂ composite powder preparation by different routes.
4.3 Characterization of Dried Gel and Calcined Powder

The dried gel was characterized for its thermal decomposition behaviour by (DSC/TG), the presence of different ions and hydroxides by FTIR, and phase analysis by XRD. Subsequently, the gel powder was calcined for 4 hrs. at different temperatures between 350-1050°C and the phase evolution, particle size distribution, surface area, compaction behaviour and particle morphology of the calcined powder has also been studied.

4.3.1 DSC/TG of Dried Gel/Precipitate

The thermal analysis of the dried gel/precipitate gives an idea about the decomposition and crystallization behavior of hydroxides present in the gel/precipitate. A small quantity of finely ground dried gel/precipitate was subjected to DSC/TG study (Netzsch STA409 C) in an ambient atmosphere at a heating rate of 10°C/minute using α-Al₂O₃ as reference material.

4.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

The different ions and metal hydroxides in the dried gel/precipitate and calcined powder have been studied through FTIR. The powder sample was mixed with KBr in an agate mortar and pressed to a pellet of 0.1 mm thickness. The spectra were taken in a diffuse reflectance (DRIFT) mode in a Shimadzu FTIR instrument (Model 84005) in the wave number range 4000 - 400 cm⁻¹.

4.3.3 Calcination

All the powder prepared by ROUTE 1- ROUTE 4 calcined at different temperature 350 – 1050°C with a 4 hrs holding time at the peak temperature.

4.3.4 Crystallite Size, Phase Analysis of Dried Gel, Precipitate and Calcined Powder

The phase analysis of dried gel, precipitate as well as calcined powder was carried out with an X-ray diffractometer (Phillips PW 1830, Holland) with Cu-Kα radiation in the 2θ range 20-80 ° at a scan speed of 2°/min. The accelerating voltage and current were 35kV and 30mA respectively. The crystallite size of the powder was calculated from X-ray line broadening using Scherrer’s formula [4.3].
\[ D = \frac{0.9 \lambda}{B \cos \theta} \]  
\[ (4.8) \]

where, \( D \) is the crystallite size, \( \lambda \) is the wavelength of the radiation, \( \theta \) is the Bragg's angle and \( B \) is the full width at half maximum.

\[ B^2 = B_{\text{meas}}^2 - B_{\text{inst.}}^2 \]  
\[ (4.9) \]

where, \( B_{\text{meas}} \) = Observed full width at half maximum from peak values, \( B_{\text{inst.}} \) = Instrumental broadening.

The fraction of tetragonal zirconia was calculated by comparing the peak intensities of tetragonal [111] and monoclinic [111] and [11\overline{1}] obtained from X-ray diffraction of calcined as well as sintered samples using the following Eqn. [4.4, 4.5].

\[ V_m = \frac{1.311 X_m}{(1 + 0.311 X_m)} \]  
\[ (4.10) \]

where, \( X_m = \frac{I_m(111) + I_m(11\overline{1})}{I_m(111) + I_m(11\overline{1}) + I_m(111)} \times 100 \]  
\[ (4.11) \]

where, \( V_m \) is the volume fraction of monoclinic ZrO\(_2\), \( I \) = integrated intensity of the respective diffracting plane, \( X_m \) is the intensity of \( m \)-ZrO\(_2\) with respect to total ZrO\(_2\), subscript \( m \) and \( t \) stands for monoclinic and tetragonal ZrO\(_2\).

### 4.3.5 Particle Size Distribution

The particle size and size distribution of the calcined powder has been studied by laser scattering technique (Malvern MASTER SIZER 2000, U.K.). The scattering of the light by the particle depend on the refractive index of the powder, dispersant and medium. The refractive index and bulk density of both the medium and samples was determined before carrying out the particle size distribution. The density of the powder was determined by pycnometer method using kerosene as medium. The calcined powder was ultrasonically dispersed in water using sodium hexametaphosphate as dispersant. The \( D_{50} \) was determined from the size frequency curve which was calculated on the basis of the surface to volume ratio of particle.
4.3.6 Surface Area of Calcined Powder

The specific surface area of the calcined powder was measured by BET surface area analyzer (Quantachrome Instruments, U.S.A.) which is based on the adsorption of nitrogen gas on the sample surface. The calcined powder was degassed at 100°C and measurement was done at five different points. The average particle size is the diameter of the spheres equivalent to exterior surface area. Assuming spherical particles, the particle size ($d_{BET}$) has also been calculated from surface area according to Eqn. (4.10).

$$d_{BET} = \frac{6}{S_p \rho} \quad \text{(Spherical approximation)} \quad (4.12)$$

where, $d_{BET}$ = average particle diameter, $S_p$ = specific surface area ($m^2 \text{ gm}^{-1}$); $\rho$ = true density of the material.

4.3.7 Compaction Behaviour of Powder

The packing characteristic of particles, stress induced flow behaviour and the agglomeration strength of calcined powder were studied from the logarithmic pressure-relative density diagram. Compaction behaviour and agglomerate strength of the powder has been measured by uniaxially compaction of the powder in circular die and punch. The weighed amount of powder was taken in a stearic acid lubricated die and punch. The powder was properly leveled and the initial height was of the powder was measured. The punch movement was measured using universal testing machine (UTM) (Hounsfield H50KT, UK) at a constant crosshead speed of 0.2 mm/min. The green density of the powder compact has been calculated from the punch movement and the initial height of the powder.

4.3.8 Microstructure of Calcined Powder

The morphology of the calcined powder i.e. agglomeration behaviour, particle size and shape were studied in TEM (PHILIPS CM200T, CANADA). The TEM sample was prepared by dispersing a small amount of powder in isopropyl alcohol followed by ultrasonication (20 KHz, 500 W) for 20 min. One drop of the well-dispersed suspension was deposited on a 400 mesh carbon coated copper grid. The grid was dried in an IR
lamp for solvent evaporation. The powder was observed in bright field at an accelerating voltage of 200 KV.

4.4 Densification Behaviour

4.4.1 Sintering Kinetics

The sintering kinetics of Al₂O₃-ZrO₂ composite powder was studied by both isothermal and constant rate heating method. In the constant rate heating method, the green rectangular bars of Al₂O₃-ZrO₂ composite was sintered at different heating rate (5, 10, 15, 20°C/min) till 1450°C in ambient atmosphere in a dilatometer (NETZSCH DL 402C). The activation energy for mass transport during initial stage of sintering was calculated from the shrinkage data at different temperatures. In isothermal method, the green compact was rapidly heated @ 20°C/min to the desired temperatures (1050-1450°C) and held at that temperature for 2 hrs.

4.4.2 Sintering of Green Compacts

The green compacts were placed on alumina substrate and heated from room temperature to 650°C at a rate 4°C/min and held there for 30 min. for binder removal. Thereafter, the samples were heated at a rate 3°C/min to the final sintering temperature (1400-1600°C) at 50°C interval with a hold time of 4 hrs. at each sintering temperatures. The samples were also sintered for various soaking periods i.e. 6 hrs, 8 hrs at 1600°C. The samples were cooled at 3°C/minute till 900°C followed by furnace cooling.

4.5 Characterization of Sintered Samples

The sintered samples were studied for phase analysis of Al₂O₃ and ZrO₂, density, mechanical properties, thermal expansion behaviour and microstructural study by SEM.

4.5.1 Phase analysis of Sintered Sample

The phase in the sintered compacts was studied by X-ray diffraction using Cu Kα radiation. The samples were scanned in the 2θ ranges 20-80° and the obtained XRD pattern was analyzed using Schmid’s formula as described in section 4.3.4.
4.5.2 Bulk Density and Relative Density of Sintered Specimen

The bulk density and apparent porosity of the sintered specimen were measured by Archimedes’ principle using kerosene as the immersion liquid. The bulk density was calculated using the suspended and soaked weights.

\[
\text{Bulk Density} = \left( \frac{D \times \text{Density of Kerosene}}{W - S} \right)
\]

(4.13)

where, \(D\), \(W\), and \(S\) are the dry weight, soaked weight and suspended weight of the sample.

The relative densities of the sintered samples were measured from the bulk density and the theoretical density calculated from the x-ray phase analysis.

\[
\text{Relative Density} = \frac{\text{Bulk Density}}{\left[ (X_t \times 6.1 + X_m \times 269) \times 0.2 \right] - (3.69 \times 0.2)}
\]

(4.14)

where, \(X_t\) and \(X_m\) are the volume fraction of tetragonal and monoclinic ZrO₂.

4.5.3 Microstructure of Sintered Specimen

The microstructures of the sintered ZTA composites were observed by SEM, FE-SEM and TEM. The samples were polished using automatic grinding & polishing unit (Buehler, Ecomet 3-Automet 3). At first, the specimen surface was ground successively using 240 and 600 grit SiC paper disks respectively. Following this, the samples were polished in 1μm diamond paste on a texmet cloth. The polished samples were washed by acetone and cleaned with in an ultrasonic bath. The polished samples were chemically etched for 15 min in a 1:1:2 :: HF: HNO₃: H₂O solution. The chemically etched samples were washed, dried and thermally etched for 20 min at 150°C below the sintering temperature.

4.5.3.1 SEM/FE-SEM Analysis

The polished and etched samples were sputter coated with palladium-platinum coating in a sputtering unit for 2-3 min. to make the surface conducting. The specimens were observed by SEM (JEOL- JSM 6480 LV, Japan) in BSE and SE mode at 15 KV accelerating voltage. Fracture and indented surface of some samples were also observed by SEM in both SE and BSE mode. Some selected sintered and thermally etched samples were also observed in FE-SEM (SIRION, PHILIPS, Eindhoven, Holland) at an accelerating voltage of 10 KV in SE and BSE mode.
4.5.3.2 TEM of bulk sintered samples

Some selected bulk sintered samples were also observed in TEM (TECNAI-G2, FEI USA), at 200 KV. The samples were prepared by argon ion milling.

4.6 Hardness, Strength and Toughness

Hardness, flexural strength and toughness of the sintered samples were measured on rectangular bars of size 45 x 4 x 4 mm³. All the surfaces of the samples were polished and the edges were also chamfered. The dimetal compression test was carried out on cylindrical pellet (2-4 mm thick and 10-12 mm dia.) which were polished to remove roughness. The longitudinal edges of the specimens were chamfered by polishing to eliminate the edge cracks and stress.

4.6.1 Vickers Hardness

The hardness was studied by a Vickers semi-macro hardness tester (LV-700 Leco, Japan). The indentations were carried out at different loads (5, 10, 15, 20 Kgf) with 15 sec dwell time. The hardness (Hv) was determined from the diagonal length using the formula given below [4.6].

\[
H_v = 0.47 \times \frac{P}{a^2}
\]  

(4.15)

where, P is the applied load in Newton and a is the half diagonal length in µm. The hardness was calculated from the slope of the plot of applied load and square of the half diagonal (a²) at no crack condition of the indent using the above relation.

4.6.2 Flexural Strength

Flexural strength was determined in three-point bending as per ASTM standard C1161-90 [4.7] and by Brazilian disk test methods in UTM (Hounsfield H10KS, U.K). For three point bending, the span length was 25 mm and cross head speed was 0.2 mm/min. The flexural strength was calculated from the following equation [4.7].

\[
\sigma_{flexural} = \left( \frac{3PL}{2WD^2} \right)
\]  

(4.16)
where, \( P \) is the fracture load, \( L \) is the span length, \( W \) is the width and \( D \) is the breadth of the sample.

The biaxial flexural strength of sintered samples was measured on the cylindrical samples. This test is also known as Brazilian disc test. In this test, the samples were broken in compression at a cross head speed of 0.2 mm/sec. The strength was calculated from the formula [4.8].

\[
\sigma_{\text{biaxial flexural strength}} = \frac{2P}{\pi Dt}
\]  

(4.17)

where, \( P \) is the breaking load, \( D \) is the diameter of the pellet and \( t \) is the thickness of the pellet.

4.6.3 Fracture Toughness

The fracture toughness of the sintered and notched specimen was determined in three point bending using SENB method [4.9] on notched samples. The notches were made using a Buehler low speed saw. The notched samples were pre-cracked by putting an indentation at notch tip. The fracture toughness \( K_{IC} \) was calculated by the following Eqn. [4.10].

\[
K_{IC} = \frac{3P}{2W D^2} \left[ L \sqrt{C + A_1 \left( \frac{C}{D} \right) + A_2 \left( \frac{C}{D} \right)^2 + A_3 \left( \frac{C}{D} \right)^3 + A_4 \left( \frac{C}{D} \right)^4} \right]
\]  

(4.18)

where, \( P \) is the breaking load, \( C \) is the notch depth, \( W \) is the width, \( L \) is the span length, \( D \) is the depth or thickness of the sample. \( A_0, A_1, A_2, A_3 \) and \( A_4 \) are the constants and their values are calculated as following:

\[
A_0 = 1.9 + 0.0075(L/D)
\]

\[
A_1 = -3.39 + 0.08(L/D)
\]

\[
A_2 = 15.4 - 0.2175(L/D)
\]

\[
A_3 = -26.24 + 0.2815(L/D)
\]

\[
A_4 = 26.38 - 0.145(L/D)
\]
4.7 Thermal Shock Resistance

The thermal shock resistance of the sintered specimen evaluates the resistance to crack initiation or its propagation under thermal stress when subjected to a thermal shock from high temperature (such as rapidly cooling down from high temperature to low temperature). The thermal shock resistance was studied by heating the samples at 5°C/min up to a temperature of 1000, 1100 and 1200°C with a soaking time of 30 min at each temperature and followed by rapid cooling in air till the samples attained room temperature following the method of Li et al. [4.11]. The thermal shock resistance was determined by measuring flexural strength, tensile strength and fracture toughness after thermal shock. The phase analysis of the thermally shocked sample was also carried out to study the phase change due to thermal shock.
References


Chapter V

Results and discussion
Section A

Processing and Characterization of Al₂O₃-ZrO₂ (undoped) Composites
5.1 Preparation of Al$_2$O$_3$-ZrO$_2$ Composite by Gelation Method (ROUTE 1)

The powder processing of Al$_2$O$_3$-ZrO$_2$ composites containing nominally equal volume fraction of Al$_2$O$_3$ and ZrO$_2$ prepared by gelation technique have been elaborated in section 4.2.1. The properties of the powder and the sintered compacts are discussed in the following sections.

5.1.1 Phase Analysis of Dried Gel

The XRD pattern of the dried gel is shown in Fig.5.1. The XRD pattern shows that the dried gel is amorphous with crystalline peaks superimposed on the amorphous broad background. These crystalline peaks were identified as NH$_4$Cl [JCPDS 73-0365], which formed during the gelation process due to the reaction between AlCl$_3$, and ZrOCl$_2$ with NH$_4$OH.

![Fig.5.1. XRD pattern of dried gel (ROUTE 1)](image)

5.1.2 Thermal Analysis of Dried Gel

Figure 5.2 shows the DSC/TG curve of as dried gel. The first broad endothermic peak at 100°C is associated with a weight loss of 13.7% (which continues till about 200°C). This endothermic peak and the weight loss is due to the dehydroxylation of Al(OH)$_3$. The governing chemical reaction is given by:
\[2AlCl_3 + 6NH_4OH = 2Al(OH)_3 + 6NH_4Cl\]  \hspace{1cm} (5.1)

\[2Al(OH)_3 = Al_2O_3 + 3H_2O\]  \hspace{1cm} (5.2)

Beside the decomposition of \(Al(OH)_3\), the other chemical reactions occurring during the gelation can be written as follows:

\[ZrOCl_2 + 2NH_3 + 3H_2O = Zr(OH)_4 + 2NH_4Cl\]  \hspace{1cm} (5.3)

The decomposition of \(Al(OH)_3\) to \(Al_2O_3\) is associated with 13.8% weight loss. The observed weight loss is 13.7% which matches well with the theoretical weight loss for the composite powder containing 40% wt% \(Al_2O_3\) and 60% wt% \(ZrO_2\). It may be mentioned here that the decomposition of \(Al(OH)_3\) to \(Al_2O_3\) is a two step process which takes place via an intermediate amorphous \(Al_2O_3\) phase formation. The exothermic peak for amorphous to crystalline \(Al_2O_3\) is masked by the strong endothermic peak at 300°C. This feature has been clearly indicated in a later section which discusses the effect of washing on the crystallization behavior.

The second endothermic peak at 194°C is a sharp one without a corresponding weight loss in the TG curve. This peak, therefore, corresponds to reactions other than

---

*Fig. 5.2. DSC/TG thermogram of as synthesized \(Al_2O_3-ZrO_2\) dried gel (ROUTE 1)*
decomposition reactions. The decomposition of NH₄Cl is a two step process involving melting (220°C) and sublimation (338°C) [5.1]. Thus the endothermic peak at 194°C corresponds to the melting and sublimation of NH₄Cl. The later peak is associated with a weight loss of 48.4% which matches well with the theoretical weight loss (47.3%) for the sublimation of NH₄Cl.

