Physicochemical Studies of Zirconia and Magnesia Doped Zirconia Ceramic Powder

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(Received 11th December, 1995, revised 27th February, 1997)

Summary: Spherical fine zirconia (ZrO_2) and 9 mol % magnesia doped zirconia (MgO-ZrO_2) ceramic powders (diameter of ~0.2 mm) have been synthesized from a hydrothermally treated sol of zirconium and magnesium salts by spray pyrolysis. The results revealed that synthesized powders can be sintered into uniformly sized fine grained ceramic of > 97% theoretical density at temperature as low as 1100°C. The phases, purity, crystallite size, agglomeration structure, particle size, specific surface area, pore size distribution and porosity of ZrO_2 and MgO-ZrO_2 ceramics were measured by XRD, SEM, N_2-gas adsorption and Hg-diffusion techniques. The results of X-ray diffraction and scanning electron microscopy showed that the ZrO_2 and MgO-ZrO_2 remained amorphous upto 700°C, but on increasing the heat treatment temperature to around 1200°C for 8 hrs. monoclinic crystals were obtained. Thermogravimetric (TG) and differential scanning calorimetric (DSC) techniques were used to measure the burnout temperatures and enthalpy (ΔH) of polyvinyl alcohol (PVA) and methylcellulose (MC) polymers used as binders. Burnout of these polymers is 100% in an oxidizing atmosphere; 90% burnout was achieved in an inert atmosphere.

Introduction

Zirconia doped with alkaline earth oxides is extensively employed in many applications because of its superior mechanical strength, chemical durability and ion conductivity [1]. It is one of the strongest and toughest oxide ceramics when properly prepared and is not susceptible to creep at the anticipated use temperatures [2]. Several wet chemical methods are being developed for synthesis and characterization of high purity, homogenous and sinterable small particle ceramic powders and glasses. Metal alkoxide [3], citrate [4], sol-gel microsphere [5], and chloride [6] processes are also being used successfully for stabilized zirconia. Sol-gel technique provides an advantageous low temperature route to a homogeneous dehydrated ZrO_2 product as compared to conventional method. Partially stabilized zirconia is one of the most promising candidate for the ceramic die. Ceramic materials, unlike clay are nonplastic when mixed with water and are thus impossible to form into any shape without the use of a binder. Organic binders function as temporary bonding media to provide "green strength" for ceramic bodies and glazes [7]. Also, the binder can affect other properties of a ceramic batch, such as wet strength of a formed body, plasticity, die lubrication, wetting, water retention etc. The role of organic binders in ceramic processes has been discussed by Pincus [8], Treischel [9], Thompson [10] and McNamara [11]. For fabricating ceramics and clay bodies by extrusion, Teter [12] studied both the use of organic binders in isostatically pressed bodies and their machinability. Commercial water soluble polymers like polyvinyl alcohol (PVA) and methylcellulose (MC) polymers have been used extensively as binders for glaze; dry, semidry, isostatic pressing, extrusion, both ram and screw type, injection moulding and more recently slip casting. Aqueous solutions of methylcellulose and polyvinyl alcohol polymers gel upon heating are pseudoplastic and surface active. This thermal gelation property makes these polymers useful and beneficial as organic binders in many industries such as food, pharmaceutical and ceramic processes [13,14]. The present work describes synthesis, characterization and the sintering behaviour of spherical zirconia and 9mol% magnesia doped zirconia ceramic powder prepared by a sol-gel technique. The study of burn-out

temperature and enthalpy (ΔH) of methylcellulose (MC) and polyvinyl alcohol (PVA) polymers used as binder materials were also ascertained.

Results and Discussion

Characterization of physical properties of a material is not only important but also necessary for the understanding of the material. These properties are the result of the interrelationships of the processing techniques used for the fabrication, the microstructures, and phases developed. These properties ultimately control the utility of the material for specific applications such as mechanical, electrical, etc. Extensive chemical analysis were performed to measure the composition of fine zirconia (ZrO_2) and 9mol% magnesia doped zirconia ($MgO\text{-}ZrO_2$) powders. The results are summarized in Table-1.

