CHAPTER 8

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

8.1 SUMMARY

A novel processing technique has been developed via oxalate sol-gel drop generation route to produce near-net-shaped prototype zirconia minispheres with smaller size and required properties that could potentially be used as grinding media. Minispheres of diameter ranging from 0.8 to 1.2 mm are produced. Formation of zirconium oxalate sol has been demonstrated as a good starting route for the preparation of zirconia minispheres stabilized with different dopants which has overcome the conventional powder compaction preparation method.

The present work reports the experimental aspects of preparation and characterization of undoped zirconia, Ce-ZrO$_2$, Y-ZrO$_2$ and Mg-ZrO$_2$ minispheres. The thesis starts with a brief discussion on ceramic processing methods, properties of zirconia, grinding process and grinding media. Transparent, physical and thixotropic ZO gel has been prepared by oxalate gelation from metal salts of chlorides, nitrates and oxalic acid in triple distilled water. Possible reasons for the various stages of the formation of the gels have been analyzed by means of DLVO theory.

Variations of viscosity and pH with ageing time for the zirconium oxalate sol have been analyzed. The suitable viscosity of gel for sphere
formation has been identified as 15cPs ideal for forming drops in a setting solution by extrusion method.

Zirconia minispheres without the addition of stabilizer fails to retain the shape and strength after sintering. This destructive effect has been attributed due to the anisotropic volume expansion accompanying the extensive microcracking caused by tetragonal to monoclinic phase transition at higher sintering temperatures. The green density of the minispheres is only 48% TD and that of the sintered zirconia minispheres prepared without sintering additives is only 82% TD.

In order to overcome the difficulties encountered for undoped zirconia, stabilizing the zirconia minispheres with tetragonal phase is essential which has been attained by adding suitable stabilizing agent. Three types of minispheres namely ceria, yttria and magnesia stabilized zirconia minispheres have been prepared following the ZO preparation procedure and characterized to reveal the physical, structural and mechanical properties.

Heat treatment has been performed in stages upto 1500°C from 300°C to analyze the property variations of 13 mol % ceria stabilized zirconia (13Ce-ZrO₂), 5 mol % yttria stabilized zirconia (5Y-ZrO₂) and 8 mol % magnesia stabilized zirconia (8Mg-ZrO₂) minispheres. The fast heating rate always leads to the lower density due to the entrapment of the residuals by the pores. The slow heating rate facilitates the smooth release of residuals before the pores start to close and ultimately reaches the near TD.

Stabilized zirconia minispheres have been extensively characterized to establish the effect of stabilizer content, binder ratio and sintering temperature on density, porosity, shrinkage, weight loss, crystallization temperature, crystallite size, phase, grain size and mechanical
properties. The phase transformation studies using DTA and X-ray diffraction method confirm the formation of t-phase in stabilized zirconia. During sintering the dopant ions are substituted for zirconium ions in the crystal structure which favours the formation of tetragonal phase. When the content of stabilizers is increased, the sintered density of the zirconia minispheres has also increased gradually and has reached a maximum of 93-96 % TD. Controlled grain growth and pore shrinkage with high mobility in the presence of sintering aid have contributed to the enhanced density. The decrease in the porosity occurs due to the increase in the addition of stabilizer content.

Investigations on weight loss and decomposition behavior have been carried out by means of TGA and DTA for the dried minispheres. Observations from the TGA studies show that there exists maximum 43 percentage of weight loss for almost all the stabilized minispheres. DTA studies show the crystallization of t-phase around 400-500°C for all stabilizer additions. Variations in percentage of weight loss, shrinkage and porosity with sintering temperature have been analyzed. Impacts of heating rate and soaking time have also been analyzed in detail.

Using BET technique, the surface area analysis has been carried out. It has been found that the surface area of all stabilized zirconia particles decreases with increase in sintering temperature and heating rate. FT-IR characterization of all stabilized dried minispheres has been carried out. It has been observed that the addition of dopant ions does not affect the structure of the zirconyl oxalate. Presence and periodic removal of volatiles for all stabilized minispheres have been confirmed by FT-IR analysis.

Crystallization behavior of all the stabilized minispheres has been analyzed by varying stabilizer concentration and sintering temperature. The
as-prepared dried minispheres are found to be amorphous. The CZO, YZO and MZO minispheres are crystallized in t phase ranging from 420 to 511°C, where ZO minispheres are crystallized in metastable t phase at 471°C and then transformed to a monoclinic phase at 750°C. Crystallization temperature is strongly depends on the heating rate. It has been observed that there is a retention of full tetragonal phase for 13Ce-ZrO$_2$ minispheres sintered at 1500°C for 5 hours whereas 5Y-ZrO$_2$ and 8Mg-ZrO$_2$ minispheres are partially stabilized with tetragonal and monoclinic phases. It is found that the percentage of tetragonal phase increase with stabilizer content and decreases as the sintering temperature is increased. Maximum density has been achieved at sintering temperature of 1500°C for 13Ce-ZrO$_2$ and 8Mg-ZrO$_2$ minispheres. In contrast, 5Y-ZrO$_2$ minispheres has achieved the maximum density with complete t phase for a sintering temperature of 900°C. It is also observed that the slow heating rate leads to good sinterability.