The third stage of weight loss starts right after the second stage of weight loss and it continues till about 425°C. The weight loss recorded in this stage is 13.3%. It is anticipated that in this stage, Zr(OH)₄ decomposes according to the following reaction:

\[ \text{Zr(OH)}_4 = \text{ZrO}_2 + 2\text{H}_2\text{O} \]  

(5.4)

The theoretical weight loss for this reaction is 22.7%. For equal volume fraction of Al₂O₃ - ZrO₂ composites, this comes out to be 13.58%, which matches well with the observed weight loss of 13.3%.

Immediately after the completion of weight loss, two broad and shallow exothermic peaks are observed between 490°C and 500°C. The exothermic peaks are because of crystallization of \( \gamma \)-Al₂O₃ and \( \alpha \)-ZrO₂ respectively which are identified from their characteristic \( d \)-spacing.

5.1.3 FTIR Spectra of Dried Gel

The FTIR spectrum of the dried gel sample is shown in Fig. 5.3. The different peaks obtained in the wave number range 3500-400 cm\(^{-1}\) are assigned to different stretching and bending vibrations listed in Table 5.1. The broad peak in the wave number range 3500 –2800 cm\(^{-1}\) is assigned to O-H stretching vibration indicating the presence of molecular water and adsorbed water [5.2].
Fig. 5.3. FTIR spectra of dried gel powder (ROUTE 1)

Table 5.1 FTIR spectra of dried gel (ROUTE 1)

<table>
<thead>
<tr>
<th>Adsorption Peak (cm(^{-1}))</th>
<th>Nature of Peak</th>
<th>Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>3500-3000</td>
<td>strong stretching</td>
<td>molecular water</td>
</tr>
<tr>
<td>2880</td>
<td>weak bending</td>
<td>H bonded OH</td>
</tr>
<tr>
<td>2813</td>
<td>sharp bending</td>
<td>N-H</td>
</tr>
<tr>
<td>2345</td>
<td>weak stretching</td>
<td>Cl(^{-})</td>
</tr>
<tr>
<td>2012</td>
<td>weak stretching</td>
<td>-OH</td>
</tr>
<tr>
<td>1773</td>
<td>shoulder peak</td>
<td>N-H</td>
</tr>
<tr>
<td>1643</td>
<td>weak bending</td>
<td>Zr-OH</td>
</tr>
<tr>
<td>1407</td>
<td>strong stretching</td>
<td>N-H bending</td>
</tr>
<tr>
<td>1070</td>
<td>weak bending</td>
<td>Al-O (six coordinated)</td>
</tr>
<tr>
<td>896</td>
<td>broad peak</td>
<td>Al-O (four coordinated)</td>
</tr>
<tr>
<td>449</td>
<td>weak bending</td>
<td>Zr-O vibration</td>
</tr>
</tbody>
</table>

The shoulder peak around 2800 – 2750 cm\(^{-1}\) as well as at 1773,1400 cm\(^{-1}\) are due to N–H bending from NH\(_3\) [5.3]. The absorption peaks at 2345 cm\(^{-1}\) correspond to the
stretching of Cl ions and that of 2012 cm\(^{-1}\) is due to bending vibration of (-OH) groups of the hydroxides [5.4]. The peak appearing at 1643 cm\(^{-1}\) is due to the bending vibration of Zr-OH group. The six and four coordinated Al-O vibrations are shown at 1070 and 800 cm\(^{-1}\) respectively [5.5]. The broad bands in the range 550-500 cm\(^{-1}\) are due to Zr-O vibration [5.6]. The weak absorption peaks of Zr-O are due to the partial masking effect by the stronger intensity of Al-O vibration.

### 5.1.4 Phase Evolution in Calcined Gel

The XRD pattern of the gel calcined at different temperature is shown in Fig. 5.4. The powder calcined at 350°C show broad peaks of cubic ZrO\(_2\) (JCPDS 81-1550), boehmite (JCPDS 83-1505) and bayerite (JCPDS 20-0011). The broadening indicates fine crystallites of ZrO\(_2\). The average crystallite size of the powder calcined at 450°C is 4.71 nm, which increases at higher calcination temperature (Table 5.2). At higher calcination temperature the ZrO\(_2\) peaks become sharp and strong in intensity due to growth of crystallites. Till 500°C, only \(\varphi\)-ZrO\(_2\) peaks could be detected and identified. At 850°C, \(t\)-ZrO\(_2\) also starts to appear. The presence of \(t\)-ZrO\(_2\) was identified on the basis of (002)\(_t\) and (200)\(_t\) split peaks. At still higher calcination temperature (950°C), a mixture of \(t\) and \(m\)-ZrO\(_2\) and \(\gamma\)-Al\(_2\)O\(_3\) could be detected. The amount of retained \(t\)-ZrO\(_2\) at this temperature is 79%. Shi et al. [5.7] and Hong et al. [5.8] have reported that the lattice distortion of ZrO\(_2\) by Al\(_2\)O\(_3\) particle restrict the crystallite growth of ZrO\(_2\) and can help to retain metastable ZrO\(_2\) phases. However, crystalline phase of transition Al\(_2\)O\(_3\) could not be detected at lower temperatures and at 750°C \(\gamma\)-Al\(_2\)O\(_3\) was observed which was retained till 950°C.
Fig. 5.4. Phase evolution of Al$_2$O$_3$-ZrO$_2$ gel as a function of calcination temperature (ROUTE 1)
Table 5.2 Crystallite size of ZrO$_2$ as a function of calcination temperature in the Al$_2$O$_3$-ZrO$_2$ composite powder (ROUTE 1)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Crystallite Size of ZrO$_2$ (nm)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>3.62</td>
<td>$c$-ZrO$_2$, boehmite, bayrite</td>
</tr>
<tr>
<td>450</td>
<td>4.71</td>
<td>$c$-ZrO$_2$, boehmite, bayrite</td>
</tr>
<tr>
<td>500</td>
<td>5.1</td>
<td>$c$-ZrO$_2$ boehmite, bayrite</td>
</tr>
<tr>
<td>850</td>
<td>15.29</td>
<td>$c$,$t$,$m$-ZrO$_2$ (tr), $\gamma$-Al$_2$O$_3$</td>
</tr>
<tr>
<td>950</td>
<td>22.99</td>
<td>$c$,$t$,$m$-ZrO$_2$, $\gamma$-Al$_2$O$_3$</td>
</tr>
</tbody>
</table>

5.1.5 Particle Size and TEM Analysis of Calcined Gel

The particle size distribution of calcined gel (Fig.5.5) is broad. The fine fraction (<10 µm) is 16 vol% and the coarse fractions (>80 µm) is 86 vol%. The mean particle size ($d_{50}$) is 35.47 µm. The characteristic features of calcined gel are given in Table 5.3. The BET surface area of the calcined gel is 49 m$^2$gm$^{-1}$ and calculated particle size ($d_{BET}$) is 51 nm.

Fig.5.5. Particle size distribution of Al$_2$O$_3$-ZrO$_2$ calcined (850°C) powder (ROUTE 1)
Table 5.3 Properties of (850°C) calcined powder (ROUTE 1)

<table>
<thead>
<tr>
<th></th>
<th>D_{50} (μm)</th>
<th>D_{BET} (nm)</th>
<th>D_{TEM} (nm)</th>
<th>P_{ij} (MPa)</th>
<th>S (m²/gm)</th>
<th>AF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35.47</td>
<td>51</td>
<td>25</td>
<td>134</td>
<td>49</td>
<td>1418</td>
</tr>
</tbody>
</table>

![TEM Photograph](image1)

**Fig.5.6. TEM photograph of calcined (850°C) Al₂O₃-ZrO₂ powder (ROUTE 1)**

The TEM micrograph of calcined powder (Fig. 5.6) show agglomerated powder containing primary particles. The electron diffraction pattern show diffused ring pattern indicating very fine crystallites. X-ray diffraction pattern shows that the fine crystallites are boehmite [JCPDS 83-1505]. The strong inter-particle bonding resulting from the inter-particle solvent removal during drying; this brings the particles closer because of capillary action resulting in particle cluster formation. Subsequently, during calcination, these particle clusters form strong bridges among themselves thereby forming hard agglomerates. It is also possible that the cluster of primary particles can have weak inter-particle bonding thereby forming soft agglomerates. The TEM microstructure of the calcined gel shows high degree of agglomeration. The degree of agglomeration is expressed by Agglomeration Factor (AF), which is the ratio of mean agglomerate or
particle size to primary particle size. A higher value of AF is an indication of greater degree of agglomeration.

5.1.6 Compaction Behaviour of Calcined Gel

Figure 5.7 shows the semi logarithmic plot of compaction pressure as a function of density of the green compacts for as prepared calcined gel. The graph of green density vs log (compaction pressure) provides important information about the powder compaction behaviour. Usually, compaction of ceramic powders takes place in two stages:

Stage-I  Granule flow and rearrangement

Stage-II  Granule deformation combined with granule densification.

The crushing strength \( P_j \) of particles is the intersection of the two linear segments and the \( P_j \) value varies with size, shape and extent of particle breakage from brittle fracture.

Fig.5.7. Compaction behaviour of calcined (850°C) Al\(_2\)O\(_3\)-ZrO\(_2\) powder (ROUTE 1)

Stage-I take place at lower pressure, where a small amount of sliding and granule rearrangement takes place. Stage-II occurs above \( P_j \) and begins with granule deformation, which subsequently shifts to granule densification process. The dependence of agglomerate break point \( P_j \) on the granule parameter during stage –II compaction can be described by the following equation [5.9].
\[ \rho_{\text{compact}} = \rho_{\text{fill}} + M \log \frac{P}{P_j} \]  

(5.5)

where, \( \rho_{\text{compact}} \) is the compact density at an applied pressure \( P_a \), \( \rho_{\text{fill}} \) is the filled density and 'M' is the compaction constant that depends on the deformability and densification characteristics of the granules.

![Relative density as a function of sintering temperature for sintered Al\(_2\)O\(_3\)-ZrO\(_2\) composites (ROUTE 1)](image)

**Fig. 5.8. Relative density as a function of sintering temperature for sintered Al\(_2\)O\(_3\)-ZrO\(_2\) composites (ROUTE 1)**

The critical pressure (\( P_j \)) or the agglomerate break point denotes the strength of the agglomerate. The lower is the agglomerate strength; the softer will be the agglomerate which will easily break under compaction load leading to better compaction and high green density. The as prepared calcined powder shows higher \( P_j \) value (134 MPa). It is usually observed that powder containing high density granules produce a high compact density with a lower value of 'm' (up to 5). Soft or low density granules, on the other hand, have 'M' in the range 7-10 [5.9]. For the gel prepared powder 'M' is 2.2 which indicate that the powder has high-density granules.
5.1.7 Densification Behaviour of Sintered Pellets

The relative density of the sintered samples as a function of sintering temperature is shown in Fig. 5.8. The relative densities were calculated using rule of mixture and the theoretical densities of monoclinic ZrO₂ (5.89 gm/cm³) and Al₂O₃ (3.98 gm/cm³). It is seen that the density increases with sintering temperature and exhibit ‘S’ type behaviour. Although a large linear shrinkage (15% - 19%) was observed during the sintering process, the sintered samples had poor sintered density. It is presumed that the presence of hard agglomerates and flaws restrict pore removal during sintering which reduces the sintered density [5.10].

![XRD pattern of Al₂O₃-ZrO₂ composites sintered at different temperature (ROUTE 1)](image)

Fig.5.9. XRD pattern of Al₂O₃-ZrO₂ composites sintered at different temperature (ROUTE 1)

5.1.8 Phases and Microstructure in the Sintered Sample

The XRD pattern of the samples sintered at different temperature is shown in Fig. 5.9. The volume fraction of m-ZrO₂ and t-ZrO₂ has been calculated using Schmid’s formula [5.11] and is shown in Fig. 5.10. X-ray diffraction pattern of sintered pellets show monoclinic ZrO₂ (d= 3.15 Å, JCPDS 83-0944) and α-Al₂O₃ (d= 2.09Å, JCPDS 82-1467) as the major phase in the sintered sample along with small amount of t-ZrO₂ phase (d= 2.96 Å, JCPDS 81-1544). The fraction of retained t-ZrO₂ decreases on increasing the
sintering temperature probably due to the combined effect of low matrix constraint provided by the porous compacts as well as due to an increase in grain size.

Fig.5.10. Tetragonal ZrO$_2$ retention as a function of sintering temperature (ROUTE 1)

Figure 5.11 show the sintered microstructure of Al$_2$O$_3$-ZrO$_2$ composite. The dark grains are Al$_2$O$_3$ and bright grains are ZrO$_2$. The microstructure is porous and shows both intergranular and intragranular ZrO$_2$. The grain size distribution of both Al$_2$O$_3$ and ZrO$_2$ has wide variation. The average grain size for ZrO$_2$ are 1.43 ± 0.45 $\mu m$ and that of Al$_2$O$_3$ are about 1.67 ± 0.57 $\mu m$. 
The present section on the processing of Al$_2$O$_3$-ZrO$_2$ composites by gelation could be concluded with the following findings. Although, the prepared Al$_2$O$_3$-ZrO$_2$ powder had fine crystallites, it also had high agglomeration strength. The maximum sintered density of the composite after sintering at 1600°C was 70% with low fraction of retained t-ZrO$_2$ (9.3%). The sintered sample had porous microstructure with both inter and intragranular ZrO$_2$ in Al$_2$O$_3$ matrix. The porous microstructure probably resulted from the sintering of agglomerated powder. Therefore, further processing optimization are needed to improve the sintered density as well as t-phase retention. It is proposed that the same may be achieved either by modifying the powder processing route or by adopting post powder preparation processing steps.
5.2 Preparation of $\text{Al}_2\text{O}_3$-$\text{ZrO}_2$ Composite by Precipitation Method Using Chloride Precursors (ROUTE 2)

In the previous section, it was observed that the composite powder prepared by gelation method did not densify to high density and it was thought that the gelation method might be responsible for poor sintered density. The logic behind this assumption is the fact that in the gelation process, upon the addition of NH$_4$OH, partial precipitation of the AlCl$_3$ and ZrOCl$_2$ to the respective hydroxide takes place. The system pH at this stage is about 6.5. Subsequently, the hydroxides forms a network and results in a gel which entraps the unreacted AlCl$_3$ and ZrOCl$_2$ as well as the solvent. The presence of residual chlorides helps in lowering the crystallization temperature of Al and Zr hydroxides. Due to low temperature crystallization, the crystal growth continues even at higher temperature and therefore, at the sintering temperature the crystallite size becomes large which most likely has affected $\alpha$-phase retention and density. Secondly, due to the large volume of the entrapped solvent (water), hard agglomerate formation is favoured and this also has affected densification. Washing of the gel to remove the excess ions and the solvent cannot be adopted here because it will also remove the water soluble unreacted salts which may affect the stoichiometry. Thus, a different powder processing route, viz, precipitation from the salt is being adopted as a process optimization step. In the precipitation process, the pH is maintained between 8.7 and 9.1 and the system is thoroughly stirred during the precipitation process so that complete reaction of AlCl$_3$ and ZrOCl$_2$ with NH$_4$OH takes place. This precipitate if required can be washed for the removal of unwanted anions. This section will therefore, discuss the properties of $\text{Al}_2\text{O}_3$-$\text{ZrO}_2$ composite powder and compact prepared from the precipitated powder.

The method of the $\text{Al}_2\text{O}_3$-$\text{ZrO}_2$ composite powder preparation by precipitation route has already been detailed in section 4.2.2. In the following sections, the thermal decomposition, crystallization, phase evolution and densification behaviour of those powder and that of the sintered compacts will be discussed.

5.2.1 Thermal Analysis of Dried Precipitates

Figure 5.12 shows the DSC/TG plot of the precipitated $\text{Al}_2\text{O}_3$-$\text{ZrO}_2$ uncalcined powder. The graph is distinctly different from that of dried gel. It has two endothermic peaks; the
first one is broad and occurs in the temperature range 30°C - 180°C followed by a sharp endothermic peak at 290°C. The TG curve exhibit a total weight loss of 52% which takes place in three stages. In the first stage (RT-180°C), the weight loss is 14%. The second stage of weight loss (24%) is observed between 180°C - 320°C and the third and final stage of weight loss (13%) is observed between 320°C - 350°C. The first endothermic peak doublet and the associated weight loss correspond to the dehydroxylation of hydrated Al₂O₃ (pseudo boehmite). The decomposition of pseudo boehmite takes place in two stages. In the first stage, pseudo boehmite loses its 15% excess water and transforms to bayerite which subsequently decomposes to amorphous Al₂O₃. The crystallization of amorphous to transition Al₂O₃ is masked by the strong endothermic peak of NH₄Cl decomposition.

