1.0 INTRODUCTION

The appropriate selection of a matrix phase and the addition of various zirconia grains to form ceramic composites with better strength and toughness has become widely recognised as a method for producing materials for engineering applications. The operating environment for high temperature reactions in metallurgy and other melting processes is increasingly becoming severe with time. Thus the need for high performance composite ceramics are finding importance in modern day technology. The oxides which play key role in refractory system are SiO₂, Al₂O₃, CaO, MgO etc. Recently the oxide that has attracted widespread attention of many scientists is ZrO₂. It has been known that the polymorphic transformation of ZrO₂ can be made use of to prepare an entirely new generation of materials. Subsequently these have become popular as transformation toughened ceramics having excellent mechanical and machinable properties. Addition of ZrO₂ to Al₂O₃, mullite and Si₃N₄ have resulted in composite systems that are effective in strengthening and toughening the ceramic matrix.

In the last few years sol-gel methods have been receiving a great deal of scientific attention. Gels are normally obtained by destabilising the colloidal sols from hydrolysis and polycondensation of metal alkoxides. This is a more expensive process but represents a wider opportunity for molecular manipulation and structural design. The preparatory conditions of the gels appear to be the most important factors in preparing the precursor powders. The starting solution has predominant effect on the attributes of a sol. Thus the sol-gel method at present is playing a vital role in the synthesis of active powders of homogeneous nature in multiphase system. Most of the work related to sol-gel process are being carried out through non-aqueous organic route which appears to be costly when the cost of the starting alkoxides are considered. Moreover these organic materials are not free from pollution.

In homogeneous precipitation of hydrous metal oxides, kinetic condition should be adjusted in such a way that the hydroxide ions are generated in situ rather than added.
as a base. Continuous hydroxylation yielding precursor to solid phase formation can be achieved in metal salt solution either by deprotonation of hydrated metal ions or by slow decomposition of molecules releasing hydroxide ions. Heating solutions of hydrolysable metal ions greatly promotes the dissociation of protons from co-ordinated water molecules. A proper combination of all the parameters such as concentration, temperature may result in solute complexes that will generate uniform colloidal particles. The major problem with current powder consolidation is that extensive agglomeration usually occurs when particle concentration is high. Ordered ceramic suspension may be used as precursors for some green compacts.

Zirconia, the dispersed phase in alumina-zirconia composites is responsible for grain growth inhibition, stress induced transformation related toughening and microcracking toughening, modification of thermal expansion coefficients, and high modulus of elasticity. These composites possess better thermal shock resistance than the matrix material. On the other hand, hydration resistance of \( \text{ZrO}_2 \) is improved by incorporation of alumina. Various routes of preparation of these composites have been explored and practised by the investigators.

The basic zirconia bearing ceramics deal with either natural or artificial powders that have been shaped into objects, and subsequently densified at a temperature close to their liquidus. Many advances have been made in the preparation of powders, forming and methods of densification. The conventional method of processing imposes a severe limit on producing products of high reliability for use in adverse environments. The important factor is the contact of the surfaces and interfaces of the materials during the early stages of production.

Alumina is one of the most important oxide ceramics used often as a structural material for withstanding mechanical load at elevated temperature, because of its high melting point, young’s modulus, hardness and chemical corrosion resistance. But lot of limitations have become evident in its applications, due to brittleness, low strength etc.
Several methods have been attempted to improve the property. One such method is the dispersion of a second phase into the brittle ceramic, which may yield considerable improvement in fracture energy.

Dispersion of ZrO$_2$ particles in Al$_2$O$_3$ is one of the suitable methods of improving the properties of Al$_2$O$_3$ bearing composites. Two polymorphic forms of zirconia i.e. the tetragonal and monoclinic significantly increase the toughness. Metastable $t$-ZrO$_2$ enhances strength as well as toughness through volume and shape changes associated with $t \rightarrow m$ transformation induced by stress field of a propagating crack. The $m$ - ZrO$_2$ increases the toughness but not strength, due to formation of microcracks around the particles. For the development of $t$ - ZrO$_2$, the particles must be smaller than a critical diameter required for homogeneous dispersion within the ceramic matrix. For obtaining the optimum property, critical diameter should be more to reduce the $t \rightarrow m$ transformation temperature. This can be achieved by stabilising zirconia with CaO, MgO, Y$_2$O$_3$, CeO$_2$.

The phase equilibrium studies in Al$_2$O$_3$-ZrO$_2$ system have shown that Al$_2$O$_3$ and ZrO$_2$ are compatible to one another. The phase diagram indicates that neither extensive solubility nor change in the ZrO$_2$ transformation temperature. But since Al$_2$O$_3$ has approximately double the elastic modulus of ZrO$_2$, theoretically it would be a much better constrained matrix than ZrO$_2$ alone. Neglecting the residual strain energy due to thermal expansion, one would expect the strain associated with the transformation to be better for Al$_2$O$_3$ constraining matrix, in contrast to ZrO$_2$ matrix. From the experimental data in ZrO$_2$-Al$_2$O$_3$ system, it is known that (i) the critical grain size in the high modulus matrix is much larger than lower modulus matrix, and (ii) the critical size decreases with increasing ZrO$_2$ addition to Al$_2$O$_3$. Inhibition of crystal growth of ZrO$_2$ and increase of modulus of elasticity of Al$_2$O$_3$ have positive contribution for the retention of tetragonal ZrO$_2$ by selective addition of dopants.
Water is an intrical part of the gel structure. The bonding energy of the associated water is strongly influenced by the surface charge of the framework structure. The dispersion phase which is bonded with relatively low energy is normally expelled during drying. The residual water controls the physical texture of the material, and is attached fairly to the hydrophilic surface of the gels. When the dried hydrogels are subjected to heat treatment, in the first phase it is characterised by the endothermic reaction relating to expulsion of water.

In the present investigation mixed hydroxide hydrogels of ZrO$_2$ :Al$_2$O$_3$ at different mole ratios have been synthesised by following the wet interaction technique in aqueous medium. The experimental conditions have been so adjusted to obtain a homogeneous gel structure. Dehydration-rehydration behaviour of the hydrogels has been studied under equilibrium condition which is related to the thermal stability.

Kinetics of the dehydration process at the particular dehydration zone has been studied through isothermal dehydration experiment. Kinetics belong to heterogeneous solid state reactions and the basis for understanding the rate processes has been the Arrhenius relationship, which states that the logarithm of the reaction rate constant k is proportional to the reciprocal of absolute temperature. The kinetic parameters including the activation energies have been determined and compared.

In the final part of the investigation, densification of these composites with and without additive has been studied by the normal pressure sintering process. To study and use the nanostructured and other metastable ceramics extensively, it is important to synthesise these materials in bulk and consolidation of particulate to produce a dense body with uniform and properly dispersed microstructure after sintering.

In compiling the zirconia alumina composite in unconventional manner, consideration has been paid to the purity, composition and proper synthesis through an inorganic colloidal route. The relevant powder characteristics and comparative sintering
behaviour in absence and presence of a particular dopant (Y$_2$O$_3$) have been studied. The transformation nature and the phases generated have influenced the important characteristics of this type of composite. Mole ratio of the ingredient oxides, amount of dopant, and the temperature of sintering have emerged as the important parameters.