Variations of crystalline size and sintered density with the sintering temperature and stabilizer concentration have been observed for all stabilized zirconia minispheres. Density variations with sintering temperature and stabilizer content have also been analyzed. SEM analysis reveals the microstructural features of stabilized zirconia minispheres for different sintering temperatures and stabilizer content. It has been observed that the existence of pores at the grain corners shows the inability of the maximum removal of pores during sintering.

The microstructure of yttria stabilized minisphe

The microstructure of yttria stabilized minispheres shows less agglomerated grain growth which results in moderate grain size and very close homogeneous microstructure. Variations in grain size with stabilizer concentration and sintering temperature have been analyzed for all the stabilized zirconia minispheres. It has been observed that the average grain size varies between 0.8 and 2.7μm for all the stabilized zirconia minispheres
with sintering temperature ranging from 900°C to 1500°C which influence the internal tensile stress produced due to the thermal expansion of zirconia.

The harness studies have been performed using Vickers indentation method. Effect of sintering schedule on the mechanical properties has been analyzed. Variations of hardness, fracture toughness and percentage of wear loss with sintering temperature and stabilizer concentration have been analyzed. It has been observed that the hardness decreases with the applied load ranging from 0.5 to 2 Kg irrespective of stabilizer concentration. Maximum hardness of 8.8, 10.9 and 8.2 MPa have been observed for zirconia minispheres stabilized with ceria, yttria and magnesia respectively. As the sintering temperature and soaking period increases, the grain size also increases. During indentation, the larger size grains transform easily from tetragonal to monoclinic phase and hence hardness decreases. Hardness value has found to be increasing linearly with density of the minispheres. It has also been observed that the hardness increases with stabilizer content.

The observations on fracture toughness have not been unique for all the stabilizers. It has been found to vary depending on the fraction of tetragonal phase present in the system for a particular sintering temperature. Maximum fracture toughness of 12.115, 9.148 and 8.71 MPam$^{1/2}$ have been achieved for zirconia minispheres stabilized with ceria, yttria and magnesia respectively. It has been observed that the percentage of wear loss slightly increases with milling time and even for 9 hours of milling only 0.41 % of wear loss has been observed. The contamination of powder is considerably negligible. The mechanical properties of stabilized zirconia minispheres have also been compared. The main reason for the high strength of the PSZ system appears to be the existence of a metastable tetragonal phase which is strongly dependent on several factors such as the percentage of stabilizer, the sintering temperatures, the soak time and the nature of the raw material.
In order to reduce the shrinkage and to improve sintered density of the zirconia minispheres, solid loading has been performed on CZO sol by adding t-zirconia powder. To study the effect of solid loading on preparation and properties different wt% (30, 50 and 70) of solid loading have been experimented. The green density and sintered density are observed as 57% and 98 %TD respectively. Maximum of 98% TD is observed for 30 wt% of solid loading and further increase in solid loading marginally reduces the sintered density of 13Ce-ZrO₂ minispheres sintered at 1500°C for 5 hours. Two different grain sizes have been observed by SEM analysis whereas the grains are arranged more compactly. Effect of binder addition has also been analyzed in detail.

A maximum hardness of 9.1 GPa has been obtained for 30 wt% of solid loading. Further increase in solid loading has been observed with marginal degrease in density, hardness and wear resistance of the minispheres. However, the contamination by the milling media has been found to be negligible. A maximum density of 98% TD has been obtained for the 13Ce-ZrO₂ minispheres prepared using 30 wt% solid loaded CZO with the addition of 35 wt% of PVA and sintered at 1500°C for 5 hours.

8.2 SUGGESTIONS FOR FUTURE WORK

Commercial production is possible when processing steps and controlling parameters are further reduced. The cost of the production can be reduced if the transformation and densification are achieved at low temperature.

The sample preparation routes for characterization and property studies can still be optimized to obtain better identification of phase, microstructure and mechanical properties.
Thermal shock resistance and creep are the two important property studies, which will give us to understand the high temperature behavior of these materials. The electrical and thermal properties can also be studied.

A systematic study needs to be carried out to understand the effect of atmospheric conditions on sol and gel formation.

Seeding the sol can be preformed to achieve enhanced density at low sintering temperature.

Non-isothermal heating regimes can also be applied in the sintering process which could improve the strength and glassy surface of the minispheres.

Automation for drop generation need to be adapted for optimizing the preparation route.