CHAPTER 7

EFFECT OF SOLID LOADING AND BINDER ADDITION ON PREPARATION AND PROPERTIES OF CERIA STABILIZED ZIRCONIA MINISPHERES

7.1 INTRODUCTION

To impart green strength to the shaped component of zirconia minispheres and to improve the properties after sintering, binder has to be added along with zirconium oxalate sol. These additives may include either organic or inorganic materials which help to retain the shape during body formulation of near-net-shaped prototype zirconia minispheres.

For compacting oxide materials, the most commonly used binder is PVA because it has a strong affinity of adsorption on oxide particles dispersed in water (Bassner and Klingerberg, 1998). Polymer molecules absorbed on the surface of particles will bridge them together in the gel. This imparts organic network between the particles which results in high green density (Morissette et al 1999).

The PVA inter-chain separation distance in solution decreases with increase in degree of hydrolysis and causes interaction between polymer-solvent and polymer-polymer system. The viscosity of the binder solution and the adhesion strength of the organic film on the particle alter the internal friction and the ultimate shear strength of the sol. When the submicron
zirconia powders are flocculated with an organic binder in the system, the plasticity is developed. When the sol is to be extruded to form the shaped components, the friction at particle contacts should not restrict the particle sliding in the sol. For a particulate system, a particular concentration of binder and liquid is required for easy plastic flow without friction.

Relatively little work has been reported on the properties of technical ceramics plasticized with organic binders. Therefore an attempt is made to study the effect of binder content on the sintered density of the stabilized zirconia minispheres.

The difficulty encountered in forming minispheres using sol-gel processing is the magnitude of the shrinkage, subsequent difficulty in maintaining dimensional control and achieving near TD. This restricts the use of zirconium oxalate sol alone as a starting route for the fabrication of dense and hard zirconia minispheres. Wistrom and Clark (1984) have also suggested that the presence of solid particulates or fibers substantially reduces the amount of shrinkage.

In the present study, the solid loading is performed in the CZO sol by the addition of t-ZrO₂ powder to reduce the shrinkage and to increase the density of the final product. The mixing of t-ZrO₂ with CZO reduces shrinkage by (a) replacing the lower specific volume CZO with t-ZrO₂ thereby changing, the total specific volume upon transformation and by (b) increasing the density with improved particle packing. However, the differential shrinkage due to the bimodal particle size distribution of the powder may be a problem when CZO is mixed with t-zirconia of different particle size. Small amount of PVA is also added to the sol to increase the plasticity and the green strength.
In this chapter, the effect of solid loading and binder addition on shrinkage, transformation temperature and enhancement of properties of the ceria stabilized zirconia minispheres are presented.

7.2 EXPERIMENTAL PROCEDURE

CZO sol was prepared following the procedure given in chapter 4. The sol was then dehydrated by heating at 80°C to remove excess amount water content appropriate for the formation of minispheres. To enhance the densification and to reduce the shrinkage and transformation temperature, the CZO sol was solid loaded using pure t-ZrO$_2$ powders. In solid loading, t-ZrO$_2$ powders of 0.5μm size were mixed with the CZO sol and stirred well to avoid mass segregation and to improve homogenous dispersion. The solid loaded CZO sol was then adjusted to a pH value of 1.5 using nitric acid. PVA was added to impart green strength and plasticity in the sol to make it appropriate for minisphere formation in the setting solution.

The gelled minispheres were then dried at room temperature for 24 hours to remove excess ammonia and converted into t-ZrO$_2$ minispheres by sintering at 1500°C for 5 hours. To study the effect of solid loading on preparation and properties different wt% (30, 50 and 70) of solid loading was used. Figure 7.1 illustrates the flow chart for the preparation of zirconia minispheres using CZO sol with solid loading.

7.3 RESULTS AND DISCUSSION

7.3.1 Thermal Analysis

Figure 7.2 shows the onset temperature at which phase transformation occurs in ceria stabilized zirconia minispheres solid loaded with t-ZrO$_2$ powder. It is observed from DTA curve that the solid loading on 13Ce-ZrO$_2$ minispheres lowers the crystallization temperature. The second
exothermic peak observed for 13Ce-ZrO$_2$ minispheres without solid loading (Figure 4.5) is reduced from 420 to 388°C. The temperature shift for t-ZrO$_2$ transformation indicates that the t-ZrO$_2$ particles do indeed act as nuclei, when the 13Ce-ZrO$_2$ minispheres solid loaded with 30wt % of pure t-ZrO$_2$ powders. It is also observed that the crystallization temperature marginally decreases with further increase in solid loading which supports the claim that solid loading do not affect the transformation temperature beyond a saturation level. Changes in oxalate decompositions temperature and volatiles removal temperatures are also observed which may be attributed to the procedural alterations adapted in the preparation route.

