6.0 SUMMARY AND CONCLUSIONS

Metastable ZrO\textsubscript{2} bearing ceramics produced by using non-equilibrium processing techniques, such as rapid solidification and chemical precursor synthesis through sol-gel route, have been known to possess interesting and potentially useful properties. The metastable phase may serve as a precursor to the desired microstructure. Synthesis appears to be a very important requirement for the generation of metastable ceramics with controlled microstructure. The conditions that allow the desired metastable phase or the nanometric grain size to be retained may not be adequate for complete densification. The present investigation has been undertaken to synthesise a precursor powder of ZrO\textsubscript{2} - Al\textsubscript{2}O\textsubscript{3} system having different mole ratios through the nonconventional sol-gel route in aqueous phase.

1. The salts selected for the aqueous phase interaction have the least tendency to hydrolyse, and as such homogeneous mixing in the solution state is possible. The hydrogel has been formed in basic pH, and all the textural characteristics of the gel have been observed, including the liberation of syneresis liquid by capillary force during ageing. The consistency of the gels has been semi-solid and optically translucent.

The formed gels have been properly processed to remove the adherent soluble impurities, and dried at low temperature to inhibit the formation of hard agglomerates. Chemicals analysis of the dried product has indicated that more or less same mole ratio of ZrO\textsubscript{2} : Al\textsubscript{2}O\textsubscript{3} is retained as that in the batch composition. The hydroxide conversions have been completed at the experimental pH, with homogenous texture for the synthesised powder.

The powders have been found to possess significantly high surface area, with the density and the surface area following a direct relationship with ZrO\textsubscript{2} content.
Infrared analysis of the hydrogel has indicated the existence of all the related band frequencies of the individual hydroxide, including OH- stretching and bending vibrations. Moreover, the absorption peaks have not exhibited major shifting, indicating no influence of variation on the nature of the spectra. X-ray diffraction analysis of the original powder has revealed the amorphous nature irrespective of molar ratio of the ingredients.

2. DTA peak temperatures for both endo and exothermic reactions have revealed the same type of high temperature reaction. Shift of peak temperature has been influenced by mole ratio of ZrO$_2$:Al$_2$O$_3$. Initial endothermic reactions have been associated with the expulsion of loosely bound gel water, and directly related to the ZrO$_2$ content. The size, number and disposition of channels are the controlling factors for expulsion of water. Generation of the crystalline phases i.e., polymorphs of ZrO$_2$ and $\alpha$-Al$_2$O$_3$ have been manifested as exothermic peaks, the temperature of which have followed an inverse relation with the oxide content.

3. Difference in peak temperature has prompted study of equilibrium dehydration-rehydration during progressive heat treatment. Dehydration involves initial loss of gel and surface water, followed by dehydroxylation of the hydroxides. Equilibrium dehydration has proceeded up to 800°C in a non linear path exhibiting a sharp inflection at 300°C resulting from the energy involved in the expulsion of different types of water. Variation of mole ratio of ZrO$_2$:Al$_2$O$_3$ has not altered the mechanism of the process, except the magnitude. The loss is related directly to the Al$_2$O$_3$ content.

4. Rehydration of the heat treated samples, as calculated on the basis of the dehydrated weight, has been found to be directly related to the humidity. The reversibility of dehydration-rehydration is related to the structural stability, which is maintained up to 300°C due to the retention of amorphous nature of the hydrogel. Along with physical adsorption, some reconstitution of OH groups might occur, thereby changing the surface characteristics.
5. Kinetics of the endothermic reaction associated with the expulsion of chemically combined water from hydrogel structure has been carried out in order to throw some light on the mechanism of the process. The results of isothermal dehydration experiments at the particular zone have been interpreted using Guggenheim equation.

\[ -kt \log dL = \ldots \ldots + \log \left[ L_\infty \left( 1 - e^{-kd} \right) \right] \]

\[ 2.303 \]

Linearity of the plots of log dL vs time has indicated that first order kinetics is valid irrespective of the nature of the hydrogel. The main observations may be summarised as:

i) Applicability of first order kinetics for the major portion of the reaction for all compositions suggests that dehydration is essentially controlled by the mutual interaction of the hydroxyl groups.

ii) The deviation from first order kinetics at certain stage appears to be due to possibility of randomness in the orientation of water molecules, and decrease in concentration of the reactants at the later stage of dehydration. The extent of validity of first order law follows the nature of true endothermic reaction, and is influenced to some extent by the composition.