The second endothermic peak and the associated weight loss is due to the decomposition of NH₄Cl (Eqns. 5.1 and 5.3) and the third stage weight loss relate to the dehydroxylation of Zr(OH)₄ (Eqn. 5.4). The observed weight loss for the dehydroxylation of Al(OH)₃ and Zr(OH)₄ matches with that of theoretical value. Since the precipitation was carried out at higher pH (8.7-9.1), it ensured complete precipitation of both AlCl₃ and
ZrOCl₂ to Al(OH)₃ and Zr(OH)₄ respectively. In this case, the dehydroxylation of Zr(OH)₄ to ZrO₂ is a single step process (Eqn. 5.4). Due to the partial removal of NH₄Cl during solvent extraction from the precipitates, the observed weight loss for NH₄Cl is less (24%) as against 48% for the gel.

5.2.2 FTIR Spectra of Dried Precipitates

The FTIR spectrum of the amorphous precipitates is presented in Fig. 5.13. The different absorption peaks and the possible vibration frequencies have been listed in Table 5.4.

![FTIR spectra of dried Al₂O₃-ZrO₂ precipitates (ROUTE 2)](image)

**Fig.5.13. FTIR spectra of dried Al₂O₃-ZrO₂ precipitates (ROUTE 2)**

A comparison of this spectrum with that of the gel (Fig. 5.3) shows that due to a lower fraction of residual water and anions in the precipitates the absorption peaks are well resolved. The absorption peaks at 3150, 3045 and 1070 cm⁻¹ are clearly distinguishable (Fig. 5.13). It is also noticed that the absorption peaks of Zr-O is weak due to the partial masking effect from the stronger intensity peaks of Al-O and N-H stretching. The shoulder peaks at 620 and 470 cm⁻¹ are due to cubic ZrO₂ [5.6].
Table 5.4 FTIR spectra of dried precipitates (ROUTE 2)

<table>
<thead>
<tr>
<th>Adsorption Peak (cm$^{-1}$)</th>
<th>Nature of Peak</th>
<th>Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>3460</td>
<td>stretching vibration</td>
<td>Molecular water</td>
</tr>
<tr>
<td>3150,3045</td>
<td>strong Bending</td>
<td>H bonded OH</td>
</tr>
<tr>
<td>2800-2850</td>
<td>shoulder peak</td>
<td>N-H</td>
</tr>
<tr>
<td>2370</td>
<td>weak stretching</td>
<td>Cl$^-$</td>
</tr>
<tr>
<td>1750</td>
<td>shoulder peak</td>
<td>N-H bending</td>
</tr>
<tr>
<td>1641</td>
<td>weak bending</td>
<td>Zr-OH</td>
</tr>
<tr>
<td>1405</td>
<td>strong stretching</td>
<td>N-H bending</td>
</tr>
<tr>
<td>1070</td>
<td>sharp bending</td>
<td>Al-O</td>
</tr>
<tr>
<td>470,620</td>
<td>weak bending</td>
<td>Zr-O vibration</td>
</tr>
</tbody>
</table>

5.2.3 Phase Evolution of Calcined powder

The XRD patterns of Al$_2$O$_3$-ZrO$_2$ calcined (350 to 950°C) precipitates are presented in Fig 5.14. The powder calcined at 350°C show broad peaks of cubic ZrO$_2$ (crystallite size 4.4 nm). The average crystallite size increases with increasing temperature due to the nucleation and growth of crystals. Tetragonal ZrO$_2$ appears at 850°C but monoclinic ZrO$_2$ could not be detected till 950°C. γ-Al$_2$O$_3$ could be detected from 850°C onwards.
Fig. 5.14. XRD pattern of Al₃O₃-ZrO₂ precipitates at different calcination temperature (ROUTE 2)
5.2.4 Particle Size and Surface Area of Calcined Precipitates

The particle size distribution of calcined precipitates is shown in Fig. 5.15. The agglomerates have a wide size distribution ranging from 1-100 µm. The distribution shows that 40% of the agglomerates are in the size range of 30-60 µm with very few (~20%) on the lower size (<10 µm) range. The specific surface area of the calcined powder is 71 m² gm⁻¹ and the calculated particle size (D_BET) is 17.42 nm.

![Particle size distribution of 850°C calcined precipitates (ROUTE 2)](image)

*Fig.5.15. Particle size distribution of 850°C calcined precipitates (ROUTE 2)*

5.2.5 TEM Analysis

Figure 5.16 (a) shows the bright field TEM image of calcined precipitates. The selected area diffraction pattern of the powder (Fig 5.16 (b)) shows ring pattern indicating polycrystalline nature of the calcined precipitates. The micrograph shows that although the primary particles are spherical, they are agglomerated. The dark particles are ZrO₂ and the lighter ones are Al₂O₃. While the crystallite size calculated from X-ray line broadening is 12.78 nm, TEM micrograph indicate that the average particles size is 22.5 nm. A larger particle size in TEM is due to the agglomeration of crystallites or primary particles caused due to the high surface energy of the fine crystallites.
Fig. 5.16. (a) TEM micrograph and (b) diffraction pattern of Al₂O₃-ZrO₂ powder calcined at 850°C (ROUTE 2)

Table 5.5 Properties of calcined (850°C) powder (ROUTE 2)

<table>
<thead>
<tr>
<th>$D_{50}$ (μm)</th>
<th>$D_{BET}$ (nm)</th>
<th>$D_{TEM}$ (nm)</th>
<th>$P_j$ (MPa)</th>
<th>$S$ ($m^2 gm^{-1}$)</th>
<th>AF</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.4</td>
<td>17.42</td>
<td>22.5</td>
<td>126</td>
<td>71</td>
<td>1216</td>
</tr>
</tbody>
</table>

5.2.6 Compaction Behaviour of Calcined Powder

Figure 5.17 shows the plot of log compaction pressure vs. green density of calcined precipitate compacts. The $P_j$ value is 126 MPa which is lower than that of gel (134 MPa). The compaction behaviour graph shows that higher initial green density of the compacts can be achieved by pressing in second segment of compaction (>126 MPa). The elimination of intergranular pores during the second stage of compaction increases the density.
Fig. 5.17. Compaction curve of precipitated $\text{Al}_2\text{O}_3$-$\text{ZrO}_2$ composite (ROUTE 2)

A wider distribution of agglomerate size is expected to increase the green density owing to better particle packing efficiency. This powder also has very high AF (1216) and ‘$M$’ (2.6) which signifies that the powder contains hard agglomerates.

Fig. 5.18. Effect of sintering temperature on relative density of $\text{Al}_2\text{O}_3$-$\text{ZrO}_2$ composite (ROUTE 2)
5.2.7 Densification Behaviour and Phase Retention of Sintered Sample

The relative density increases with sintering temperature as shown in Fig. 5.18. At 1600°C, the linear shrinkage of the sample is 25% and the relative density is 88%.

![Fig.5.19. Tetragonal ZrO₂ retention as a function of sintering temperature (ROUTE 2)](image)

5.2.8 Microstructure of Sintered Sample

The microstructure of sintered pellet in Back Scattered Electron (BSE) mode is shown in Fig. 5.20. The bright grains are ZrO₂ and the dark grains are Al₂O₃. A near uniform distribution of ZrO₂ and Al₂O₃ grains is observed throughout the matrix. The average grain size of Al₂O₃ and ZrO₂ is 1.7 ± 0.74 μm, and 1.9 ± 0.61 μm respectively. The ZrO₂ mostly appears at the grain boundaries of Al₂O₃. However, some submicron intragranular ZrO₂ grains are also found within the Al₂O₃ matrix and very few intragranular Al₂O₃ grains are also found in ZrO₂. Micropores are present at the triple junctions of the ZrO₂ grains. The presence of pores tends to increase the diffusion distance between particles thereby reducing the driving force for pore shrinkage. SEM observation also revealed that many of these pores could not be removed even during the later stage of sintering.
This section discussed the powder processing and characterization of Al₂O₃-ZrO₂ composites prepared by precipitation route using AlCl₃ and ZrOCl₂. DSC/TG of the as precipitated powder show single stage decomposition of Zr(OH)₄. The calcined powder shows a wide size distribution of agglomerate and low agglomeration strength (126 MPa). It was expected that a finer initial particles and removal of entrapped anions may improve the densification of composites. However, the maximum sintered density was only 88% after sintering at 1600°C with only 4% t-ZrO₂ retention. The sintered samples have porous microstructure with both intragranular and intergranular ZrO₂ dispersed in Al₂O₃ matrix and vice versa. The relative density of the composite although is higher than gelation route but is still low enough for mechanical property evaluation of the composite. It was also noticed that the composites undergoes a weight loss of 7.7 % during the sintering stage which is more as compared to binder content. This may be due to the removal of chlorides at higher temperature. Similar observations have been made by Scott and Reed [5.12] while working on the effect of laundering on the densification of ZrO₂. Sarkar also noted that OH- remains attached to Al₂O₃ till 1000°C [5.22]. Thus the additional weight loss during sintering of the composites can be linked to these two factors and therefore, it is necessary to remove chloride as well as hydroxyls after the complete precipitation and before calcination and sintering.
Thus the precipitated powders were subjected to hot water and alcohol washing to remove the chloride ions as well as for minimizing the hard agglomerates formation by changing the nature of surface bonding.

5.3 Effect of Hot Water and Alcohol Washing on Al₂O₃-ZrO₂ Composite Prepared by Precipitation Using Chloride Precursors (ROUTE 3)

As discussed in the previous section, Al₂O₃ - ZrO₂ composite has been prepared by precipitation route at pH 8.7-9.1 using AlCl₃ and ZrOCl₂.8H₂O as the precursor. The precipitate was washed with hot water to remove the excess NH₄OH and NH₄Cl followed by propanol washing for removing the surface hydroxyl groups from Al(OH)₃ and Zr(OH)₄ (which are likely to produce hard agglomerate after drying). The effect of washing on the properties of Al₂O₃-ZrO₂ composite is discussed in the following sections.

5.3.1 Thermal Analysis of Dried Washed Precipitates

The DSC/TG plot of the as dried washed precipitates is shown in Fig. 5.21. The DSC plot shows two broad exothermic peaks at 105°C and 209°C (this is indicated by a slope change and a peak in the derivative DSC curve), a combination of exothermic, endothermic and exothermic peak between 280 and 305°C and another broad exothermic peak at 800°C. The first endothermic peak refers to pseudo boehmite to bayerite transformation. This bayerite further transforms to boehmite with a weight loss of 6% at 209°C. Subsequently, bayerite crystallizes to γ-Al₂O₃ at 280°C. The next endothermic peak is for Zr(OH)₄ decomposition followed by another exothermic peak due to the crystallization of cubic ZrO₂. The TG plot shows a total weight loss of 28.6% which takes place in two stages. X-ray diffraction pattern of 'as dried' precipitate shows that pseudo-boehmite is present. The pseudo-boehmite has a disordered structure and it contains >15% water in the lattice. On heating, dehydroxylation of pseudo-boehmite takes place and the structure changes to bayerite. On further heating, bayerite changes to Al₂O₃ through the intermediate step of boehmite [5.13, 5.14]. Assuming that there are no impurities (i.e.NH₄Cl or NH₄OH, which have been mostly removed during washing), the weight loss in TG is due to two processes, viz. decomposition of Al(OH)₃ (single stage decomposition) and decomposition of Zr(OH)₄. For equal volume fraction of Al₂O₃ and ZrO₂, Al(OH)₃ dehydroxylation weight loss should be 13.9% (Eqn. 5.2).
The observed weight loss of 14% matches well with theoretical value and thus the first stage weight loss up to 300°C corresponds to the decomposition of Al(OH)$_3$ and its crystallization to Al$_2$O$_3$. The DSC curve also shows an exothermic peak at the end of the first stage weight loss. The second stage weight loss is 14.6%. For the Zr(OH)$_4$ decomposition reaction (Eqn. 5.4), the calculated weight loss is 13.82% for powder having equal volume fraction of Al$_2$O$_3$ and ZrO$_2$. The observed weight loss 14.6% corresponds well with the theoretical value. This weight loss is also associated with an exothermic peak at 400°C. Thus the exothermic peak at 400°C and the weight loss of 14.6% between 300 and 400°C is due to the decomposition of Zr(OH)$_4$ and the crystallization of ZrO$_2$. XRD confirms that cubic ZrO$_2$ is formed at around that temperature. The exothermic peak at 825°C is due to the transformation of cubic to tetragonal ZrO$_2$. The phase transition of amorphous to cubic and tetragonal follows the reported transformation sequence [5.15].

5.3.2 FTIR Analysis

The nature of the surface radicals of the washed precipitates (uncalcined and calcined) was observed using FTIR spectroscopy (Fig. 5.22). The crystallization behaviour and
phase evolution during calcination is dependent on the nature of bonding in the Zr and Al hydroxides in the raw powder.

![IR spectra of dried and calcined washed precipitates (ROUTE 3)](image)

**Fig.5.22. IR spectra of dried and calcined washed precipitates (ROUTE 3)**

The stretching positions of raw powder as well as calcined powder are quite similar to those reported in earlier sections (Sections 5.1.3 and 5.2.2). The relative intensity of all possible peaks is higher for calcined powder. A comparative study of the different peak positions for both the powder is given in Table 5.6. The broad band at 3200-3600 cm⁻¹ in the raw powder is due to asymmetric and symmetric stretching vibration of (OH)⁻¹ group, and this broad peak became narrow on calcination. The sharp peaks at 2361 and 2343 cm⁻¹ are due to coupled effect of stretching and bending vibration of (OH)⁻¹ group. The calcined powder does not have any H-bonded (OH)⁻¹ group. The bending at 3430 and 3110 cm⁻¹ are the non-hydrogen bonded (OH)⁻¹ group which confirms the presence of Zr(OH)₄ in raw powder. The peaks at 1070 and 735 cm⁻¹ correspond to Al-OH and Al-O bonds. The stretching vibration at 605 and 472 cm⁻¹ in calcined powder is attributed to cubic ZrO₂. There is no N-H stretching for both the powder which confirms the absence of ammonium chloride.
Table 5.6 FTIR spectra of dried and calcined (260°C) washed precipitates (ROUTE 2)

<table>
<thead>
<tr>
<th>Adsorption Peak (cm⁻¹)</th>
<th>Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Powder</td>
<td>Calcined at 260°C</td>
</tr>
<tr>
<td>3000-3500</td>
<td>Molecular water</td>
</tr>
<tr>
<td>3430</td>
<td>-OH</td>
</tr>
<tr>
<td>3110</td>
<td>-OH</td>
</tr>
<tr>
<td>2360, 2343</td>
<td>Cl-</td>
</tr>
<tr>
<td>2084</td>
<td>H bonded OH</td>
</tr>
<tr>
<td>1634</td>
<td>Sharp Zr-OH</td>
</tr>
<tr>
<td>1636</td>
<td></td>
</tr>
<tr>
<td>1377</td>
<td>Zr-OH</td>
</tr>
<tr>
<td>1072</td>
<td>Al-OH</td>
</tr>
<tr>
<td>1070</td>
<td></td>
</tr>
<tr>
<td>735</td>
<td></td>
</tr>
<tr>
<td>614, 478</td>
<td>Zr-O</td>
</tr>
</tbody>
</table>

5.3.3 Phase Evolution of Calcined Washed Precipitates

The XRD pattern of washed Al₂O₃-ZrO₂ washed precipitates is shown in Fig. 5.23. The as dried precipitates have pseudoboehmite. This precipitate when heated at 260°C, the pattern changes to that of bayerite. At 550°C, broad peaks consisting of cubic ZrO₂ and transition Al₂O₃ appears. At 850°C, while ZrO₂ changes to a mixture of cubic + tetragonal, Al₂O₃ is present as γ-Al₂O₃. At 1050°C, the XRD pattern is consists of all the three forms of ZrO₂ (m, t and c) as well as γ-Al₂O₃. The crystallite size of ZrO₂ is 21.55 nm at this temperature.
Fig. 5.23. X-ray diffraction of Al₂O₃-ZrO₂ washed precipitates calcined at different temperature (ROUTE 3)
Table 5.7 Properties of calcined washed precipitates (ROUTE 3)

<table>
<thead>
<tr>
<th>D_{50} (µm)</th>
<th>D_{BET} (nm)</th>
<th>D_{TEM} (nm)</th>
<th>P_j (Mpa)</th>
<th>S (m² gm⁻¹)</th>
<th>AF</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.25</td>
<td>10</td>
<td>10-20</td>
<td>99</td>
<td>123</td>
<td>770</td>
</tr>
</tbody>
</table>

5.3.4 Particle Size, Pore Size distribution and Surface Area Analysis of Calcined Washed Precipitates

The particle size distribution of calcined washed precipitates is shown in Fig. 5.24. The agglomerate size has a wide distribution ranging from 1-100 µm. It is seen that 50% of the agglomerates are in the size range of 1-19 µm. The finer size fractions (1-3 µm) become distinct on water and alcohol washing.