It is evident from the DTA curve that the net percentage of weight loss decreases from 41.80 to 34.69 which implies that the solid loading (30 wt%) improves the residual weight of the 13Ce-ZrO$_2$ form 58.20 to 65.31 %. It is observed that the hydroxylation procedure adopted in the present study does have an impact on the percentage weight loss in water removal stage. Weight loss on water removal stage is observed as 6.81% which is nearly 3% less than that observed for 13Ce-ZrO$_2$ without solid loading (Figure 4.5). In addition, shift in the first endothermic peak (~100°C) is also observed which may be due to the removal of entrapped residual ammonia and water. Variations in percentage of weight loss and shrinkage have been analyzed with increase in amount of solid loading. It is observed that the weight loss percentage and shrinkage decreases with increase of solid loading. Figure 7.3 shows the comparison on residual weight, shrinkage and density of 13Ce-ZrO$_2$ minispheres sintered at 1500°C with various amount solid loading. It is observed that the residual weight of 13Ce-ZrO$_2$ minispheres increases to nearly 7 % for 30 wt % of solid loading and further increase in amount of solid loading is not yielding considerable increase in residual weight. Nearly 12% reduction in shrinkage is observed for the addition of 50 wt% of solid loading.
Figure 7.1  Flow chart for the preparation of zirconia minispheres using CZO sol with solid loading
7.3.2  Density Studies

The density of the 13Ce-ZrO₂ minispheres varies considerably with the increase in the solid loading as shown in Figure 7.3. A maximum of 98% TD is obtained for the minispheres formed using ceria doped zirconium oxalate sol with 30 wt% of t-ZrO₂ solid loading sintered at 1500°C for 5 hours. The densification of the zirconium oxalate - zirconia has been formed to depend greatly on the intrinsic densification behavior of the t-ZrO₂ powder. Solid loading in the range of 50-70wt% leads to the marginal reduction in the density of the final product which may be due to the imbalance occurs in the ratio of residual weight and shrinkage. The difference in densification behavior is believed to be due to the degree of differential shrinkage. The critical value of solid loading is observed as 30 wt% for obtaining maximum density (98%) with the moderate shrinkage.

Figure 7.2  TGA/DTA curves for the dried 13Ce-ZrO₂ with solid loading (30 wt%)
Figure 7.3 Variations on residual weight, shrinkage and density of 13Ce-ZrO$_2$ minispheres with different solid loading

Enhanced dimensional control has been achieved due to the reduction in sintering shrinkage of the final product. However, the desired density can be obtained with reasonable shrinkage by using appropriate (wt %) addition of t-ZrO$_2$ powder. Table 7.1 gives the density of the 13Ce-ZrO$_2$ minispheres prepared with and without solid loading sintered at 1500°C for different soaking time. The impact of soaking time on density is also observed.

7.3.3 Effect of Binder and Sintering Temperature

The concentration of the binder in the sol strongly influences the green density of the shaped minispheres which in turn, increases the sintered density of the final product. Higher green density gives more initial particle contacts and smaller initial pores which requires less sintering temperature to
obtain final density. Figure 7.5 shows the dependence of sintered density of 13Ce-ZrO$_2$ minispheres (30wt% solid loading sintered at 1500°C for 5 hours) with the concentration of PVA as binder. The density increases as the binder concentration is increased. A maximum density of 98% TD is obtained for the samples prepared with 35 wt% PVA. Further increase in the concentration results in high friction in the gel which is not ideal for drop formation in the setting solution. Figure 7.4 shows the variation of density with sintering temperature for 13Ce-ZrO$_2$ minispheres prepared with 30wt% solid loading. The green density of the minisphere is 57% TD and it gradually increases with sintering temperature and reaches a maximum of 98% TD for the spheres sintered at 1500°C.

![Variation of Density with Sintering Temperature](image)

**Figure 7.4** Variation of density with sintering temperature (13Ce-ZrO$_2$ minispheres prepared with 30 wt% solid loading)
Figure 7.5  Dependence of sintering density with the concentration of PVA as binder for 13Ce-ZrO$_2$ minispheres (30 wt% solid loading and sintered at 1500°C for 5 hours)

Table 7.1  Dependence of density with and without solid loading for different soaking period

<table>
<thead>
<tr>
<th>Type of sol used for forming</th>
<th>Green density (TD%)</th>
<th>Density (TD%) – Sintering temperature 1500°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Soaking time (hours)</td>
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<tr>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>CZO</td>
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<td>93.61</td>
</tr>
<tr>
<td>CZO with solid loading</td>
<td>57</td>
<td>94.32</td>
</tr>
</tbody>
</table>
7.3.4 Microstructural Analysis