iii) In the final stage of dehydration due to the decrease in the concentration of the reacting species, higher energy is required for dislodging the water molecules, and as such \( k_2 \) values are always lower than the corresponding \( k_1 \) values. Due to the porous structure of the hydrogel, the escaping water molecules face very little diffusion barrier at the initial stage, minimising the compositional effect.

iv) The activation energies at the initial and final stages of dehydration i.e. \( E_1 \) and \( E_2 \) have been found to be in conformity with the earlier conclusion. Hence,
the ratio $E_2/E_1$ has always been greater than 1.0. It is to be noted here that both the hydroxides in the mixture undergo dehydroxylation at the temperature region of the kinetic study.

There is an increasing trend in recent years for the preparation of fine powders to satisfy the requirement of demanding properties. The powders thus synthesised in ZrO$_2$-Al$_2$O$_3$ system with wide compositional variations have been characterised properly with respect to their physical and chemical properties. The powders with desirable chemical composition are fine particles with high surface area (indicative of minimum agglomeration). The reactivity of the precursor powder samples obtained through inorganic route has been ascertained from their non crystalline nature along with high moisture absorption capacity. The distribution of the individual phases developed in this process has been homogeneous, since the hydrogel is generated from the homogeneous phase.

6. The hydrated precursor powder has been calcined to remove bulk water in order to avoid flaws which might result during sintering. Particle agglomeration has occurred during calcination, but without producing hard agglomerate. Mechanical compaction of the dried powder has been effected by uniaxial pressing in a hydraulic press. In this type of fabrication applied force might not be transmitted uniformly because of friction between the particles. But the particles derived from hydrogels are generally possess minimum anisometry. Moreover the fabricated shapes are too small to exhibit the faults. Sintering has been performed in the ambient atmosphere at 1400 - 1600°C. In all cases shrinkage has been a positive function of temperature. Removal of residual OH groups and particle migration causing grain growth and crystallisation are the contributing factors. The mole ratio of ZrO$_2$:Al$_2$O$_3$ and the amount of the additive play a significant role because of its relation to phase generation.

7. The magnitude of densification as a function of composition, sintering temperature and amount of dopant is reflected through the measurement of both bulk
and true densities. The relative density has been found to be maximum for the 1:2 mole ratio sample having 4 mole% Y₂O₃ at 1600°C. The change of bulk density with temperature has not been linear, showing an inflection at 1500°C in all cases. The highest bulk density of Al₂O₃ - ZrO₂ is attributed to faster rate of sintering through the direct sites (oxygen vacancy). The transformational features of the individual oxide in the present composite system has influenced the bulk density change.

8. The evolution of pores in this type of sintered compact is difficult to analyse. Although porosity generation and elimination are related to the loss of water, particle migration, crystallisation and grain growth, no direct correlation has been achieved possibly due to overlapping of the processes. The rate of decrease of porosity is not uniform throughout the entire course of sintering. Shrinkage associated with the elimination of pores is manifested by the identical inflection point at 1500°C. 4 mole% Y₂O₃ has been found to be optimum with respect to reduction of porosity indicating thereby that it is contributed by the transformation of ZrO₂ and formation of solid solution with Y₂O₃.

9. Thermal expansion curves of the composites exhibit hysteresis effect related to the phase transformation of ZrO₂. In ZrO₂:Al₂O₃ (1:2) sample containing 4 mole % Y₂O₃, the hysteresis effect is negligible, which may be due to retention of tetragonal phase on cooling. The coefficient of expansion follows a direct relationship with the Al₂O₃ content.

10. It is evident from the experimental results that Y₂O₃ plays a vital role in the densification of ZrO₂ - Al₂O₃ composites. As there is no tendency for compound formation among the ingredient oxides except the dopant, the true density change is purely an additive function of the formed phases. Among the ingredients, ZrO₂ possesses higher density in any polymorphic form, and as such the compositional effect is evident up to 1550°C. The true density which is an intrinsic property, continuously increases.
followed by slight decrease at 1600°C. The latter phenomenon appears to be related to
vacancy creation in the ZrO₂ lattice during phase transformation.