Thus the washing process is at least partially effective in breaking the agglomerates and reducing the apparent particle size. The specific surface area of the calcined powder is 123 m² gm⁻¹ and the calculated particle size (D_{BET}) is 10 nm. The predominant pore width is around 1.5, 2.7 and 6.2 nm indicating a combination of micro and mesopore (pore size >2 nm).

Fig.5.24. Particle size distribution of washed precipitates calcined at 850°C (ROUTE 3)
5.3.5 TEM Analysis

Figure 5.25 (a, b) shows the bright field image and diffraction pattern respectively of the calcined powder. Both Al₂O₃ and ZrO₂ have comparable particle sizes (10 – 20 nm). Thus the particle size obtained from TEM matches well with the crystallite size (7.53 nm) obtained from X-ray line broadening. The corresponding electron diffraction pattern shows distinct ring pattern. Thus the calcined composite powder is well crystallized at 850°C.

![TEM micrograph and diffraction pattern of Al₂O₃-ZrO₂ washed precipitates calcined at 850°C (ROUTE 3)](image)

5.3.6 Compaction Behaviour of Calcined Washed Precipitates

The calcined powder was uniaxially pressed and the green densities were plotted as a function of log applied pressure (Fig. 5.26). The agglomerate strength of the powder is found to be 99 MPa. The agglomerate strength is much lower than the unwashed powder (126 MPa). The calcined powder has smaller AF (770) which signifies lesser agglomeration tendency of these powders. The water washing followed by alcohol washing prevents strong interparticle bonding during drying process thereby reducing the capillary forces. The dried powder is fluffy and softly agglomerated.
5.3.7 Sintered Density and Microstructure

The effect of sintering temperature on the density of $\text{Al}_2\text{O}_3$–$\text{ZrO}_2$ composite is shown in Fig. 5.27. The sintering of the pellets showed nearly isotropic shrinkage over the temperature range 1400-1600°C with the anisotropy factor (ratio of radial to transverse shrinkage) varying between 1.03-1.04. The relative sintered density increases with temperature with complete transformation of tetragonal $\text{ZrO}_2$ to monoclinic phase. In the present study, the $\text{Al}_2\text{O}_3$–$\text{ZrO}_2$ composite could be densified only up to 90%, the lower sintered density resulted from the incomplete pore removal. It may be noted that during the sintering process, a further sample weight loss of 9.4% was recorded. This magnitude of the weight loss is definitely more than that expected for the binder burnout. It is postulated that this extra weight loss comes from the residual chlorides or hydroxyl ions (in hydrated $\text{Al}_2\text{O}_3$) which go off at high temperature leaving behind a porous structure. This enables the grains to grow at a rapid rate without a corresponding decrease in porosity or pore removal. Thus the final microstructure becomes porous with relatively large grains (in $\mu$m) of $\text{Al}_2\text{O}_3$ and $\text{ZrO}_2$. The microstructure of polished and etched sample of sintered $\text{Al}_2\text{O}_3$–$\text{ZrO}_2$ composites is shown in Fig. 5.28. The $\text{Al}_2\text{O}_3$ has a narrow grain size distribution.

![Graph showing compaction behaviour of calcined $\text{Al}_2\text{O}_3$–$\text{ZrO}_2$ washed precipitates](image.png)

**Fig.5.26. Compaction behaviour of calcined $\text{Al}_2\text{O}_3$–$\text{ZrO}_2$ washed precipitates (ROUTE 3)**
Fig. 5.27. Relative density and \(t\)-ZrO\(_2\) phase retention as a function of sintering temperature for the Al\(_2\)O\(_3\)-ZrO\(_2\) composites (ROUTE 3).

Fig. 5.28. (A) SEM micrograph of Al\(_2\)O\(_3\)-ZrO\(_2\) composite sintered at 1600°C.

The microstructure is homogeneous but has both inter and intragranular ZrO\(_2\) was observed in the matrix Fig. 5.28 (A) TEM image shows that microcracks are present at the Al\(_2\)O\(_3\)-ZrO\(_2\) grain boundary [Fig. 5.28 (B)] along with twining cracks (arrow marked). The coarsening of the microstructure probably results due to the limited solid solubility of
Al₂O₃ and ZrO₂ phases. The average grain size of Al₂O₃ and ZrO₂ are 1.9 ± 0.7 µm, 1.5 ± 0.60 µm respectively.

**Fig. 5.28. (B) TEM micrograph of sintered Al₂O₃-ZrO₂ composite (ROUTE 3)**

5.3.8 Hardness and Biaxial Flexural Strength

The Vickers hardness of the sintered Al₂O₃-ZrO₂ composite sample is shown in Fig. 5.29.

**Fig. 5.29. Variation of hardness with sintering temperature (ROUTE 3)**
Although the fraction of retained $t$-ZrO$_2$ decreases with sintering temperature, the hardness as well as sintered density continuously increases with sintering temperature till 1600°C. The above increase in the hardness of the Al$_2$O$_3$-ZrO$_2$ composite could be related to the density increment. It appears that the phases of the sintered composite have least influence on the hardness. The biaxial flexural strength of the sintered sample was determined on circular specimen. The strength increases with increase in sintering temperature (Fig. 5.30). The lower value of strength is due to the combined effect of porous microstructure and microcracking (the later resulting from spontaneous $t\rightarrow m$ ZrO$_2$ transformation).

![Fig. 5.30. Effect of sintering temperature on biaxial flexure strength of Al$_2$O$_3$-ZrO$_2$ composite (ROUTE 3)](Fig. 5.30. Effect of sintering temperature on biaxial flexure strength of Al$_2$O$_3$-ZrO$_2$ composite (ROUTE 3))

The strength of the composite show an exponential relationship with porosity and the highest biaxial strength of the composite was 55 MPa. The three point bending strength at 1600°C was 63.7± 2.6 MPa, which is higher than that of biaxial strength. Since the biaxial flexure takes place due to more severe tensile stress state in the sample, its value is usually lower than that obtained with three point bending test. Thus it is observed that the Al$_2$O$_3$–ZrO$_2$ composite powder prepared by precipitation route using chloride precursors at higher pH (8.7-9.1) has fine crystallites and high surface area as compared to the powder prepared by gelation method. The subsequent post precipitation treatment
of water and iso propyl alcohol washing resulted in soft and porous agglomerates which improved the densification.

SENB fracture toughness ($K_{IC}$) measured in three point bending (1600°C sintered sample) was 1.75 MPa√m, which is lower than pure and dense Al$_2$O$_3$ ceramics. It thus appears that the extensive matrix microcracking due to spontaneous transformation of ZrO$_2$ associated with low density porous microstructure has resulted in poor toughness.

The density of the samples could be increased to 90% of the theoretical. However, even then $\tau$-ZrO$_2$ phase could not be retained in the significant fraction in the sintered sample. As already mentioned, residual chlorides may affect the densification. Thus it was decided to partially reduce the chloride content of the precursors by replacing AlCl$_3$ with Al(NO$_3$)$_3$.

5.4 Al$_2$O$_3$-ZrO$_2$ Composite Prepared by Precipitation using Nitrate and Chloride Precursors: Effect of Hot Water and Alcohol Washing (ROUTE 4)

As already mentioned, the presence of residual chloride in the powder affects its densification behaviour. Therefore, it was decided to replace one of the precursors (AlCl$_3$) with Al(NO$_3$)$_3$ to study the effect of precursor on density and phase retention of the sintered Al$_2$O$_3$-ZrO$_2$ composites. Since zirconyl nitrate is costly and difficult to work with, Al(NO$_3$)$_3$ (because of its ready availability and better workability) replaced AlCl$_3$ while ZrOCl$_2$ was retained as ZrO$_2$ precursor for Al$_2$O$_3$-ZrO$_2$ composite processing.

The Al$_2$O$_3$-ZrO$_2$ composite was prepared by precipitation at higher pH 8.7-9.1 from a mixed solution of Al(NO$_3$)$_3$ and ZrOCl$_2$.8H$_2$O. The precipitate was washed with hot water to remove the excess NH$_4$OH and NH$_4$Cl followed by washing with propanol. The effect of washing on the properties of Al$_2$O$_3$-ZrO$_2$ composite is discussed in the following sections.

5.4.1 Thermal Analysis of Dried Washed Precipitates

The DSC/TG plot of the as dried washed precipitates is shown in Fig. 5.31. The DSC curve in this case shows an endothermic peak at 110°C, a sharp exothermic peak at about 260°C and another endothermic peak at 280°C respectively. In between the first
endothermic peak at 100°C and first exothermic peak at 260°C there is another endothermic peak at 122°C (indicated by slope change). At higher temperature the DSC curve shows a sharp endothermic peak at 280°C and broad endothermic peak at 357°C followed by exothermic peaks at 420°C and 780°C respectively. Finally there is a broad hump around 1000°C. The TG curve of the gel shows a gradual weight loss of about 14.58% in the temperature range 30 - 250°C which takes place in two stages. The first stage weight loss is 9% and second stage weight loss (between 100-225°C) is 5.4%.

![DSC/TG thermogram of dried washed precipitates (ROUTE 4)](image)

**Fig.5.31. DSC/TG thermogram of dried washed precipitates (ROUTE 4)**

A sharp weight loss of 5.6% is recorded in the temperature range 250 – 300°C followed by another weight loss of 5.5% occurring between 300 and 500°C. The X-ray diffraction pattern of as dried uncalcined powder shows the presence of disordered bayerite. It is reported [5.16] that the dedydroxylation of bayerite (Al₂O₃·3H₂O) took place in two stages. In the first stage, bayerite decomposes to boehmite according to the reaction:

\[
\text{Al(OH)}_3 \rightarrow \text{AlO(OH)} + \text{H}_2\text{O}
\]  

(5.6)
In the present study, the weight loss for this stage is 9.4%. In the second stage, boehmite decomposes to form amorphous Al\(_2\)O\(_3\) with a weight loss of 6% following the reaction given below:

\[
2\text{Al}^3\text{O}^4\text{(OH)} = \text{Al}_2\text{O}_3 + \text{H}_2\text{O}
\] (5.7)

The total weight loss is 15.4%. Subsequently the amorphous Al\(_2\)O\(_3\) crystallizes to \(\gamma\)-Al\(_2\)O\(_3\) at 260°C. The observed weight loss (14.58%) matches well with the calculated weight loss.

Following this exothermic peak, a sharp endothermic peak occurs at 280°C associated with a total weight loss of 11.1% occurring in two stages. The most probable reaction which will describe the decomposition of Zr(OH)\(_4\) [5.17,5.18] are as follows:

\[
\text{Zr(OH)}_4 = \text{ZrO(OH)}_2 + \text{H}_2\text{O}
\] (5.8)

\[
\text{ZrO(OH)}_2 = \text{ZrO}_2 + \text{H}_2\text{O}
\] (5.9)

The first stage of weight loss (5.54%) takes place between 250°C and 300°C, the second stage of weight loss (5.56%) is between 300°C and 450°C. Since the weight loss of ZrO\(_2\) takes place in two stages, it can be assumed that Zr(OH)\(_4\) first completely decomposes to ZrO(OH)\(_2\) (Eqn. 5.8) and subsequently ZrO(OH)\(_2\) decomposes to ZrO\(_2\) (Eqn. 5.9). The weight loss for Eqn. (5.8) and (5.9) would have been 6.9% and 7.8% respectively for equal volume composition. However, since the observed weight loss is less than the theoretical weight. It is possible that some overlapping of reaction (5.8) and (5.9) takes place and the following sequence is proposed:

In the first stage a small fraction of Zr(OH)\(_4\) directly convert to ZrO\(_2\) according to the reaction (Eqn. 5.4) and the remaining fraction of Zr(OH)\(_4\) converts to ZrO(OH)\(_2\) according to the reaction (Eqn.5.8). This ZrO(OH)\(_2\) subsequently decomposes to ZrO\(_2\) in the second stage according to the reaction (Eqn. 5.9).

On back calculating from the final product, it is found that weight loss of 5.54% in the first stage corresponds to decomposition of 16.8% of Zr(OH)\(_4\). This fraction of Zr(OH)\(_4\) directly converts to ZrO\(_2\) and the remaining 83.2% of Zr(OH)\(_4\) converts to ZrO(OH)\(_2\). In the second stage, this 83.2% ZrO(OH)\(_2\) converts to ZrO\(_2\).
5.4.2 FTIR Analysis

The nature of bonds present in dried washed precipitates was studied by FTIR analysis and shown in Fig. 5.32. The broad band at 3200-3600 cm$^{-1}$ in raw powder is assigned to asymmetric and symmetric stretching vibration of (OH)$^{-1}$ group. The sharp peaks at 2362 and 2335 cm$^{-1}$ are due to bending vibration of Cl$^{-}$ group. The peak positions at 1628 and 1384 cm$^{-1}$ result from the bending vibration of Zr-OH group. The stretching vibrations are
also present in the 260°C calcined powder but the peaks become sharp and strong [Table 5.8].

**Table 5.8 FTIR spectra of Al$_2$O$_3$-ZrO$_2$ powder calcined at different temperature (ROUTE 4)**

<table>
<thead>
<tr>
<th>Raw powder</th>
<th>Calcination Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>260°C</td>
</tr>
<tr>
<td>3911</td>
<td>3751</td>
</tr>
<tr>
<td>3478</td>
<td>3435</td>
</tr>
<tr>
<td>3092</td>
<td>3085</td>
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<tr>
<td>2425</td>
<td>2854</td>
</tr>
<tr>
<td>2362</td>
<td>2366</td>
</tr>
<tr>
<td>2335</td>
<td>2343</td>
</tr>
<tr>
<td>2082</td>
<td>2099</td>
</tr>
<tr>
<td>1628</td>
<td>1636</td>
</tr>
<tr>
<td>1384</td>
<td>1384</td>
</tr>
<tr>
<td>1068</td>
<td>1068</td>
</tr>
<tr>
<td>872</td>
<td>1408</td>
</tr>
<tr>
<td>760</td>
<td>734</td>
</tr>
<tr>
<td>610</td>
<td>613</td>
</tr>
<tr>
<td></td>
<td>478</td>
</tr>
</tbody>
</table>

The stretching positions of raw powder as well as calcined powder are quite similar. The relative intensity of all possible peaks is higher for calcined powder. The peaks at 1068 and 734 cm$^{-1}$ correspond to Al-OH bond. In the powder calcined at 450°C, the stretching vibrations at 613 and 478 cm$^{-1}$ were attributed to cubic ZrO$_2$. The peaks at 3420 and 1670 cm$^{-1}$ were present till 950°C corresponding to the Al-OH stretching vibration. The stretching of crystalline Zr–O bonds show absorption bands at lower frequencies of 760 and 538 cm$^{-1}$ and 573 cm$^{-1}$, which is an Al-O octahedral band at 950°C. IR spectra show that a trace amount of (OH)$^{-1}$ group still remains in the structure of Al$_2$O$_3$-ZrO$_2$ composites even after heating at 1000°C. Similar results have also been observed by
Sarkar [5.22]. This causes a weight loss of Al$_2$O$_3$-ZrO$_2$ composites samples during sintering which is explained in later sections.

**Table No 5.9 Properties of calcined powder (ROUTE 4)**

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{50}$ (µm)</td>
<td>$D_{BET}$ (nm)</td>
<td>$D_{TEM}$ (nm)</td>
<td>$P_j$ (MPa)</td>
<td>$S$ (m$^2$ gm$^{-1}$)</td>
<td>AF</td>
<td></td>
</tr>
<tr>
<td>3.54</td>
<td>7.27</td>
<td>10-15</td>
<td>98</td>
<td>170</td>
<td>120</td>
<td></td>
</tr>
</tbody>
</table>

**5.4.3 Phase Evolution of Calcined Powder**

The XRD pattern of dried washed precipitates is shown in Fig. 5.33 as a function of calcination temperature. The dried precipitates contain disordered bayerite (JCPDS 22-0011), while ZrO$_2$ is in amorphous state. At 260°C, the bayerite changes to boehmite. A mixture of poorly crystalline cubic ZrO$_2$ and transitional Al$_2$O$_3$ is observed at 550°C. At 750°C cubic ZrO$_2$ appears along with $\gamma$-Al$_2$O$_3$. Finally at 1050°C, ZrO$_2$ consists of a mixture of cubic + tetragonal while Al$_2$O$_3$ is present as $\gamma$-Al$_2$O$_3$

**5.4.4 Particle Size, Pore Size Distribution and Surface Area Analysis of Calcined Powder**

The particle size of washed calcined precipitates is distributed between 1-20 µm. The calcined powder had monomodal particle distribution with average size of 3.54 µm. The specific surface area of the calcined powder is 170 m$^2$ gm$^{-1}$ and the calculated particle size ($D_{BET}$) is 7.27 nm. Both micro and meso pores are present in the calcined powder. The agglomeration factor AF is much lower (120) than the precipitated and washed powder prepared from all chloride precursors indicating that residual chloride ion play a role in determining the agglomerate strength.
Fig. 5.33. X-ray diffraction of Al₂O₃-ZrO₂ powder calcined at different temperature (ROUTE 4)
Fig. 5.34. FTIR spectra of calcined Al₂O₃-ZrO₂ precipitates (a) for all chloride precursors and (b) for chloride-nitrate combination precursor (ROUTE 4)

A rough estimate of the relative chloride concentration in the two type of calcined powders (i.e. one prepared from all chloride precursors and the other prepared from the
combination of nitrate and chloride precursors) was made by studying the FTIR study of calcined powders of the above two types. The results are reproduced in Fig 5.34(a) (for all chloride precursors) and 5.34(b) (for chloride-nitrate combination precursor). The chloride peak is detected from the shoulder peak 2360 and 2330 cm\(^{-1}\) [5.2]. The Fig shows that the relative concentration of chloride is less when the precursor is a combination of chloride and nitrate. The lower amount of chloride in chloride-nitrate combination helps in achieving a higher density of the latter samples.