Table-1: Elemental analysis in (ppm) of ZrO_2 and $MgO\text{-}ZrO_2$ ceramic powder

Sample/Elements	Al	Cu	Mg	Mn	Fe
ZrO_2 ceramic powder	180	625	N.D	3181	4248
$MgO\text{-}ZrO_2$ ceramic powder	180	657	7007	3383	4431

Thermal analysis is an appropriate technique to investigate the water molecules absorbed during the washing of the synthesised powder of ZrO_2 and removal of organic binders occluded in $MgO\text{-}ZrO_2$ ceramics. As the electrolyte is not completely removed from the zirconium solution pyrolyzed at relatively low temperature (700°C) within limited duration. It may be difficult to eliminate the remaining electrolyte by controlling reaction temperature and flow rate of carrier gas only, without a major improvement in the existing apparatus. Thus the powder produced by the present method needs the calcination to remove the electrolyte. All the volatiles were completely removed at 1000°C as observed on TG-DTA curves, Figures 1-2. The total weight loss (%water) for ZrO_2 and $MgO\text{-}ZrO_2$ powder was observed to be 5.11% and 4.96% respectively.

Densities of compact powder were estimated by using the equation

$$\rho/\rho_{th} = \rho_o/\rho_{th}[1 - \Delta\, 1/1_o]^{-3}$$

where ρ_o/ρ_{th} was the initial density $\Delta 1/1_o$ was the total relatively shrinkage measured from dilometry and ρ/ρ_{th} was the relative density of the sintered compact [15]. Some characteristics of sintered ceramic bodies are summarized in Table-2. The results revealed that the $MgO\text{-}ZrO_2$ sintered microstructure is composed of uniformly sized grains and is >91% of theoretical density. Results of densities of powder compacts were found to be similar with the work of Abraham *et al* [16]. The specific surface areas of zirconia (ZrO_2) and magnesia doped zirconia powders were found to be 27.11 and 41.23 m^2g^{-1} respectively and the results were found to be consistent with literature [17]. In present work no ageing study was made, Fegley [18] suggested that the larger surface area resulted from a surface coating of fine spherical precipitate formed by the rapid hydrolysis of residual titanium ethoxide on the particle surface upon contact with water in the initial washing step. Figures 3-4 describe the particle size distribution of ZrO_2 and

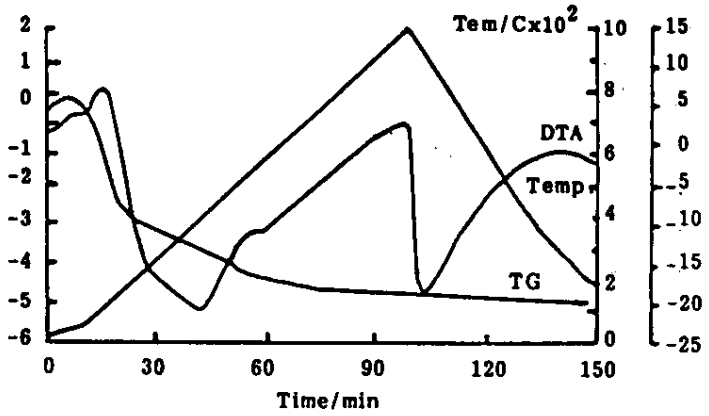

Fig. 1: Simultaneous thermal analysis (TG-DTA) of zirconia.

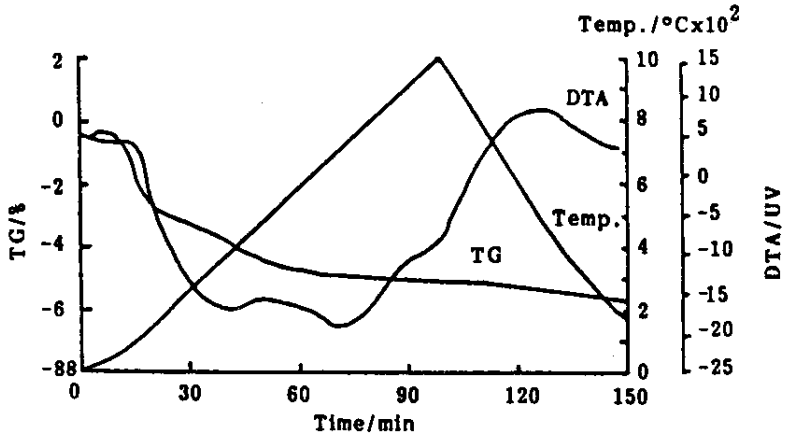

Fig. 2: Simultaneous thermal analysis (TG-DTA) of magnesia doped zirconia.

