Study on process development and property evaluation of sol-gel derived magnesia stabilized zirconia minispheres

J. JUDES¹∗, V. KAMARAJ²

¹Department of Physics, University VOC college of Engg., Anna University, Tuticorin – 628008, India
²Department of Ceramic Technology, Anna University, Chennai – 600025, India

In order to overcome limitations in the processing parameters of powder compaction method, a novel processing technique based on sol-gel route has been developed to produce near-net-shaped prototype fine zirconia minispheres with required properties that could potentially be used as grinding media. Impact of magnesia concentration and sintering temperature on the final product has been analyzed in detail. Zirconia minispheres have been characterized to establish a correlation between physical, structural and mechanical properties. Sintering temperature, soaking period, heating rate and viscosity of the sol apparently influence the characteristics of the magnesia stabilized zirconia minispheres. The phase identification, density variation, chemical decomposition, functional group specification, surface area, porosity, shrinkage and microstructural features of the dried and sintered final product have been studied. It has been observed that magnesia content, sintering temperature, density and the grain size of the sintered minispheres have a significant impact on the mechanical properties of the final product.

Keywords: zirconia minispheres; sol-gel synthesis; zirconium oxalate sol; magnesia stabilization

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1. Introduction

The conventional powder compaction method used for fabrication of grinding media (less than 1 mm in diameter) has major setbacks such as variety of size, density and non-uniformity in shape, since slight change in processing parameters leads to drastic structural changes. In order to overcome the limitations, a novel processing technique based on sol-gel drop generation method [1, 2] has been developed in the present study to prepare near-net-shaped nano-crystalline zirconia minispheres as grinding media. Sol-gel drop generation method is found to be very economical and effective. This method enables greater control of the process at the molecular level and avoiding impurities. Crystalline structures and catalytic properties can also be optimized. Among the ceramic oxides, zirconia is one of the most fascinating materials because of its excellent properties such as high fracture toughness, strength, stability in hostile environments etc. Various potential sol precursors were investigated and characterized for the preparation of zirconia minispheres as grinding media. The optimum was an aqueous sol made from hydrolyzed zirconium oxalate (ZrO(COO)₂) [3]. Sol-gel processing has the advantage of producing ultra-fine zirconia minispheres of required size by extruding zirconium oxalate sol.

To use zirconia to its full potential the properties of the oxide have been modified extensively by the addition of stabilizing oxides. One of the widely studied ceramic materials is magnesia stabilized zirconia (Mg–ZrO₂). Mg–ZrO₂ received considerable attention in the literature for its dominant mechanical property, which is widely held to be transformation toughening during tetragonal to monoclinic transformation [4]. Structural and mechanical properties of magnesia stabilized zirconia can be easily tailored by systematic doping and temperature treatment, which makes the material very facile for the use as a grinding medium [5].

In general, zirconia can be synthesized using different methods. The traditional precipita-
tion technique gives rise to microcrystalline zirconia, while the sol-gel method, produces nanocrystalline zirconia that is very attractive for novel applications since nanocrystalline structures often exhibit properties different from that observed in the microcrystalline ones. In the present study, the preparation of near-net-shaped prototype zirconia minispheres has been achieved by the sol-gel drop generation route. The characterization studies revealed the information about stabilization and enhancement of structural, physical and mechanical properties of zirconia minispheres.

2. Experimental procedure

Water soluble metal salts of chlorides and nitrates have been selected because compared with the alkoxides, the cost of the salts of inorganic material is quite low and hence the final product is cost effective. The starting material used for the preparation of zirconia sol was zirconium oxychloride octahydrate (ZrOCl₂·8H₂O) of 1M concentration. Oxalic acid ((COOH)₂·2H₂O) was refluxed in deionised water at 60 °C to obtain 1M concentration solution.

Magnesium nitrate hexahydrate (Mg(NO₃)₃·6H₂O) was used as a stabilizing agent to study the effect of transformation toughening property and processing conditions. The magnesium nitrate was stirred and mixed thoroughly with the solution of zirconyl chloride (1M) as a parent sol in such a way that the final sintered product contained 5, 8 and 10 mol % of magnesia stabilized zirconia (Mg–ZrO₂). The desired quantity (1:0.7 vol/vol ratio) of oxalic acid was then added dropwise, under constant stirring, to the parent sol at room temperature (~29 °C), which produced white flocculates and disappeared immediately [6]. The addition of stoichiometric ratio of oxalic acid with the mixed cation solution led to the formation of an unclear sol that then turned to be a white opaque gel. On the other hand, a transparent sol and gel were observed when the addition of oxalic acid was sufficient to form the magnesia doped zirconyl oxalate (MZO) gel. In order to understand more clearly the nature of dopants in the oxalate sols structure, Tohge et al. suggested that the dopant was uniformly distributed on the porous surface of the zirconyl-oxalate gel structure. During calcinations the dopant ions were substituted for zirconium ions in the crystal structure which favored the formation of the stabilized zirconia [7].

As the addition of oxalic acid was continued, the rate of disappearance of white flocculates decreased and finally a white opaque gel was obtained. The gel transformed into a clear sol on continuous stirring. A probable reason for the variation of the rate of disappearance of the flocculates might be the higher ionic concentration of the solution and an uneven distribution of the ions. As the time increased, the clear gel again became slightly opaque. The formed sol was transformed into a transparent thixotropic gel at room temperature by physical gelation. Since many factors influenced the solutions, a possible qualitative explanation for the disappearance of the white flocculates at the beginning stage, the formation of the white thick gel at the middle stage and the clear sol at the final stage, can be discussed on the basis of DLVO theory presented by Li and Messing [8].

It had also been noticed that the atmospheric conditions had a remarkable effect on the formation of the transparent sol, gel and gelation time. For example, if the humidity of the atmosphere was more than 95 %, the formed sol and gel were highly transparent at room temperature and the time taken for gelation was longer and if the humidity was less than 90 %, the formed sol was of aggregative nature and the gel was opaque. The viscosity measurements of the sol as a function of time were carried out using Brookfield viscometer which indicated that the viscosity of the sol increased with time. The gradual increase in the viscosity was due to the transformation of the particles from randomly aggregated state to ordered state with parallel orientation. The required viscosity could be obtained by adding a suitable binder, polyvinyl alcohol PVA (35 wt.%) based on the formation of a sphere in the setting solution and retention of the shape after sintering. It might be considered that the formed hydrochloric acid was one of the reasons for the co-