5.4.5 TEM Analysis

The TEM microstructure of the calcined washed precipitates is shown in Fig. 5.35. The micrograph shows fine spherical shaped particles in the range of 10-15 nm size. There is no difference in particle size and that of the crystallite size calculated from XRD and particle size from surface area. Hence the particles behave like individual crystal without clustering. The particle size shows a narrow range distribution.

*Fig. 5.35. TEM micrograph and diffraction patterns of Al\(_2\)O\(_3\)-ZrO\(_2\) 850°C calcined power (ROUTE 4)*
5.4.6 Compaction Behaviour of Powder

The compaction behaviour of the calcined washed precipitates is shown in Fig. 5.36. As the powder was less agglomerated (AF 120), the powder was soft and fluffy and compaction was easy. The linear behaviour of the curve at lower pressure range signifies that the packing is done by rearrangement of particle which behaves like loose mass instead of a coherent mass. Hence, it may be said that \( P_j \) value decreases with decreases in agglomerate size. But it was difficult to exactly find out \( P_j \) value due to the rounding of the curve. However, it appears to be about 98 MPa. The compaction constant ‘\( M \)’ calculated from Eqn. 5.5 is 7.4 which is in the range of soft agglomerate.

![Fig.5.36. Compaction behaviour of the Al\(_2\)O\(_3\)-ZrO\(_2\) power during uniaxial compaction (ROUTE 4)](image)

5.4.7 Sintering and Microstructure

The densification behavior of Al\(_2\)O\(_3\)-ZrO\(_2\) composites as a function of sintering temperature is shown in Fig. 5.37. The relative density increases linearly with temperature till 1500°C. The anisotropy factor decreased with increase in sintering temperature till 1450°C (90% theoretical density) and remained unchanged thereafter. The microstructure of polished and etched sintered sample (1600°C) (Fig. 5.38) shows that the average grain size of Al\(_2\)O\(_3\) and ZrO\(_2\) are 1.77 ± 0.79 µm, 1.27± 0.25 µm respectively. The spherical ZrO\(_2\) was present mostly in intergranular position. The
improvement in density in Route 4 samples (as compared to Route 3 samples) is due to the combined effect of water and alcohol washing. It has already been discussed in the literature review section of the powder processing chapter that the presences of both chloride ions as well as hard agglomerates affect the density improvement. While water washing has reduced the chloride content alcohol washing has produced the soft agglomerates. The presence of soft agglomerates has improved the sintered density. The M value is 3% which indicate the soft agglomerate.

Fig. 5.37. Relative density of Al$_2$O$_3$-ZrO$_2$ composites as a function of sintering temperature (ROUTE 4)

Fig. 5.38. SEM micrograph of Al$_2$O$_3$- ZrO$_2$ composite sintered at 1600°C (ROUTE 4)
TEM microstructure (Fig. 5.39) shows that the microcracks (generated due to the spontaneous transformation of $t$-ZrO$_2$ on cooling) are present at the Al$_2$O$_3$- ZrO$_2$ grain boundary and show a twin like appearance.

![TEM micrograph of sintered Al$_2$O$_3$-ZrO$_2$ composite (ROUTE 4)](image)

**Fig.5.39. TEM micrograph of sintered Al$_2$O$_3$-ZrO$_2$ composite (ROUTE 4)**

![Effect of sintering temperature on hardness of Al$_2$O$_3$-ZrO$_2$ composite (ROUTE 4)](image)

**Fig.5.40. Effect of sintering temperature on hardness of Al$_2$O$_3$-ZrO$_2$ composite (ROUTE 4)**
5.4.8 Hardness and Biaxial flexural strength

The Vickers hardness of the sintered Al₂O₃-ZrO₂ composite sample is shown in Fig. 5.41. The hardness variation of the present samples (prepared from nitrate chloride precursor combination) exhibit similar hardness trend observed for the samples prepared from all chloride precursors. However, in this case, the increase in hardness is slow between 1400-1450°C (4.08 to 4.46 GPa), followed by a rapid increase to 8.7 GPa at 1600°C and finally between 1500 to 1600°C the increase is steady and linear although, the rate of increase is slow. The above increase in the hardness of the Al₂O₃-ZrO₂ composite could be related to the density increment. It appears that the phases of the sintered composite have least influence on the hardness.

![Fig.5.41. Effect of sintering temperature on biaxial flexure strength of Al₂O₃-ZrO₂ composite (ROUTE 4)](image)

The biaxial flexural strength of the sintered sample increases with sintering temperature and also have a porosity dependence as shown in Fig.5.41. The lower strength value is due to the porous microstructure and high density of microcracks generated due to the spontaneous transformation of \( t \rightarrow m \) ZrO₂ as well due to the thermal expansion between the two phases.

SENB fracture toughness \( (K_{IC}) \) measured in three point bending (1600°C sintered sample) was 1.9 MPa√m, which is lower than pure and dense Al₂O₃ ceramics. It thus
appears that the extensive matrix microcracking due to spontaneous transformation of ZrO_2 associated with low density porous microstructure has resulted in poor toughness. The Al_2O_3-ZrO_2 composite prepared from precipitation of Al(NO_3)_3 and ZrOCl_2 followed by hot water and alcohol washing crystallized at higher temperature. TEM microstructure of the calcined powder showed monomodal particle distribution having 10-15 nm primary particles. The composite had been densified to 95% of the theoretical density at 1600°C. Thus the Al_2O_3-ZrO_2 composite prepared from the combination of Al(NO_3)_3 and ZrOCl_2 showed better densification in comparison to Al_2O_3-ZrO_2 composites prepared from all chloride precursors. However, even with high density, t-ZrO_2 could not be retained. This was probably due to the low matrix modulus of the composite. The calculated composite modulus (assuming t-ZrO_2) was 296 GPa. The failure to retain t-ZrO_2 caused matrix microcracking which is responsible for the observed poor mechanical behavior of the composite. Thus, it was decided to use Y_2O_3 as stabilizer for ZrO_2. The Al_2O_3-Y_2O_3-ZrO_2 composites having nominally equal volume fraction of Al_2O_3 and Y-ZrO_2 will be prepared using the same process flow diagram as before and the properties will be evaluated.

Table 5.10 Physical properties of the calcined powder at a glance

<table>
<thead>
<tr>
<th>ROUTE</th>
<th>Av Particle size calculated from</th>
<th>BET Surface area S (m²/gm)</th>
<th>Agglomeration strength P_j (MPa)</th>
<th>TEM micrograph DTEM (nm)</th>
<th>Agglomerate factor AF</th>
<th>Surface area measurement DBET (nm)</th>
<th>Particle size measurement D_s0 (μm)</th>
<th>Agglomerate factor AF</th>
</tr>
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<tbody>
<tr>
<td>1</td>
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</tr>
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<td>2</td>
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<td>1216</td>
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</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>4</td>
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<td>98</td>
<td>170</td>
<td>10-15</td>
<td>120</td>
<td>7.27</td>
<td>7.27</td>
<td></td>
</tr>
</tbody>
</table>
Section B

Effect of Y$_2$O$_3$ doping on the properties of Al$_2$O$_3$-ZrO$_2$ Composites
5.5.1 Processing of Al$_2$O$_3$-Y-ZrO$_2$ Composites

In the previous sections the densification behavior, mechanical properties and microstructure of Al$_2$O$_3$-ZrO$_2$ composites was discussed. It was observed that the precursors (especially anions) as well as the processing route controlled the density, microstructure as well as the mechanical properties of the sintered composite. The poor mechanical properties in an otherwise reasonably dense composite were attributed to extensive microcracks resulting from the spontaneous $t\rightarrow m$ transformation during cooling from the sintering temperature as well as to the residual pores. Due to higher volume percentage of ZrO$_2$, the reduced elastic modulus of matrix could not retain $t$-ZrO$_2$, although the grain size was small. Therefore, it was decided to add Y$_2$O$_3$ (1, 2, 2.5, and 3 mol %) for stabilizing $t$-ZrO$_2$. All the Y$_2$O$_3$ doped composites were prepared by precipitation route using Al(NO$_3$)$_3$, ZrOCl$_2$, and Y(NO$_3$)$_3$ as the precursors and the precipitates were washed as before (Modified ROUTE 4 Section 4.2.4) prior to calcination.

5.5.2 Densification Behaviour of Al$_2$O$_3$-Y-ZrO$_2$ composites

The sintered density of Al$_2$O$_3$-Y-ZrO$_2$ composites as a function of sintering temperature is shown in Fig. 5.42. The sintered density increases with the increase in sintering temperature from 1400 to 1600°C. At any fixed sintering temperature, sintered density is higher for samples having higher Y$_2$O$_3$. The higher density of the Al$_2$O$_3$-Y-ZrO$_2$ composites is attributed to the oxygen vacancy concentration in the Y$_2$O$_3$ doped samples. Although Y$_2$O$_3$ addition did not alter the densification mechanism (or the activation energy), the density increased with Y$_2$O$_3$ content.
5.5.3 Tetragonal-ZrO₂ phase retention in sintered Al₂O₃-Y-ZrO₂ composites

The $t$-ZrO₂ phase retention as a function of sintering temperature and $Y₂O₃$ content of the Al₂O₃-Y-ZrO₂ composites has been given in Fig. 5.43. The $t$-ZrO₂ retention also increases with $Y₂O₃$ addition with the trend similar to that observed for density variation. The maximum $t$-ZrO₂ retention is ~100% at 3 mol% $Y₂O₃$ addition. The $t$-ZrO₂ retention is very low in the composites prepared with 1.0 mol% $Y₂O₃$ and remain almost constant throughout the sintering temperature. However, the $t$-ZrO₂ retention for the samples prepared with 2 mol% $Y₂O₃$ decreases with increase in sintering temperature. The decrease in $t$-ZrO₂ retention with sintering temperature is attributed to the grain growth ZrO₂ grains. The samples prepared with high $Y₂O₃$ content the retention is high nearly 100% retention was observed in the sintering temperature studied.

*Fig.5.42. Relative Density of Al₂O₃-Y-ZrO₂ composites as function of Y₂O₃ content*
5.5.4 Effect of Y$_2$O$_3$ addition on the sintering kinetics of Al$_2$O$_3$-ZrO$_2$ composites

The non-isothermal densification behaviour of Al$_2$O$_3$-3Y-ZrO$_2$ was shown in Fig.5.44. The densification starts around 900°C and continues till 1450°C. It could be seen from the Fig.5.44 that Y$_2$O$_3$ doped composite has higher shrinkage as compared to undoped Al$_2$O$_3$-ZrO$_2$ composites. The higher shrinkage observed in these samples is due to the enhanced densification of the samples resulting from the creation of oxygen defects due to addition of Y$_2$O$_3$ in the composites. The duplex densification behavior is also observed in these samples. An attempt has also been made to calculate the densification kinetic parameters for Al$_2$O$_3$-3Y-ZrO$_2$ composites from the isothermal densification behavior during initial stage of sintering. It has been observed that the Y$_2$O$_3$ addition did not affect the sintering mechanism during the initial stage. The analysis of the isothermal dilatometric data in the temperature range 900 to 1050°C with a 50°C interval revealed that the kinetic parameter $n$ varied from 4.76 to 5.0. This observed $n$ value indicates that the volume diffusion is the dominant densification mechanism of Al$_2$O$_3$-3Y-ZrO$_2$ composite.
Fig. 5.44. Non-isothermal densification behavior of Al$_2$O$_3$-3Y-ZrO$_2$ composites
Section C

Densification Kinetics of $\text{Al}_2\text{O}_3$-$\text{ZrO}_2$ Composites
5.6.1 Densification behavior of Al$_2$O$_3$-ZrO$_2$ composite prepared from different processing routes.

The non-isothermal densification behaviour of Al$_2$O$_3$-ZrO$_2$ composites has shown in Fig.5.45 as a function of different processing routes.

![Fig.5.45. Non-isothermal densification behavior of Al$_2$O$_3$-ZrO$_2$ composites prepared by different processing routes](image)

Figure 5.45 shows that in the lower temperature range (room temperature to 800°C), Al$_2$O$_3$-ZrO$_2$ compact under goes a small initial expansion due to the thermal expansion of the Al$_2$O$_3$-ZrO$_2$ composite powder compact followed by the onset of the shrinkage. The densification of Al$_2$O$_3$-ZrO$_2$ composite compact occurs in the temperature range 950 - 1130°C and the onset varied with the powder synthesis route. This onset temperature was related to the initial particle size and/or surface area of the powder and thus, the precipitated washed powder having higher specific surface area (123 m$^2$ gm$^{-1}$) along with finer particle size distribution showed a lower onset temperature for densification as compared to precipitated powder having lower specific surface area (71 m$^2$ gm$^{-1}$) [5.19]. The densification of Al$_2$O$_3$-ZrO$_2$ composite powder compact showed a duplex sintering behavior. The first stage of densification started between 950 - 1130°C and continued up to 1200-1250°C at an enhanced rate. The second stage of densification started between 1200-1250°C and continued till 1450°C or higher temperature at a slower rate.
Shi et al. [5.20] had also reported the similar duplex sintering behaviour of ZTA composite containing 15 or higher mole% \( \text{Al}_2\text{O}_3 \). The shrinkage was reported to be small for composites containing more than 45 mole% \( \text{Al}_2\text{O}_3 \) and it was higher at lower \( \text{Al}_2\text{O}_3 \) content. Among all the different types powder processing route studied in the present investigation, precipitated washed powder exhibited the highest shrinkage (21%) at 1450°C followed precipitation route and gelation route. The observed shrinkage range for different powder correlated well with the agglomerate size and agglomerate strength of the starting powder and the powder having hard and larger agglomerate size ended up with a smaller shrinkage during sintering process. Tables 5.3, 5.5 and 5.7 showed that the agglomerate strength were 134, 126 and 99 MPa and agglomerate size were 35, 30 and 19 \( \mu \text{m} \) for gelation, precipitation and precipitated washed routes respectively. The lower agglomerate strength and smaller agglomerate size of precipitated washed powder produced higher shrinkage in the compacts. The shrinkage was found to increase rapidly in the temperature range 950 - 1250°C, thereafter the shrinkage slope changed and shrinkage increment continued at slower rate till 1450°C and above. The slope change in temperature range 1250-1300°C could be either due to \( m \rightarrow t \) \( \text{ZrO}_2 \) phase transformation and/or to the \( \gamma \) to \( \alpha \)\( \text{Al}_2\text{O}_3 \) phase transformation (both the effects are expected to take place in the said temperature region). In order to substantiate the exact phenomena responsible for the observed duplex densification behavior, the densification behavior of the pure \( \text{Al}_2\text{O}_3 \) and \( \text{ZrO}_2 \) powder prepared by precipitation washed route was also studied. The sintering behaviour of pure \( \text{ZrO}_2 \) (Fig.5.46) shows a single stage densification behavior, where as the \( \text{Al}_2\text{O}_3 \) powder showed a double stage densification behavior similar to that of the composite powder with the onset of the second stage occurring around 1270°C. Thus the duplex densification is due to the \( \gamma \rightarrow \alpha \) \( \text{Al}_2\text{O}_3 \) phase transition.
Fig. 5.46. Dilatometric curves for Al₂O₃ and ZrO₂

The observed low temperature (1250°C) γ→α Al₂O₃ phase transition in the Al₂O₃-ZrO₂ composite compacts may be due to the presence of ZrO₂ in the composite powder which reduces the transformation temperature by 20°C.