11. Regarding the mechanical properties, measurement of flexural strength shows
that the magnitude is dependent on the relative proportion of ingredient oxides, sintering
temperature and dopant characteristics. Even the minor variation in the consolidation
process might affect the strength. The results reflect strength increase up to 1550°C
sintering temperature, followed by slight decrease at 1600°C. The presence of Y₂O₃ at 4
mole % increases the mechanical strength at all compositions. In this case the stabiliser
has prevented the formation of microcracks in the matrix, and has strengthened the grain
boundaries. Reduction of hot strength both in the absence and presence of additives is
significant, which might be due to elastic failure of the composite material in the
transgranular brittle fashion. Grain boundary sliding does not appear to be responsible
due to the absence of glassy phase.

12. One of the important characteristics of materials intended for use as refractory is
the thermal shock resistance. In zirconia bearing composites thermal stress always
developes at the surface during sudden cooling, resulting in its fracture. During water
quenching after 8 cycles the retained strength varies from 45 to 30%, and it decreases
continuously with increase of Al₂O₃ content. Similar trend is maintained with samples
containing 4 mole % Y₂O₃. But in this case strength retention is higher 50 to 35%. The
reduction in strength in both the cases might be attributed to conversion of tetragonal
ZrO₂ to monoclinic symmetry during quenching. Moreover the thermal mismatch
between the particles increases during quenching, and this creates a stress field. The
thermal stress is large enough to propagate crack. The propagating crack experiences
decreasing strength with depth, and grows to a large size resulting in low retained
strength.

13. The precursor hydrogel powder as synthesised through aqueous phase route has
been completely non-crystalline in nature, exhibiting very intimate mixing of the
ingredient oxides on earlier heat treatment. Crystallisation starts during the last stage of dehydroxylation. The hydroxyl derived oxide has a tendency for agglomerate formation to a certain extent, which might lead to heterogeneous nucleation. The nucleation rate of the two oxides are not same, and as such there has been positive overlapping of nucleation and crystallisation stages. The dehydration process yields a variety of metastable transitional phases of Al₂O₃. The transitional phases have ultrafine particle sizes. The ultimate phase transformation to α-Al₂O₃ is accompanied by particle coarsening which normally affects sinterability. In the composite bodies sintered at 1600°C, Al₂O₃ is converted to stable α-Al₂O₃ irrespective of composition. Higher the ZrO₂ content lesser is the tendency for conversion of m-ZrO₂ into other forms. Thus m-ZrO₂ becomes the minor phase at 1:4 ratio. With the addition of 4 mole % dopant, the conversion and retention of t-ZrO₂ is possible for all the compositions, signifying the role of Y₂O₃. At higher temperature (1600°C) with higher ZrO₂ content, 2 mole % is found to be optimum for conversion and retention of favourable t-ZrO₂. Higher Y₂O₃ content is thought to result in enhanced solid solubility, which favours the stress-induced transformation.

14. The comparative microstructural features of the sintered samples with and without additives have revealed the distribution of the individual phases along with their growth. In all the microstructures, zirconia grains are visible as bright rounded or subrounded grains dispersed in non spherical alumina matrix. Both intra and intergranular zirconia have been observed, and the amount of the former increases with increase in Al₂O₃ content. ZrO₂ concentration enhances the grain growth influenced by particle migration. Distribution and sizes of grains are influenced by the presence of Y₂O₃. The latter has been found to sharpen the grain boundaries. Monoclinic zirconia particles retained at higher ZrO₂ content have been found to be twinned. Y₂O₃ has contributed to more or less uniform microstructure with greater compactness. Even the morphology of the pores are influenced by Y₂O₃.
Thus it is evident that proper dispersion of zirconia in alumina substantially improves the strength through manipulation of the microstructure. The grain growth of alumina is controlled by zirconia densification rate influenced by the relative proportions of the oxides. The intergranular zirconia particles at high concentration appear to coarsen through coalescence. It is evident from the microstructure that intragranular particles coarsen at a much slower rate. Thus addition of 4 mole % $\text{Y}_2\text{O}_3$ has been beneficial in retaining tetragonal zirconia with uniform microstructure. The pressureless sintering of $\text{ZrO}_2$-$\text{Al}_2\text{O}_3$ composites at certain ratio has produced $\text{Al}_2\text{O}_3$ matrix embeded with $\text{ZrO}_2$ grains. Most of the thermomechanical properties have been found to be dependent on the grain size of $\text{ZrO}_2$. 