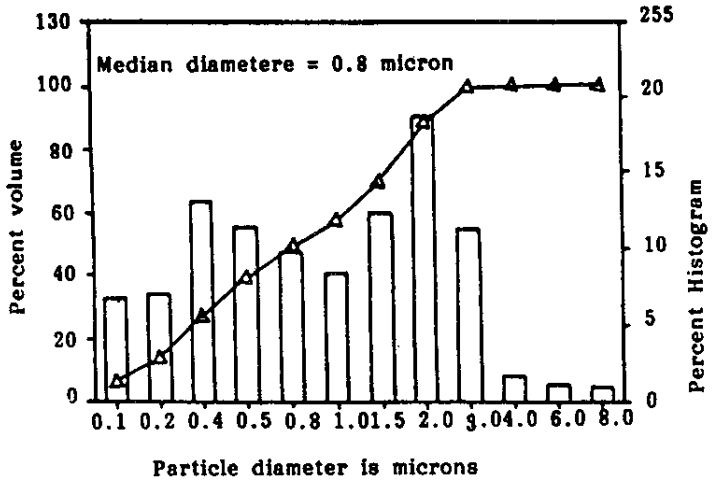

Fig. 3: Particle size distribution of spherical zirconia.

Table-2: Green density and sintered density of 9mol% magnesia doped zirconia

Sample	$MgO-ZrO_2$ -A*	$MgO-ZrO_2$ -B*
Sintering temperature (°C)	1200	1200
Green density (g cm^{-3})	2.61	2.61
Sintered material density(gcm^{-3})	4.94	4.97
Relative density (% theoretical density)	91.14	91.69

A* = Sintering for 2 hrs at 1200°C
B* = Sintering for 3 hrs at 1200°C
Theortical density = 5.42 g cm^{-3}

$MgO-ZrO_2$ ceramics. $MgO-ZrO_2$ ceramic powder indicates higher porosity than zirconia. In general, the particles produced by a spray pyrolysis method tend to be perfectly hollow or at least have more porosity [19].

The SEM micrographs of ZrO_2 and $MgO-ZrO_2$ ceramic powders (9 mol% MgO) calcined at 1200°C for 8 hrs are presented in Figures 5-6. The figures indicate that particles made by spray pyrolysis method were composed of spherical (mean dia - ≈ 0.23 μm) agglomerated and highly dispersed. The particle size distribution seemed to be uniform. When aqueous solutions of inorganic salts such as nitrate, chloride and sulphate were used as starting solutions, hollow or porous particles are especially formed. This is because the thermal decomposition begins first around the outer surface of the droplet and solid shells are firmly produced during the very short period of reaction. The density of sintered body of such powder does not increase. However, the particles produced by spray pyrolysis of zirconium sol seem to be dense and less porous. The denitration of sol increases powder density slightly. Further, very fine mist drops (3.8 μm) produced by the ultrasonic