5.6.2 Effect of precursors on densification behavior of Al₂O₃-ZrO₂ composite

The effect of precursors on densification behavior could be seen from Fig. 5.47. The samples have been prepared following precipitation and washing technique. Curve A shows the densification behavior of the compact prepared using AlCl₃ and ZrOCl₂ precursors and curve B is that prepared with Al(NO₃)₃ and ZrOCl₂. It could be seen from the figure that curve B has a higher shrinkage. Entrapped gases (caused by some volatile materials) at the sintering temperature affect the end point densities [5.21]. Scott and Reed [5.12] also reported that the presence of residual chlorine in the ZrO₂ powders (made by the chloride process) is detrimental to the sintering of ZrO₂ powders. The result of simultaneous DSC/TG analysis on the chloride precursor derived powder is shown in Fig.5.21. The gradual weight loss in the high temperature above 1000°C is attributed to the loss of residual chlorides as well as to the removal of OH- from hydrated Al₂O₃ [5.22]. Although both the powders had ZrOCl₂ as one of the precursors, the amount of chloride
ions (in the mixed nitrate chloride precursor derived samples) was partially reduced when AlCl₃ was replaced by Al(NO₃)₃.

![Graph showing non-isothermal densification behavior of Al₂O₃ - ZrO₂ composites prepared by different precursors](image)

**Fig. 5.47. Non-isothermal densification behavior of Al₂O₃ - ZrO₂ composites prepared by different precursors**

5.6.3 Effect of heating rate on densification behavior of Al₂O₃-ZrO₂ composite

The shrinkage behavior of green compacts as a function of sintering temperature and heating rate has been shown in Fig. 5.48. The onset of shrinkage was found to be independent of the heating rate. However, the temperature at which the maximum shrinkage rate was observed during first stage of sintering was found to be dependent on the heating rate and it shifted towards high temperature (1220 to 1253°C) with increase in heating rate (from 10 - 20°C /min). The maximum shrinkage rate was also found to increase with increase in heating rate during this stage.
5.6.4. Determination of sintering mechanism and activation energy - theoretical background

The generalized form of neck growth can be expressed from the two-sphere densification/sintering model [5.23, 5.24].

\[
\left( \frac{X}{R_p} \right)^n = \frac{Bt}{R_p^m}
\]  

(5.10)

where, \( X \) is the neck radius, \( R_p \) is the particle radius, \( t \) is the time, \( m \) and \( n \) are constants and the value of \( m \) and \( n \) depended on the kinetic mechanism of the initial stage of sintering, \( B = B_0 T^a \), where \( B_0 \) corresponds to the combined material and numerical constants and is related to the temperature (\( T \)) through the Arrhenius law. The exponent \( n \) (kinetic constant) of Eqn. (5.10) identifies the sintering mechanism. The value of \( n \) for different mechanism and the corresponding values of the temperature exponent ‘\( a \’ \) have been given in Table 5.11.

The neck growth and the shrinkage for the densification can be correlated by Eqn. (5.11), where, \( L_0 \) is the initial dimension of the green compact and \( \Delta L \) is the shrinkage at time \( t \).
\[
\frac{\Delta L}{L_0} = \left( \frac{X}{2R_p} \right)^2
\]  

(5.11)

Equation (5.10) and (5.11) can be combined to yield Eqn. (5.12)

\[
\frac{\Delta L}{L_0} = \left( \frac{B_0 T^a t}{2^n R_p^m} \right)^{2/n}
\]  

(5.12)

and this describes the densification behavior for isothermal conditions.

Table 5.11 Dependence of frequency factor with temperature corresponding to the kinetics models used in literature [5.24]

<table>
<thead>
<tr>
<th>Kinetic Model</th>
<th>( a )</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscous flow</td>
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<td>2</td>
</tr>
<tr>
<td>Plastic flow</td>
<td>-1</td>
<td>2</td>
</tr>
<tr>
<td>Volume diffusion</td>
<td>-1</td>
<td>5</td>
</tr>
<tr>
<td>Grain boundary diffusion</td>
<td>-1</td>
<td>6</td>
</tr>
<tr>
<td>Evaporation condensation</td>
<td>-3/2</td>
<td>3</td>
</tr>
<tr>
<td>Surface diffusion</td>
<td>-1</td>
<td>7</td>
</tr>
</tbody>
</table>

The time derivative of Eqn. (5.12) is

\[
\frac{d(\Delta L/L_0)}{dt} = \frac{d}{dt} \left[ \frac{B_0 T^a t}{2^n R_p^m} \right]^{2/n} = k \left( \frac{\Delta L}{L_0} \right)^{1-n/2}
\]  

(5.13)

where, \( k = \frac{B_0 T^a}{2^n R_p^m} \). \( B_0 \) can be expressed by the Arrhenius type relationship

\[
k = A e^{Q/RT}
\]  

(5.14)

where, \( Q \) is the activation energy and \( A = A_0 T^{a} \). The pre-exponential factor \( A \) of the Arrhenius equation is dependent on the exponent ‘\( a \)’ describing the dependence with the absolute temperature \( T \). Substitution of Eqn. (5.14) into eqn. (5.13) results in the following equation.
\[
\frac{d(\Delta L/L_0)}{dt} = A_0 T^\alpha e^{Q/RT} \left( \frac{\Delta L}{L_0} \right)^{-n/2} \tag{5.15}
\]

Equation (5.15) describes the time rate of shrinkage \((\Delta L/L_0)\) at a certain temperature and gives the generalized expression applicable for both isothermal and non-isothermal densification condition [5.25-5.27]. Thus, any set of data \(d(\Delta L/L_0)/dt \cdot \Delta L/L_0\) should fit Eqn. (5.15) independent of the experimental conditions (i.e., isothermal, non-isothermal conditions).

The dilatometric curve obtained from a linear-heating rate \((\beta = dT/dt)\), i.e., non-isothermal condition can be described by the Eqn. (5.17) (which is obtained by integrating (5.16) followed by rearrangement).

\[
T^2 \left( \frac{d(\Delta L/L_0)}{dt} \right) = \frac{2\beta Q}{nR} \left( \frac{\Delta L}{L_0} \right) \tag{5.16}
\]

The sintering activation energy and the mechanism of densification can be determined from the value of the \(Q\) and \(n\) respectively. The linear plot of \(T^2 \left( \frac{d(\Delta L/L_0)}{dt} \right)\) vs \(\frac{\Delta L}{L_0}\) as a function of heating gives an idea of \(\left( \frac{Q}{n} \right)\) ratio; however, the individual value is difficult to determine. In order to find the densification mechanism and densification activation energy, one needs to know the value of either \(Q\) or \(n\). The simultaneous determination of \(Q\) and \(n\) is only possible using the modified eqn. (5.15).

Freeman and Carroll [5.28] proposed that the sintering kinetics could be determined from a single CRH curve by modifying the Eqn. (5.15).

The differentiation of the logarithmic form of Eqn. (5.15) with respect to \(d \ln (\Delta L/L_0)\) gives

\[
\frac{d \ln d(\Delta L/L_0)}{d \ln (\Delta L/L_0)} - a \left( \frac{d \ln T}{d \ln (\Delta L/L_0)} \right) = - \left( \frac{Q[d(1/T)]}{R[d \ln (\Delta L/L_0)]} \right) + 1 \cdot \frac{n}{2} \tag{5.17}
\]

or

\[
\frac{\Delta \ln d(\Delta L/L_0)}{d \ln (\Delta L/L_0)} - a \left( \frac{\Delta \ln T}{\Delta \ln (\Delta L/L_0)} \right) = - \left( \frac{Q[\Delta (1/T)]}{R[\Delta \ln (\Delta L/L_0)]} \right) + 1 \cdot \frac{n}{2} \tag{5.18}
\]
For a fixed value of ‘a’, the plot of LHS of Eqn. (5.17) or (5.18) against \( \frac{d(1/T)}{d \ln (\Delta L/L_0)} \) or \( \frac{\Delta(1/T)}{\Delta \ln (\Delta L/L_0)} \) respectively, yields a straight line whose slope is \( \frac{Q}{R} \) and \( (1-n/2) \) is the intercept. The straight line thus obtained gives \( \frac{Q}{R} \) as slope and \( (1-n/2) \) as the intercept. Thus, \( Q \) and \( n \) can be simultaneously determined from this model (Eqn. (5.17) or (5.18)) using a single dilatometric curve. However, the parameter ‘a’ is to be assumed from the Table-10 for fitting into these equations.

**5.6.5 Determination of initial stage sintering kinetic parameter from CRH sintering**

The kinetic analysis of initial stage sintering is limited to the fractional shrinkage \( \Delta L/L_0 \leq 3 \% \), implying densification without grain growth. The initial stage sintering kinetics for \( \text{Al}_2\text{O}_3-\text{ZrO}_2 \) composites for different heating rates has been analyzed from dilatometric studies using Eqn. (5.16). The shrinkage data \( \Delta L/L_0 \leq 3 \% \) has been obtained from the nonisothermal sintering curve at different heating rate (Fig.5.48). The shrinkage rate has been calculated from the fitted time dependent shrinkage curve using numerical differentiation. The graph of \( T^a \left( \frac{d(\Delta L/L_o)}{dt} \right) \) vs \( \frac{\Delta L}{L_o} \) as a function of heating rates yields a straight line (Fig.5.49). The ‘a’ parameter has been assumed to be -1 as the viscous flow (\( a = 0 \)) and evaporation and condensation (\( a = -1.5 \)) are forbidden mechanism for densification in \( \text{Al}_2\text{O}_3-\text{ZrO}_2 \) composites. The slope, \( r \) (regression coefficient) and hence \( \frac{Q}{n} \) value calculated from the fitted equation has been tabulated in Table 5.12. The \( \frac{Q}{n} \) value has been found to be independent of the heating rate. Although it yields consistent values of \( \frac{Q}{n} \) ratio but the value of both \( Q \) and \( n \) cannot be determined simultaneously from the fitted eqn. (5.17).
Fig. 5.49. Analysis of the dilatometric curve (constant rate heating sintering) of Al₂O₃-ZrO₂ composites obtained at different heating rates using eqn. (5.16).

Table 5.12 The slopes and \( \frac{Q}{n} \) from the Fig.5.46 using Eqn. (5.16)

<table>
<thead>
<tr>
<th>Rate (( \beta )) (^\circ\text{C/min} )</th>
<th>Slope=( \frac{2\beta Q}{nR} )</th>
<th>( r )</th>
<th>( \frac{Q}{n} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>113273</td>
<td>0.998</td>
<td>47089</td>
</tr>
<tr>
<td>15</td>
<td>179136</td>
<td>0.999</td>
<td>49647</td>
</tr>
<tr>
<td>20</td>
<td>237609</td>
<td>0.999</td>
<td>49389</td>
</tr>
</tbody>
</table>

5.6.6 Determination initial stage sintering kinetic parameter from isothermal densification behaviour

The isothermal shrinkage behavior of the Al₂O₃-ZrO₂ composite has also studied in order to confirm the validity of the diffusion mechanisms. The sintering rate equation during isothermal sintering (initial stage) is given by

\[
\frac{\Delta L}{L_0} = \left( \frac{B_2 T^2 t}{2^n R_p} \right)^{\frac{2}{n}} = At^{\frac{2}{n}}
\]  

(5.12)
The logarithms of eqn. (5.13) yields

\[
\log \left( \frac{L}{L_0} \right) = \log A + \frac{2}{n} \log t \quad (5.19)
\]

Eqn. (5.19) is applicable for fractional shrinkage < 3%, a condition which satisfies the initial stage of sintering.

**Fig. 5.50.** Isothermal densification behaviour of Al$_2$O$_3$-ZrO$_2$ composites (a) Isothermal dilatometric curve (b) analysis of isothermal curve using Eqn.5.19.
Figure 5.50 (a) shows the change in shrinkage with holding time of isothermal sintering in the temperature ranges 900 to 1050°C with an 50°C interval. The isothermal shrinkage data obtained from the isothermal study has been plotted in Fig.5.50 (b) following Eqn. (5.19). The kinetic parameter ‘n’ value was determined from the slope of the fitted straight line. The value n varied between 4.45- 5.12 for different temperature. According to Table 5.11, n = 5 indicate that the densification is governed by volume diffusion. Thus, the activation energy for densification could be calculated from the $Q/n$ ratio obtained by analyzing the constant rate heating sintering dilatometric curves.

5.6.7 Simultaneous determination of initial stage sintering kinetic parameter from constant rate heating sintering dilatometric data

Figure 5.51 shows the plot of LHS of Eqn. (5.17) for $a = -1$ as a function of $\Delta (1/T)/\Delta \ln(\Delta L/L_0)$. The slope ($Q/R$) at different heating rate and intercept $(1- n/2)$ thus obtained is given in Table 5.12.

![Graph showing dilatometric analysis](image)

**Fig.5.51.** Analysis of the dilatometric curve (constant rate heating sintering) of $\text{Al}_2\text{O}_3-\text{ZrO}_2$ composites obtained at different heating rates using Eqn. 5.17.
According to Table 5.12, the ratios of $Q/n$ as well as $n$ were very close to the calculated ($Q/n$) (obtained using Eqn. 5.16). The value of $n$ varied between 5.02 and 5.22 thereby confirming that volume diffusion is the dominant sintering mechanism (as per Table 5.12).

Table 5.13 The value of slope, intercept and $Q/n$ from the Fig.5.46 using Eqn. (5.21) at different heating rate for $a = -1$.

<table>
<thead>
<tr>
<th>Heating Rate $(\beta)$ °C/min</th>
<th>Slope=$Q/R$</th>
<th>$r$</th>
<th>$n$ (calculated from intercept)</th>
<th>$Q/n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>30173</td>
<td>0.999</td>
<td>5.02</td>
<td>49974</td>
</tr>
<tr>
<td>15</td>
<td>30633</td>
<td>0.999</td>
<td>5.08</td>
<td>50138</td>
</tr>
<tr>
<td>20</td>
<td>30760</td>
<td>0.997</td>
<td>5.22</td>
<td>48994</td>
</tr>
</tbody>
</table>

Matsui [5.29] reported similar densification kinetics of ZrO$_2$ with 0.25 wt% Al$_2$O$_3$ addition. The densification rate increased with the addition of Al$_2$O$_3$ and the activation energy decreased as the kinetics changed from grain boundary diffusion (GBD) to volume diffusion (VD). The transformation of transition Al$_2$O$_3$ was not observed during the initial stage sintering temperature range. The activation energy $Q$ thus calculated from $Q/n$ ratio was found to vary between 236-258 kJ mol$^{-1}$.

5.6.8 Grain Growth Behavior of Al$_2$O$_3$-ZrO$_2$

The grain growth kinetics for normal grain growth obey a power-law relationship

$$G^N - G_0^N = Kt$$

$$G^N - Kt$$

Where, $G$ represents the grain size at time $t$, $G_0$ is the initial grain size at $t = 0$, $K$ is a constant which depended on the temperature and the activation energy of grain growth, and $N$ the grain growth exponent characterizing the growth mechanism. The grain size of both Al$_2$O$_3$ and ZrO$_2$ increased as the function of the sintering time increasing. The grain growth has almost parabolic behavior (Fig.5.52). The grain growth exponent $N$ is
calculated from the slope of the log ($\alpha$) versus log ($t$) line plot, which is equal to $1/N$ which was given in Fig. 5.53.

Fig. 5.52. Average grain sizes of the (a) ZrO$_2$ and (b) Al$_2$O$_3$ phases of the composite sintered at 1600°C for different times.
The grain growth during sintering can be described by Eqn. 5.21 [5.30]. The grain growth exponent, $N$, for ZrO$_2$ and Al$_2$O$_3$ phase were 3.17 and 4.22, respectively, indicating that different mechanisms are responsible for grain growth of each phase.

*Fig. 5.53. Log (grain size) vs. log (time) of ZrO$_2$ and Al$_2$O$_3$ sintered at 1600°C*

A growth exponent of $N = 4$ indicates a grain boundary diffusion controlled process, while an exponent of $N = 3$ indicates a volume diffusion controlled process. The grain growth exponents for the ZrO$_2$ and Al$_2$O$_3$ found in this work are in agreement with the works of Alexander et al [5.30].
References


5.4. Q. Qu, L. Li, W. Bai, C. Yan, and C. Cao, “Effects of NaCl and NH₄Cl on the initial atmospheric corrosion of zinc”, Corrosion Science, 47, 2832–2840 (2005).


Chapter VI

Results and discussion-
$\text{Al}_2\text{O}_3$-$\text{Y}$-$\text{ZrO}_2$ Composites
6.1. Flexural Strength

The effect of Y$_2$O$_3$ content on the flexural strength of Al$_2$O$_3$-Y-ZrO$_2$ composites is shown in Fig. 6.1.

