ABSTRACT

The need for the development of materials technology is gaining interest day by day due to the ever increasing demand for the high performance quality products. The superiority of the ceramic based products over the metal based products enable them for the high tech structural and functional applications. While operating in severe environments, a good ceramic material should possess, high hardness, high strength, high fracture toughness, dimensional stability, corrosion and erosion resistance, high elastic modulus, and generally low coefficient of friction and these features ultimately rely on the better processed parent materials. Indeed, the understanding of the complex solution chemistry is an essential step for the development of better ceramic powders which will lead to the fabrication of high tech devices.

Although various liquid precursor methods are available for the preparation of variety of ceramic powders, the sol-gel technique provides a suitable route to produce highly sinteractive powders because it yields better quality powders with homogeneous mixing at the molecular or atomic level, high surface area, desired size, shape and size distribution of the particles, extremely high purity etc. Over the conventional methods to prepare the solid solutions which have higher melting point, the sol-gel technique paves a simple way at extremely lower temperatures, especially, for coating and preparation of glasses. Recently this method has been adopted to produce powders, particularly of spherical shape with free flow characteristics which are used for plasma spray coating.
Zirconia is one of the pioneering-fascinating oxide ceramic materials having excellent properties such as high fracture toughness, strength, stability in hostile environment, etc. The discovery of stress induced transformation toughening of the zirconia while changing from tetragonal to monoclinic phase due to the volume expansion has resulted in the resurgence of interest for researchers on this particular material. Among the numerous important problems associated with the study of this oxide ceramic material, special attention has been paid on the powder processing of these materials since it dictates the final properties of the finished structural and functional devices.

One of the non-conventional techniques, sol-gel method, has been used to prepare pure ZrO$_2$, 10 mole% of CeO$_2$-ZrO$_2$, 5 mole% of Y$_2$O$_3$-ZrO$_2$, 4 mole% of Y$_2$O$_3$-7 mole% of CeO$_2$-ZrO$_2$ amorphous precursor powders from metal salts of chlorides, nitrates and oxalic acid as parent materials. Dried amorphous gel powders have been used to prepare concentrated sols of these materials by means of repeptization. Chloride ion concentration as a function of gelation time has been discussed.

Concentration of dried gel powders of pure zirconyl oxalate (ZO) and 5 mole% of Yttrium-Zirconyl oxalate (YZO) could not be increased because of their high viscous nature, whereas for cerium containing oxalate gel powders, the concentration has been increased upto 10 wt.% of metal oxide. The variation of gelation time with the repeptized and parent sols has been discussed.
Thermal decomposition and phase transition studies are discussed in detail by means of TGA and DTA analysis. Weight loss up to 53% has been observed for almost all the four dried precursor powders. DTA studies reveal the crystallization of metastable tetragonal phase of pure zirconia around 425°C whereas other doped powders crystallize in stable tetragonal phase around 450°C. Pure zirconia transforms to a monoclinic phase around 850°C whereas others do not. The cerium doped zirconyl oxalate decomposes in a different fashion as compared with others. Exothermic oxidation of Ce$^{3+}$ has been observed around 300°C along with the decomposition of oxalate.

Powder X-ray diffraction studies confirm the crystallization of metastable tetragonal phase of pure zirconia with a transformation to a monoclinic phase and other doped powders having stable tetragonal phase at and above 450°C. Higher angle powder X-ray diffraction shows the existence of cubic phase for the YZ and YCZ powders calcined at 850°C. Estimation of surface area and IR studies have also been conducted.

Sintering studies have been reported for three samples, namely, 10 mole% of CeO$_2$-ZrO$_2$ (CZ), 5 mole% of Y$_2$O$_3$-ZrO$_2$ (YZ), 4 mole% of Y$_2$O$_3$-7 mole% of CeO$_2$-ZrO$_2$ (YCZ) under various experimental conditions. Powders used for this study have been obtained by calcining the dried precursors at 700°C for 1 hr. Two types of powders, such as dry milled and wet milled (in methanol) have been used to analyze the sinterability. Better sinterability has been achieved for the wet milled powders than the dry milled one. Wet milled samples have been sintered to near theoretical density (TD) at 1400°C for a soaking period of 3 hours whereas the dry milled samples have
been sintered only at 1500°C for a soaking period of 5 hours. The influence of particle size distribution on the final sintered density has been discussed. Effect of heating rate on the sinterability reveals that the slow heating rate is a better way to sinter the samples. X-ray diffraction studies confirm that the sintered samples of CZ are completely in tetragonal phase whereas the YZ and YCZ samples showed mixed phases of tetragonal and cubic. Grain sizes are calculated from the SEM photographs.

Studies on hardness, fracture toughness and bend strength reveal that they primarily depend on powder processing, sintering temperature and composition. The Vickers hardness value for the YZ samples are higher than the CZ and YCZ samples whereas the fracture toughness is lower for the yttria containing samples. Higher fracture toughness value has been observed for the CZ samples. SENB and CVNB notches are prepared on the green compacted samples in order to avoid detrimental effects due to grinding on the sintered samples, and are then subsequently sintered. Fracture toughness has been evaluated by breaking the samples using three point bending mode. Flexural strength and Weibull modulus are also reported for these samples. Studies on mechanical behavior show that the wet milled samples have better mechanical properties than the dry milled samples. Part of the findings of these work has been published in National/International Journals and discussed in conferences.