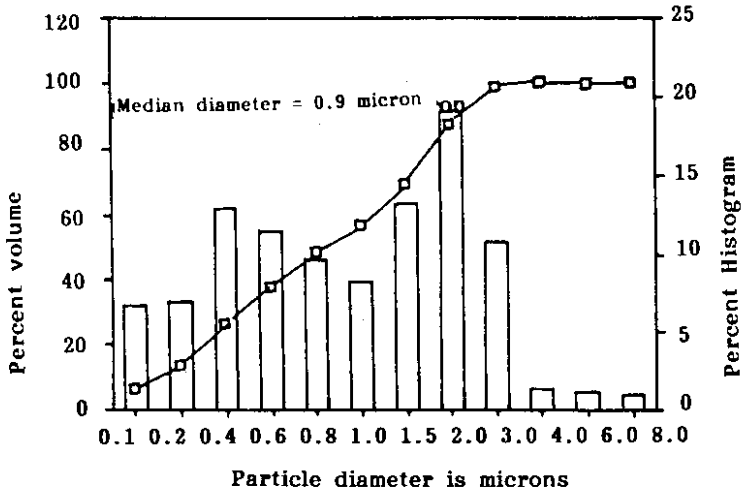

Fig. 4: Particle size distribution of magnesia doped zirconia (9 mol % magnesia).

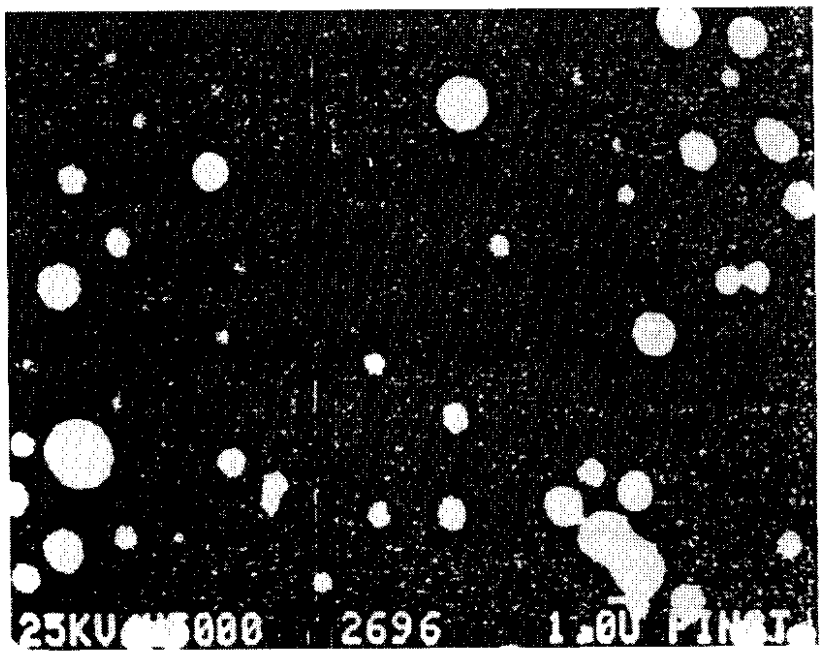

Fig. 5: Scanning electron micrograph of spherical zirconia.

vibrator and relatively slow heating rate of mist, compared with atomizer, cause high particle density. Atomizers with presurised-nozzles, relatively large size droplets are generated and their heating rate is very fast due to large flow rate of carrier gas.

The phases present in heat treated samples were determined by X-ray diffraction. XRD profiles of "as synthesized" and heat treated (calcined at 1200°C for 8 hrs) samples of ZrO_2 and MgO-ZrO_2 are shown in Figures 7-9. The "as synthesized" powders were found to remain amorphous after calcining at 400°C, but began to crystallize to the tetragonal structure near 600°C. The calcination at 800°C resulted only in a narrowing of the diffraction peaks, indicating an increase in crystallite size. ZrO_2 and MgO-ZrO_2 were found to