Figures 7.6 (a, b and c) show the SEM micrographs of the fracture surface of 13Ce-ZrO$_2$ minispheres sintered at 1500°C for 5 hours with 30, 50 and 70 wt% solid loading respectively. The microstructures reveal that two different size grains are present. The smaller grains of size 0.5 micrometer and the large grains of size ~2 micrometer are observed with reduced porosity. The presence of grains of two different sizes is due to the difference in the size of the t-ZrO$_2$ powder (used for solid loading) added directly and the t-ZrO$_2$ produced from zirconium oxalate sol used for binding the powder. However, the grains are arranged more compactly due to the difference in the grain sizes as compared with minispheres without solid loading which may be the major reason for increase in density. Further increase in amount of solid loading (>30wt%) leads to the reduction in compactness of grains because of overcrowding which may be the reason for marginal decrease in the density of the minispheres.

7.3.5 Hardness

Figure 7.7 shows the variation in Vickers hardness for the 13Ce-ZrO$_2$ minispheres sintered at 1500°C with solid loading. It is observed that the hardness of the 13Ce-ZrO$_2$ minispheres sintered at 1500°C with 30 wt% solid loading varies from 6.8 to 9.1 GPa (applied load of 2 to 0.5 kg). Increase in hardness with the addition of 30 wt % solid loading may be attributed to the elevated density (98%).

During indentation, small grain size of t-ZrO$_2$ powder restricts tetragonal to monoclinic phase transformation and hence improves the hardness of the minispheres with 30 wt% solid loading. The decrease in hardness with increase in solid loading (above 30 wt%) may be due to the marginal decrease in the sintered density. It is observed that the variation of solid loading above 30 wt% have insignificant effect on the hardness.
Figure 7.6 (a) SEM micrograph of 13Ce-ZrO$_2$ minispheres sintered at 1500°C with 30wt% solid loading

Figure 7.6 (b) SEM micrograph of 13Ce-ZrO$_2$ minispheres sintered at 1500°C with 50wt% solid loading

Figure 7.6 (c) SEM micrograph of 13Ce-ZrO$_2$ minispheres sintered at 1500°C with 70wt% solid loading
Figure 7.7  Variation of Vickers hardness with applied loads and different solid loadings for 13Ce-ZrO$_2$ minispheres sintered at 1500°C

7.3.7 Wear Resistance

Effect of solid loading on material loss of the minispheres during grinding has been analyzed which gives the extent of contamination in the milled powder. 100gm of grinding media (minispheres) are subjected to milling in a planetary mill at the speed of 100rpm for 9 hours and the wear occurred for different milling intervals are measured. It has been found that the wear loss of the 13Ce-ZrO$_2$ minispheres with 30wt% of solid loading decreases as the time of the milling increases. Figure 7.8 shows the % of wear with different solid loading occurred for different milling time interval.

It is observed that the wear resistance of 13Ce-ZrO$_2$ improves with 30 wt% of solid loading. Maximum wear of only 0.20% occurs during 9 hours of milling. It indicates that the contamination during milling by the milling media is minimal.
 variation in % of wear with different solid loadings and different milling time intervals 

The increase in the wear resistance of the material is due to the high density as reported by Zum Gahr et al (1993). Further increase in solid loading above 30 wt% leads to the reduction in wear resistance and the wear loss reaches nearly 0.37 % for 70wt% of solid loading. It is also observed that the wear loss increases with grinding time irrespective to the amount of solid loading.

7.4 CONCLUSION

The solid loading using t-ZrO₂ powder in the zirconium oxalate sol reduces the shrinkage and increases the sintered density of 13Ce-ZrO₂ minispheres. It is also observed that the density of the 13Ce-ZrO₂ minispheres increases with the binder content. The green density and sintered density are observed as 57% and 98 %TD respectively. Maximum of 98% TD is
observed for 30 wt% of zirconia solid loading and further increase in solid loading marginally reduces the sintered density of 13Ce-ZrO₂ minispheres sintered at 1500°C for 5 hrs.

The microstructure shows two different grain sizes but the grains are arranged more compactly. A maximum hardness of 9.1 GPa is obtained for 30 wt% of solid loading. Wear resistance studies shows that only 0.2% wear has occurred even after 9 hrs of milling for 13Ce-ZrO₂ minispheres sintered at 1500°C with 30 wt% of solid loading. It indicates that the solid loading has a positive effect on wear resistance of 13Ce-ZrO₂ minispheres. Further increase in the solid loading leads to the marginal decrease in density, hardness and wear resistance of the minispheres. However, the contamination by the milling media is found to be very small.

A maximum density of 98% TD has been obtained for the minispheres prepared using 30 wt% solid loaded zirconium oxalate with addition of 35 wt% PVA and sintered at 1500°C for 5 hours. It shows that the t-ZrO₂ acts as nucleus which results in high density.