![Graph showing the effect of Y$_2$O$_3$ addition on flexural strength of Al$_2$O$_3$-Y-ZrO$_2$ composites.]

Fig. 6.1. Effect of Y$_2$O$_3$ addition on flexural strength of Al$_2$O$_3$-Y-ZrO$_2$ composites

The strength gradually increases with Y$_2$O$_3$ addition till 1.0 mol% Y$_2$O$_3$ (102 MPa) followed by a rapid increase for 2, 2.5, and 3 mol% Y$_2$O$_3$ compositions which are 467, 537 and 645 MPa respectively. The low density till 1.0 mol% Y$_2$O$_3$ addition probably causes a spontaneous microcracking of the samples. In Al$_2$O$_3$-1Y-ZrO$_2$ composites, the sintered density at 1600°C is 94.5% and retained $t$-ZrO$_2$ is 10%. For Al$_2$O$_3$-2Y-ZrO$_2$ composites, under similar sintering conditions, the density is 95.4% and $t$-ZrO$_2$ retention is 16.4%. In both these composites, the combined effect of lower Y$_2$O$_3$ and lower sintered density resulted in poor $t$-ZrO$_2$ retention. This causes a spontaneous $t\rightarrow m$ ZrO$_2$ transformation giving a microcracked microstructure.
For any brittle ceramics, the fracture strength is controlled by the size of the largest flaw (controlled by the largest flaw size). The fracture toughness and fracture toughness ($K_{IC}$) and fracture strength ($\sigma_f$) are related by the following Eqn. 6.1.

$$K_{IC} = Y \sigma_f c^{1/2}$$  \hspace{1cm} (6.1)

where, $Y$ is a shape related geometrical factor (constant for all the compositions) and $c$ is the half flaw size of the most critical flaw from which fracture initiates. Therefore, for any particular composition if $K_{IC}$ and $\sigma_f$ are experimentally known then the relative value of half critical flaw size can be computed. The normalized critical flaw size for $\text{Al}_2\text{O}_3$-$\text{Y-ZrO}_2$ ($Y = 1, 2, 2.5$ and $3$ mol%) are tabulated in Table 6.1 and 6.2 using the data of three point bending strength ($\sigma_f$) as well as biaxial flexural strength ($\sigma_f$) respectively.

The Tables 6.1 and 6.2 show that the normalized flaw size variation is very small for $\text{Al}_2\text{O}_3$-$\text{Y-ZrO}_2$ composites with $Y = 2, 2.5$ and $3$ mol%. However, in $\text{Al}_2\text{O}_3$-$1\text{Y-ZrO}_2$ the flaw size is large (by an order of magnitude for three point bend test and by three times for biaxial flexural strength) as compared to other compositions.
Thus, it is proposed that in Al\textsubscript{2}O\textsubscript{3}-1Y-ZrO\textsubscript{2} composite the large flaws appear to be partially responsible for low strength in this composition. However, in Al\textsubscript{2}O\textsubscript{3}-Y-ZrO\textsubscript{2} composites with Y = 2, 2.5 and 3 mol\%, flaw size appear to have less effect on the final strength.

**Table 6.1 Normalized critical flaw size (Y\textsuperscript{2}c) of Al\textsubscript{2}O\textsubscript{3}-Y-ZrO\textsubscript{2} sintered composites (three point bending strength)**

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Three point bending strength (σ\textsubscript{f}) (MPa)</th>
<th>Fracture Toughness (K\textsubscript{IC}) (MPa√m)</th>
<th>Normalized Y\textsuperscript{2}c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}-1Y-ZrO\textsubscript{2}</td>
<td>102</td>
<td>5.68</td>
<td>3.02 x 10\textsuperscript{-3}</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}-2Y-ZrO\textsubscript{2}</td>
<td>467</td>
<td>8.45</td>
<td>3.27 x 10\textsuperscript{-4}</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}-2.5Y-ZrO\textsubscript{2}</td>
<td>537</td>
<td>9.46</td>
<td>2.97 x 10\textsuperscript{-4}</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}-3Y-ZrO\textsubscript{2}</td>
<td>640</td>
<td>13.04</td>
<td>4.38 x 10\textsuperscript{-4}</td>
</tr>
</tbody>
</table>

**Table 6.2 Normalized critical flaw size (Y\textsuperscript{2}c) of Al\textsubscript{2}O\textsubscript{3}-Y-ZrO\textsubscript{2} sintered composites (biaxial flexural strength)**

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Biaxial flexural strength (σ\textsubscript{f}) (MPa)</th>
<th>Fracture Toughness (K\textsubscript{IC}) (MPa√m)</th>
<th>Normalized Y\textsuperscript{2}c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}-1Y-ZrO\textsubscript{2}</td>
<td>102</td>
<td>5.68</td>
<td>3.1 x 10\textsuperscript{-3}</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}-2Y-ZrO\textsubscript{2}</td>
<td>190</td>
<td>8.45</td>
<td>1.97 x 10\textsuperscript{-3}</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}-2.5Y-ZrO\textsubscript{2}</td>
<td>264</td>
<td>9.46</td>
<td>1.28 x 10\textsuperscript{-3}</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}-3Y-ZrO\textsubscript{2}</td>
<td>335</td>
<td>13.04</td>
<td>1.51 x 10\textsuperscript{-3}</td>
</tr>
</tbody>
</table>
Fig. 6.3. SEM microstructure of $\text{Al}_2\text{O}_3$-1Y-ZrO$_2$ composites

Fig. 6.4. SEM microstructure of $\text{Al}_2\text{O}_3$-2Y-ZrO$_2$ composites

Fig. 6.5. SEM microstructure of $\text{Al}_2\text{O}_3$-2.5Y-ZrO$_2$ composites
Fig. 6.6. SEM microstructure of Al$_2$O$_3$-3Y-ZrO$_2$ composites

At higher Y$_2$O$_3$, not only the retention of $t$-ZrO$_2$ was higher, but also the sintered density was also high as well as the grain sizes were also finer. In Al$_2$O$_3$-Y-TZP composite the $t$-ZrO$_2$ retention among other factors, is also critically dependent on the mole fraction of Y$_2$O$_3$, its distribution within the ZrO$_2$ grains and not only on grain size alone. It has been observed and reported by many that the stabilizer distribution in ZrO$_2$ varies from grain to grain and also within a grain and this distribution of stabilizer content gives rise to different degree of stabilization of different grains as well as different level of transformability. Thus it is quite possible that some of the grains of Al$_2$O$_3$-1Y-TZP composite had lower amount of Y$_2$O$_3$ than required for stabilization and some of these grains possibly have transformed to $m$-ZrO$_2$ during cooling. Thus in spite of having lower grain size and some grains possibly have transformed to $m$-ZrO$_2$ during cooling and $t$-ZrO$_2$ retention was less in Al$_2$O$_3$-1Y-TZP composition. All this combined effect gave rise to higher strength. The inter dependence of strength and sintered density becomes more clear on comparing relative density and flexure strength as a function of sintering temperature. Both the graphs exhibit an increasing strength thereby suggesting that the fracture strength of Al$_2$O$_3$-Y-ZrO$_2$ composites is controlled by sintered density (or in the other words residual flaw size). Since the flaw size in dense composites (composition 2, 2.5 and 3Y) is small and nearly constant, the strength appears to be independent of flaw size and is controlled by transformation toughening.
Fig. 6.7 Grain size distribution of Al$_2$O$_3$-1Y-ZrO$_2$ sintered (1600°C) composites

Fig. 6.8. Grain size distribution of Al$_2$O$_3$-2Y-ZrO$_2$ sintered (1600°C) composites

Fig. 6.9. Grain size distribution of Al$_2$O$_3$-2.5Y-ZrO$_2$ sintered (1600°C) composites
Fig. 6.10. Grain size distribution of Al$_2$O$_3$-3Y-ZrO$_2$ sintered (1600°C) composites

The grain size variations (separately for Al$_2$O$_3$ and ZrO$_2$) are shown in Fig. 6.7-6.10. The grain size distribution of Al$_2$O$_3$ and ZrO$_2$ for all Al$_2$O$_3$-Y-ZrO$_2$ compositions. The distribution shows that the grain size did not vary much with compositions and majority of the grains were between 1-2.5 µm. Thus it appears that the grain size did not affect the strength in a significant way.

6.2 Biaxial Flexural Strength

The biaxial flexural strength of the composite as a function of Y$_2$O$_3$ content is shown in Fig. 6.11.

Fig. 6.11. Biaxial flexural strength of Al$_2$O$_3$-Y-ZrO$_2$ composites as a function of Y$_2$O$_3$ content
The biaxial flexural strength values show similar trend to that observed for three point bend strength. Highest strength is 345 MPa for Al$_2$O$_3$-3Y-ZrO$_2$ composites sintered at 1600°C.

![Fig.6.12. Biaxial flexural strength of Al$_2$O$_3$-3Y-ZrO$_2$ composites as a function of sintering temperature](image)

Figure 6.12 shows the strength of Al$_2$O$_3$-3Y-ZrO$_2$ composites as a function of sintering temperature. The low strength value at lower sintering temperature (<1600°C) is due to incomplete densification. However, the strength values are lower in this mode (in comparison to three point bend strength) because mixed mode fracture (Mode I and Mode II) take place in these cases. Thus tensile strength required to initiate crack propagation is lower in this case leading to lower strength.

6.3 Fracture Toughness of Al$_2$O$_3$-Y-ZrO$_2$ Composites

The SENB fracture toughness as a function of Y$_2$O$_3$ content is shown in Fig. 6.13 for samples sintered at 1600°C. The fracture toughness increases with Y$_2$O$_3$ content at first gradually (1.8 MPa$\sqrt{m}$ to 5.5 MPa$\sqrt{m}$) till 1 mol% Y$_2$O$_3$ followed by rather rapid increase to 8.5 MPa$\sqrt{m}$ at 2 mol% Y$_2$O$_3$ which further increases to 9 MPa$\sqrt{m}$ at 2.5 mol% Y$_2$O$_3$. Thereafter, the fracture toughness steeply rises to 13.04 MPa$\sqrt{m}$ at 3 mol% Y$_2$O$_3$ addition. The fracture toughness as a function of
sintering temperature could not be determined because at lower sintering temperatures the composites did not attain the required density for toughness measurement.

![Fracture Toughness of Al$_2$O$_3$-Y-ZrO$_2$ Composites as a Function of Y$_2$O$_3$ Content](image)

**Fig. 6.13. Fracture toughness of Al$_2$O$_3$-Y-ZrO$_2$ composites as a function of Y$_2$O$_3$ content**

The observed toughness values are quite high and it is possible that more than one toughening mechanism is operative in this composite. Besides transformation toughening, additional toughening effect that may arise from some grain boundary phase which either change the crack propagation path (intergranular to transgranular) or may cause crack deviation, microcrack toughening and/or combined action of these mechanisms. In order to compute the contribution of transformation toughening ($\Delta K_{ICTT}$) to the overall toughness, the fraction of transformable $t$-ZrO$_2$ was measured on the ground surface for the two high toughness compositions, viz, Al$_2$O$_3$-2.5Y-ZrO$_2$ and Al$_2$O$_3$-3Y-ZrO$_2$. The volume fraction of transformed $t$-ZrO$_2$ was found by measuring the volume fraction of net $m$-ZrO$_2$ on the ground surface using Eqn. 4.10 and 4.11. Although Al$_2$O$_3$-2Y-ZrO$_2$ also had high toughness but due to the presence of large monoclinic phase on the sintered surface (Table 6.3), the zone depth could not be accurately calculated and theoretical evaluation of toughness was made only on Al$_2$O$_3$-2.5Y-ZrO$_2$ and Al$_2$O$_3$-
3Y-ZrO₂ samples. The volume fractions of transformed t-ZrO₂ for those three compositions are shown in Table 6.3.

**Table 6.3 Volume fraction of transformed t-ZrO₂ on the ground surface of sintered A₂O₃-Y-ZrO₂ compositions**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Fraction m-ZrO₂ phase on sintered surface</th>
<th>Fraction m-ZrO₂ phase on ground surface</th>
<th>Fraction t-ZrO₂ transformed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃-2Y-ZrO₂</td>
<td>0.86</td>
<td>0.94</td>
<td>0.08</td>
</tr>
<tr>
<td>Al₂O₃-2.5Y-ZrO₂</td>
<td>0.07</td>
<td>0.50</td>
<td>0.43</td>
</tr>
<tr>
<td>Al₂O₃-3Y-ZrO₂</td>
<td>0</td>
<td>0.39</td>
<td>0.39</td>
</tr>
</tbody>
</table>

Using the above data and the transformation toughening model of Mc Meeking and Evans [6.1] and considering shear and dilation stress, the transformation toughening contribution was evaluated from the following equation:

\[ \Delta K_{IC_{TT}} = \frac{0.38EV_f \sqrt{h} e^T}{(1 - \nu)} \]  

(6.2)

The composite elastic modulus \(E\) was calculated using the volume fraction of each phase (viz. Al₂O₃ and ZrO₂) and their respective \(E\) values (\(E_{Al₂O₃} = 380\) GPa and \(E_{ZrO₂} = 210\) GPa), \(V_f\) is the volume fraction of transformed t-ZrO₂ phase obtained from Table 6.1, \(e^T\) is the transformation strain (\(e^T = 0.06\)), \(h\) is the transformation zone depth. The transformation zone depth was calculated using Mori’s formula [6.2].

\[ h = \frac{\tan \theta \left[ X_{meas} - X_{bulk} \right]}{2 \mu \left[ Y_{bulk} - X_{meas} \right]} \]  

(6.3)

where, \(X\) and \(Y\) denotes the fraction of monoclinic and tetragonal ZrO₂ and the subscript refer to their position. \(\mu\) is the linear absorption coefficient and for Al₂O₃-50 vol% ZrO₂ composite, \(\mu\) is taken to be 0.037, \(2\theta\) is the diffraction angle for t-ZrO₂ [6.3]. The calculated zone depth \((h)\) for all the two levels of Y₂O₃ doping is listed in Table 6.4.
Table 6.4 Transformation zone depth of sintered Al$_2$O$_3$-Y-ZrO$_2$ compositions

<table>
<thead>
<tr>
<th>Y$_2$O$_3$ (Mol%)</th>
<th>Zone depth ($h$) (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>2.99</td>
</tr>
<tr>
<td>3</td>
<td>4.69</td>
</tr>
</tbody>
</table>

The contribution of transformation toughening ($\Delta K_{ICT}$) to the overall toughening was evaluated on the basis of Eqn. 6.2 using the data provided in Table 6.3 and 6.4. The calculated $\Delta K_{ICT}$ values for the three compositions of Al$_2$O$_3$-Y-ZrO$_2$ composites are listed below:

Table 6.5 Comparison of the experimental and calculated fracture toughness of sintered Al$_2$O$_3$-Y-ZrO$_2$ compositions

<table>
<thead>
<tr>
<th>Composition</th>
<th>Experimental $K_{IC}$ (MPa√m)</th>
<th>Calculated $K_{IC}$ (MPa√m)</th>
<th>Difference (MPa√m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$-2.5Y-ZrO$_2$</td>
<td>9.46</td>
<td>7.36</td>
<td>+2.10</td>
</tr>
<tr>
<td>Al$_2$O$_3$-3Y-ZrO$_2$</td>
<td>13.04</td>
<td>9.21</td>
<td>+3.83</td>
</tr>
</tbody>
</table>

Thus, it could be seen that besides transformation toughening some other toughening mechanism is also helping the toughness increment. In an attempt to understand the other possible mechanisms resulting in the toughness increment, detailed microstructural analysis was carried out through FE-SEM and TEM. The FE-SEM images (SE mode) of Al$_2$O$_3$-2.5Y-ZrO$_2$ and Al$_2$O$_3$-3Y-ZrO$_2$ are shown in Fig. 6.14 (a, b) and (c, d) respectively. The lower magnification images Fig. 6.14 (a, c) shows that the ZrO$_2$ grains (0.53 µm) are smaller than that Al$_2$O$_3$ (0.69 µm). It has also been observed that in Al$_2$O$_3$-3Y-ZrO$_2$ (Fig. 6.14 d), both intergranular and transgranular cracks are present which is absent in Al$_2$O$_3$-2.5Y-ZrO$_2$ (Fig. 6.14 b). The intergranular cracks are present at Al$_2$O$_3$-ZrO$_2$ interface and the transgranular cracks are found to start mostly from the ZrO$_2$ grains (bright grains, arrow marked). This feature is not present in Al$_2$O$_3$-2.5Y-ZrO$_2$ composite.
It was also observed (through EDAX) that in $\text{Al}_2\text{O}_3$-$3\text{Y-ZrO}_2$, there was $\text{Y}^{3+}$ concentration gradient from $\text{ZrO}_2$ to $\text{Al}_2\text{O}_3$ grains through the $\text{ZrO}_2$-$\text{Al}_2\text{O}_3$ interface. The presence of both intergranular (curve) and transgranular cracks (arrow marks) as well as $\text{Y}^{3+}$ concentration gradient suggests the possibility of new compound formation at the interface definitely in $\text{Al}_2\text{O}_3$-$3\text{Y-ZrO}_2$ and possibly in $\text{Al}_2\text{O}_3$-$2.5\text{Y-ZrO}_2$. Therefore, it was decided to further study the microstructure of these two compositions through TEM with the possibility of looking more minutely at the interface. Figure 6.15(a) shows the HR-TEM microstructure of $\text{Al}_2\text{O}_3$-$2.5\text{Y-ZrO}_2$. The upper image represents the lattice image of $\text{ZrO}_2$ grain ($d=1.88\text{ Å}$) and the lower image represents the $\text{Al}_2\text{O}_3$ ($d=4.07\text{ Å}$) grain. But it is also seen that at the interface a third structure also exists.