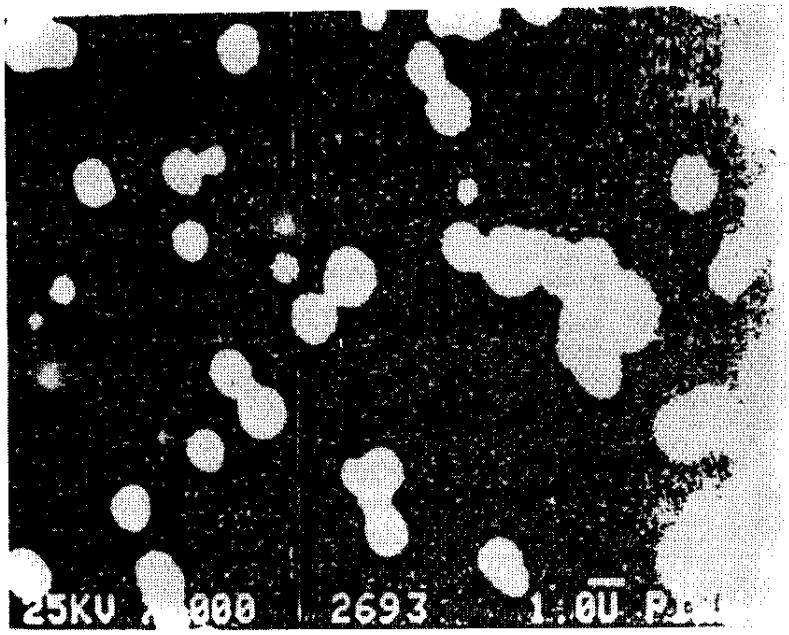

Fig. 6: Scanning electron micrograph of 9 mol% MgO doped zirconia.

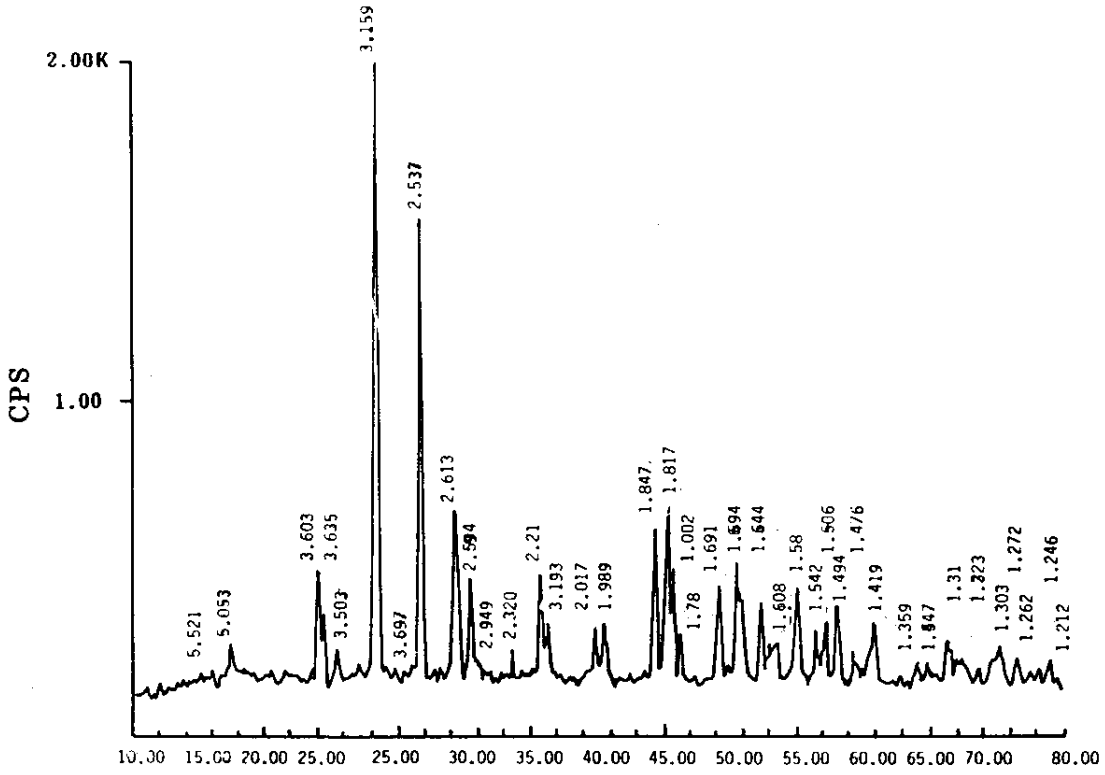

Fig. 7: X-ray diffraction pattern of ZrO_2 ceramic powder.

Table-3: Physical properties of ZrO^2 and 9mol% MgO-ZrO^2

Physical properties	ZrO_2	9mol %MgO-ZrO_2
Percent weight loss (H_2O)	5.11	4.96
Percent weight loss (PVA)		7.58
Percent weight loss (MC)		9.31
Δ H for PVA (J g^{-1})		-293.76
Δ H for MC (J g^{-1})		-105.00
Particle size (μm)	0.5 - 2.0	0.5 - 2.0
Symmetry of particles	Monoclinic	Monoclinic
Unit cell volume $(nm)^3$	0.14074	0.14283
Lattice parameters		
a (nm)	0.51471	0.51382
b(nm)	0.52111	0.52231
c(nm)	0.53144	0.53468
Shape of particle	Spherical	Agglomerates
Median diameter of particle (μm)	0.8	0.9
Total intrusion volume (mlg^{-1})	0.5323	0.586
Total pore area	100.52	104.7
Average pore diameter (μm)	0.0194	0.0224
Bulk density of particle (g ml^{-1})	1.7564	1.8827
Surface area (m^2 g^{-1})	27.11	41.23

be monoclinic when calcined at 1200°C. These results are in good agreement with the work of Scott [20] and Nogami [21]. The least-squares structure and profile refinement were performed with a modified version of the Rietveld analysis program using a refinement procedure described by Hill [22]. The calculated lattice parameters for zirconia and magnesia doped zirconia are presented in Table-3.

Burnout characteristics of MC and PVA polymers

Clean burnout is an important criterion in the choice of an organic binder in ceramics. Residues of ash and carbon can adversely affect critical properties of the ceramics. MC and PVA are both water soluble and nonionic in structure. Figures 10-11 show the TG-DTA thermograms obtained at heating rate of 1.5°C min^{-1} in an air atmosphere for (-9 mol % MgO) MgO-ZrO_2 ceramic using polyvinyl alcohol and methyl-cellulose polymers as binder. In TG traces there are two weight loss regions, the first, weight loss of