**Fig.6.14.** FE-SEM microstructure of $\text{Al}_2\text{O}_3$-$2.5\text{Y-ZrO}_2$ (a, b) and $\text{Al}_2\text{O}_3$-$3\text{Y-ZrO}_2$ composites (c, d).
Fig. 6.15. HRTEM image of (a) Al$_2$O$_3$-2.5Y-ZrO$_2$ (b) Al$_2$O$_3$-3Y-ZrO$_2$ composites

Figure 6.15(b) shows the HR-TEM image of Al$_2$O$_3$-3Y-ZrO$_2$ interface. As before, the lower image is Al$_2$O$_3$ (d=4.08Å) and upper image are ZrO$_2$ (d=1.88Å). At the interface, a secondary phase is clearly seen which is identified as YAG (d=4.21Å). It appears that the migration of Y$^{3+}$ across the Al$_2$O$_3$-ZrO$_2$ interface at the high sintering temperature resulted in nano-YAG formation at the interface. Similar results have been reported by Gao et al. [6.4] and Moya et al. [6.5] while working with Al$_2$O$_3$-25 vol% Y$_2$O$_3$ composites. At high sintering temperature, Al$_2$O$_3$ and Y$_2$O$_3$ react to form YAG. However, in the present investigation, since the amount of Y$_2$O$_3$ is very less (2 -3 mol%) in comparison to the reported study and only a certain fraction of the Y$_2$O$_3$ is diffused, the interface layer will be very thin (in angstrom level). The presence of YAG appears to have helped in enhancing the toughness by three possible mechanisms: (a) the YAG improves the grain boundary strength, (b) the presence of YAG (due to higher $\alpha$) also induces a residual stress on ZrO$_2$ (ZrO$_2$ grains are put in tension) and this might have helped in higher transformability of ZrO$_2$ grains there by leading to higher toughness and (c) the migration of Y$^{3+}$ towards Al$_2$O$_3$-ZrO$_2$ interface lowers the overall Y$^{3+}$ concentration in ZrO$_2$ to less than 3 mol%. Thus the Y$_2$O$_3$ distribution in ZrO$_2$ grains becomes inhomogeneous making it more susceptible to transformation under the applied stress (the stress level to initiate the transformation decreases). The effect of inhomogeneous dopant distribution on the enhanced transformability
has also been reported by Lange et al. [6.6] and Basu et al. [6.7]. Moreover, Nihara et al. [6.8, 6.9] have investigated the microstructure and properties of different kinds of nanocomposites and reported significant improvements of mechanical properties when nano-size dispersions were present in the composite within the matrix grains and at the grain boundaries. It has also been reported that among the different type of nano-composites; the inter-type had improved mechanical properties like strength, toughness and hardness.

![Fig.6.16. TEM Microstructure of sintered Al₂O₃-Y-ZrO₂ composites (a) 2.5 Y (b) 3 Y. The microstructure shows the grains are of sub micron size with nano intragranular dispersion](image)

The microstructure (Fig.6.16 (a, b)) of the composites in the present investigation also suggests that these composites are of nano intra type. Thus it appears that presence of intragranular nano phase as well as the intergranular YAG phase has caused the improvement of strength and toughness of Al₂O₃-Y-ZrO₂ composites. The possible strengthening and toughening mechanisms are grain boundary strengthening (due to grain boundary YAG phase), existence of both intergranular and transgranular fracture mode, enhanced transformability of Y-ZrO₂ grains (due to Y³⁺ migration) as well as the unique combination of micro-nano composites as suggested by Nihara [6.8].
6.4 Hardness of $\text{Al}_2\text{O}_3$-$\text{Y}$-$\text{ZrO}_2$ Composites

The Vickers hardness of $\text{Al}_2\text{O}_3$-$\text{Y}$-$\text{ZrO}_2$ composites as a function of sintering temperature is shown in Fig. 6.17. The hardness increases with sintering temperature as well as $\text{Y}_2\text{O}_3$ content. The increase in hardness is due to the increased density of the composite. The hardness increases both due to sintering temperature as well as $\text{Y}_2\text{O}_3$ addition. The maximum hardness is 14 GPa for $\text{Al}_2\text{O}_3$-$3\text{Y}$-$\text{ZrO}_2$ composites sintered at 1600°C.

![Graph showing Vickers hardness as a function of sintering temperature](image)

*Fig.6.17. Vickers hardness of $\text{Al}_2\text{O}_3$-$\text{Y}$-$\text{ZrO}_2$ composites as a function of sintering temperature*
Fig. 6.18 Crack propagation path in indented $\text{Al}_2\text{O}_3$-3Y-$\text{ZrO}_2$ composites. The central figure is the combined picture showing the crack propagation paths and the different zones (A, B, C, D) are enlarged in the four corners.

At the same sintering temperature, the hardness values for $\text{Al}_2\text{O}_3$-2Y-$\text{ZrO}_2$ and $\text{Al}_2\text{O}_3$-2.5Y-$\text{ZrO}_2$ composites are 9 and 12 GPa respectively. Similar trend in hardness has also been observed by Basu et al. [6.10].

The nature of the crack propagation (on impact) in $\text{Al}_2\text{O}_3$-Y-$\text{ZrO}_2$ was also studied by SEM. Figure 6.18 shows the crack propagation behavior from the corner of an indent for $\text{Al}_2\text{O}_3$-3Y-$\text{ZrO}_2$ composites (Zone A). A careful observation of the crack propagation path reveals that the crack path is tortuous – i.e. the crack deviates from its main path (Zone A-D), the crack cuts through the particle (Zone B) or the crack branches out (Zone C) or the crack bypasses a particle (Zone D). Similar
observations have also been made on the indentations carried out on $\text{Al}_2\text{O}_3$-2.5Y-ZrO$_2$ composites Fig. 6.19 (a, b), where most of the above features (as observed in $\text{Al}_2\text{O}_3$-3Y-ZrO$_2$ composites) such as tortuous crack path, crack either bypassing a particle or cutting through a particle is also observed [Fig. 6.19 (b)]. The above observation suggests that due to multiple toughening mechanism operating simultaneously in $\text{Al}_2\text{O}_3$-3Y-ZrO$_2$ composites; the crack propagation is not easy in this composites and high toughness values are obtained.

*Fig. 6.19 Crack propagation paths in indented $\text{Al}_2\text{O}_3$-2.5Y-ZrO$_2$ composites. The upper figure (a) shows the indent with crack and the crack path are enlarged in the bottom figure (b).*
6.5 Thermal Shock Resistance of Al₂O₃-3Y-ZrO₂ Composites

The thermal shock resistance of Al₂O₃-3Y-ZrO₂ (because it has the proper combination of high strength and toughness) was studied by air quenching method. The samples were heated to three different temperatures (1200, 1100, and 1000°C) and air quenched from that temperature. Strength and toughness (SENB method) were measured on these quenched samples.

Table 6.6 Effect of thermal quenching temperature on the strength and toughness of Al₂O₃-3Y-ZrO₂ composites

<table>
<thead>
<tr>
<th>Quenched from temperature (°C)</th>
<th>σ_f (MPa)</th>
<th>K_{IC} (MPa\sqrt{m})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>547</td>
<td>7.28</td>
</tr>
<tr>
<td>1100</td>
<td>485</td>
<td>4.55</td>
</tr>
<tr>
<td>1200</td>
<td>473</td>
<td>4.02</td>
</tr>
<tr>
<td>No quenching</td>
<td>645</td>
<td>13.04</td>
</tr>
</tbody>
</table>

Table 6.5 shows the results of thermal quenching temperature on the strength and toughness of Al₂O₃-3Y-ZrO₂ composites. It is seen from the Table that although the toughening is drastically affected by quenching temperature, the strength degradation is less due to the quenching. The decrease in toughness on quenching appears to be due to the generation of microcracks but these microcracks did not affect the strength that much. This hints at strengthening of grain boundary by nano YAG [6.4]. However, the results show that this composition retains significant strength and toughness even when quenched from 1000°C. The strength and toughness trends are different from the usual trend observed for quenched samples (the loss of strength on quenching is less drastic)> it is possible that the presence of nano YAG (due to its high strength both at room and high temperature) at the grain interfaces might have caused high strength.
References


Chapter VII

Conclusions and Scope of Further Work
7.1 Conclusions

The present study on the powder processing densification behavior and mechanical properties of Al₂O₃-high zirconia composites were undertaken to study the following:

a) Use of different powder processing methods on the powder properties, its optimization and \( t \) -ZrO₂ retention.

b) Effect of precursor type (or nature of anions) on the metastable phase evolution and densification behavior as well as properties of similar composites.

c) Detailed densification mechanism of the composites during initial stage sintering.

d) Effect of stabilizer on the composite properties, microstructures, strength, toughness and hardness.

e) Exploring the possible strengthening and toughening mechanism in these composites.

In this present study, Al₂O₃- 50 vol% ZrO₂ composites were processed through soft chemistry routes using AlCl₃ or Al(NO₃)₃ and ZrOCl₂ as the respective precursors. Three different processing routes, viz. gelation (ROUTE 1), precipitation (ROUTE 2) and precipitation followed by washing (ROUTE 3) of the precipitates were adopted. Only the ROUTE 3 gave the desired composite with 88% sintered density (for AlCl₃/ZrOCl₂ precursor combination). Microstructural analysis showed residual porosity in the sintered samples and FTIR of the calcined powder confirms the presence of residual chloride ions. It has been well documented that the presence of residual chloride ions can adversely affect the densification behavior. In the present study, it was found that not only the removal of chloride ions but also the removal of (OH)⁻ groups of Al³⁺ causes weight loss during the later stage of sintering. Chloride ions were partially reduced when Al(NO₃)₃ replaced AlCl₃ as the precursor for Al₂O₃ (ROUTE 4). FTIR study showed lesser amount of chlorides in the calcined powder and the sintered density increased to 95% of theoretical. The washing of the precipitates by water and alcohol reduced the agglomeration tendency of the powders thereby increasing their sinterability. This specific feature was elaborately studied through TEM photography of the calcined powder, determination of agglomeration strength and SEM microstructure of sintered samples. The TEM picture showed less agglomerated powder and the agglomeration
strength was 97 MPa. This marks the end of the first section and it was observed at this stage that due to the low elastic modulus of the composite (260 GPa). The matrix could not provide constraint to arrest the spontaneous $t\rightarrow m$ ZrO$_2$ transformation. So, all the sintered composites had very small fraction of retained $t$-ZrO$_2$ (5 to 10 vol%). This factor coupled with existence of extensive microcracking (as a result of spontaneous $t\rightarrow m$ transformation) could not improve the mechanical properties of the composites in specific strength and toughness, which were very low ($\sigma_f =$88.7 MPa, $K_{IC} =$ 1.9 MPa\text{$\sqrt{m}$}).

The densification of Al$_2$O$_3$-ZrO$_2$ composite showed duplex sintering behavior for all processing routes. However, the onset temperature was different and could be correlated with surface area, particle size and agglomeration strength of the calcined powder. The densification kinetics and activation energy of Al$_2$O$_3$-ZrO$_2$ composites was determined from isothermal and non-isothermal dilatometry study. The value of kinetic parameter ‘$n$’ varied between 5.02 and 5.22 which indicate that volume diffusion is the dominant mass transfer mechanism and the activation energy for initial stage of sintering was 236-258 kJ mol$^{-1}$.

The second part of the study involved the addition of Y$_2$O$_3$ (1, 2, 2.5 and 3 mol %) to the precursor solution of Al and Zr salt, so that Y-TZP could form during calcination and subsequent sintering process. It was observed that the addition of Y$_2$O$_3$ not only helped to retain large fraction of $t$-ZrO$_2$ in the sintered composites but the sintered density was also significantly improved and all the Y-doped compositions had high sintered density (>90%) and while Al$_2$O$_3$-2.5Y-ZrO$_2$ composition could retain 93% of $t$-ZrO$_2$ it was 100% for Al$_2$O$_3$-3Y-ZrO$_2$. Both flexural as well as biaxial flexural strength had improved with Y$_2$O$_3$ doping and the highest values were 645 and 335 MPa respectively. It was noted that only for Al$_2$O$_3$-1Y-ZrO$_2$ composites the strength was flaw controlled while for others it was transformation controlled. The fracture toughness (SEN method) increased from 5.68 MPa$\sqrt{m}$ (at 1 mol% Y$_2$O$_3$) to 9.46 MPa$\sqrt{m}$ in Al$_2$O$_3$-2.5Y-ZrO$_2$ composites which further increased to 13.04 MPa$\sqrt{m}$ in Al$_2$O$_3$-3Y-ZrO$_2$ composites. The $K_{IC}$ results were analyzed in terms of transformation toughening model of Evans and Mc Meeking and it was found that transformation toughening was not able to account for the entire toughness increment. Thus some other toughening mechanisms were also
simultaneously operative. Assuming that there might be some additional microstructural features, selected samples (with 2.5 and 3 Y$_2$O$_3$ doping) were observed in FESEM and TEM. FESEM indicated that Al$_2$O$_3$-3Y-ZrO$_2$ had some transgranular cracks in ZrO$_2$ grains. EDAX analysis revealed a concentration gradient of Y$^{3+}$ from ZrO$_2$ grain to Al$_2$O$_3$ grain. TEM picture of bulk Al$_2$O$_3$-2.5Y-ZrO$_2$ and Al$_2$O$_3$-3Y-ZrO$_2$ samples revealed the presence of a third phase at the interface of Al$_2$O$_3$ and ZrO$_2$. HR lattice image of the interface area confirmed that YAG has formed at the interface. Thus it appears that the formation of YAG in situ and its deposition along grain boundary of Al$_2$O$_3$/ZrO$_2$ is responsible for property improvement as it allows the simultaneous operation of a number of additional mechanisms like grain boundary strength, generation of residual tensile stress at ZrO$_2$ grain and the initiation of transgranular fracture.

The hardness of all Al$_2$O$_3$-Y-ZrO$_2$ composites increased at higher sintering temperature as well as at higher Y$_2$O$_3$ content. This implies that addition of Y$_2$O$_3$ promotes densification due to enhanced mass transport augments densification of the composites.

The study of thermal shock resistance behavior for Al$_2$O$_3$-3Y-ZrO$_2$ composites showed that the thermal shock resistance is high till $\Delta T = 1000$°C where the retained fracture toughness is 7.28 MPa$\sqrt{m}$ and fracture strength is 540 MPa.

**7.2 Scope of Further Work**

The present study reveals that powder processing is an important step for achieving a dense microstructure. The anions (particularly chlorides and hydroxyl groups) affect the sintered density and phase retention as the above ions go off at high temperature where pore coalescence is not possible. Y$_2$O$_3$ doping improves the situation through the formation of YAG phase at Al$_2$O$_3$/ZrO$_2$ interface. The doping also results in significant improvement of strength, toughness, hardness and thermal shock resistance. However, it is felt that some more questions needs to be answered and these are suggested as the possible future work:

(i) Is it possible to improve the densification behavior and phase retention ($\gamma$-ZrO$_2$) of the Al$_2$O$_3$-undoped ZrO$_2$ composites by either hot pressing or vacuum sintering
or spark plasma sintering? Will the anions still affect the densification and phase retention?

(ii) What may be the effect of two stage rapid sintering on the density, microstructure and properties?

(iii) Y$_2$O$_3$ doping results in the property enhancement, but the amount of Y$_2$O$_3$ need to be optimized.

(iv) Will this type of behavior still exist if prereacted Y$_2$O$_3$ doped ZrO$_2$ is dispersed in Al-sol for preparing the composites?

(v) What will be the tribological behavior of these composites?

(vi) The composites had a good combination of strength, toughness and hardness. Thus it may be used as a cutting tool material. However it is possible that this material have some bioactive properties or in other words can it be used in biomedical applications where dense prostheses are used?
Publications resulting from the Ph.D. work


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