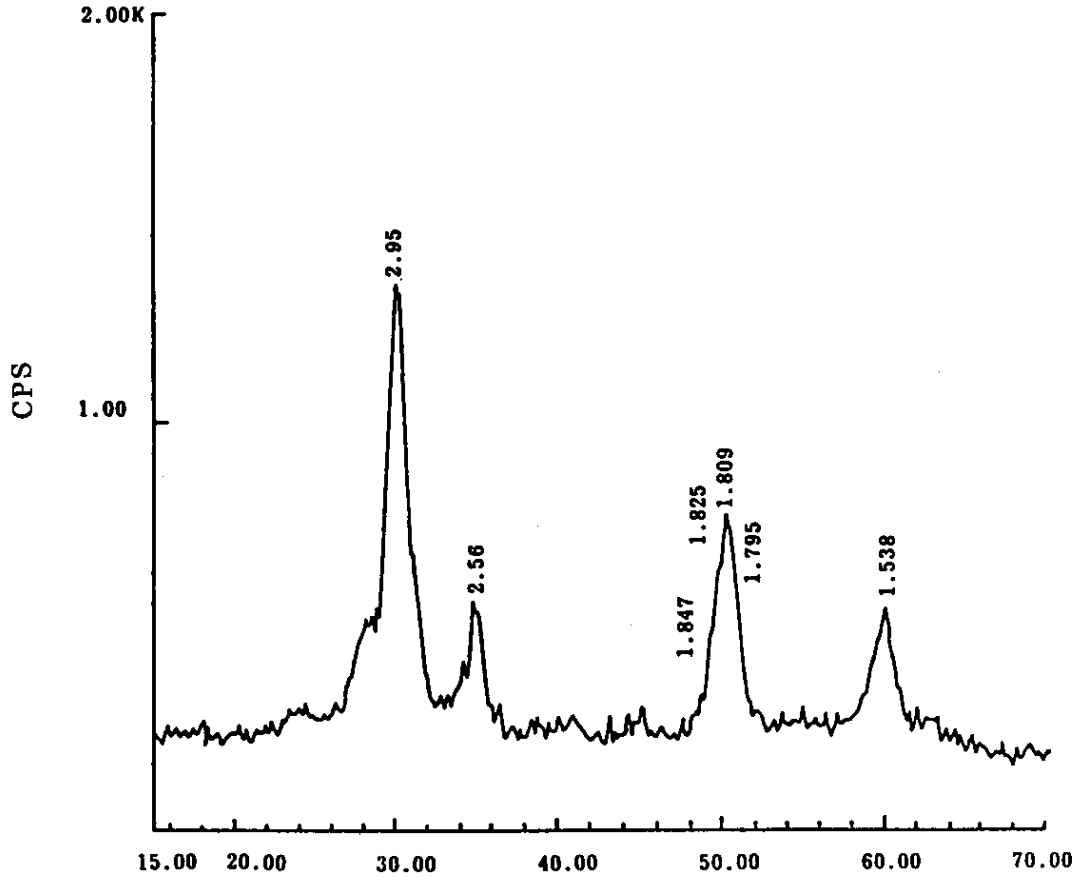

Fig. 8: X-ray diffraction pattern of "as synthesised" sample of MgO-ZrO_2 ceramic powder.

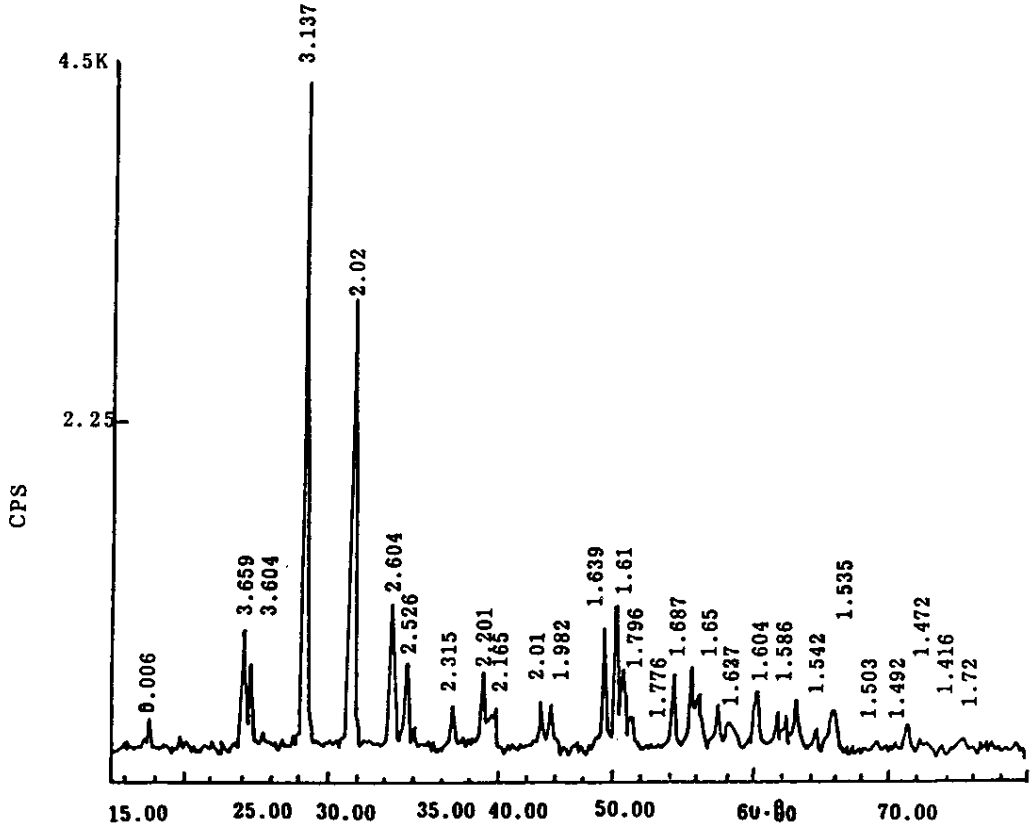

Fig. 9: X-ray diffraction pattern of calcined (8 hours at 1200°C) sample of $MgO\text{-}ZrO_2$ ceramic powder.

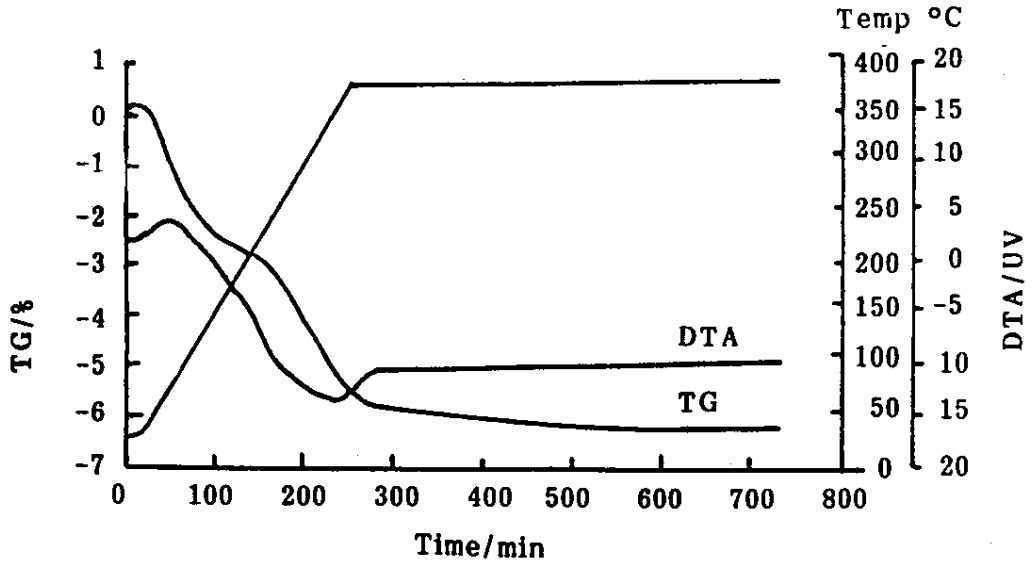

Fig. 10: Simultaneous thermal analysis (TG-DTA) of magnesia partially stabilized zirconia binded with polyvinyl alcohol.

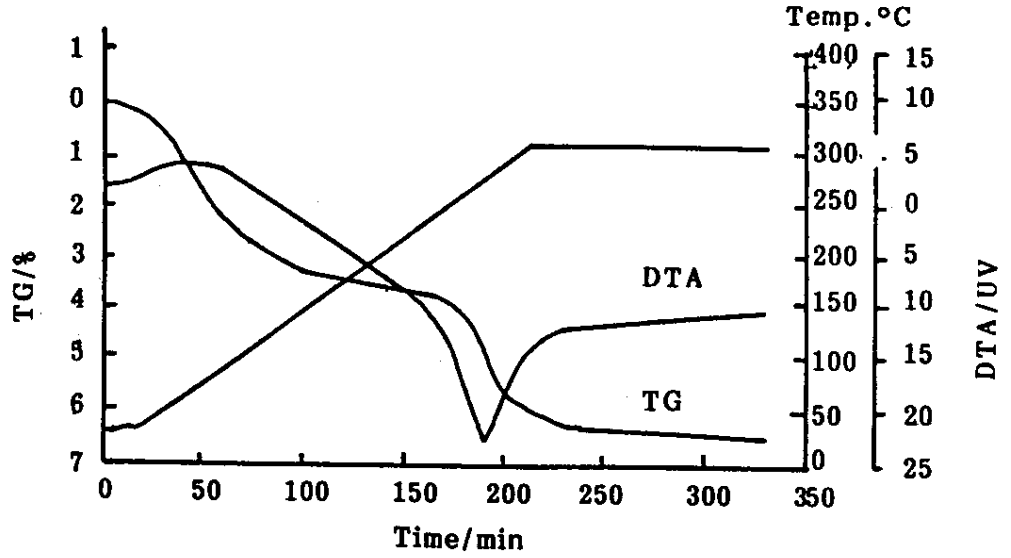

Fig. 11: Simultaneous thermal analysis (TG-DTA) of magnesia partially stabilized zirconia binded with methylcellulose.

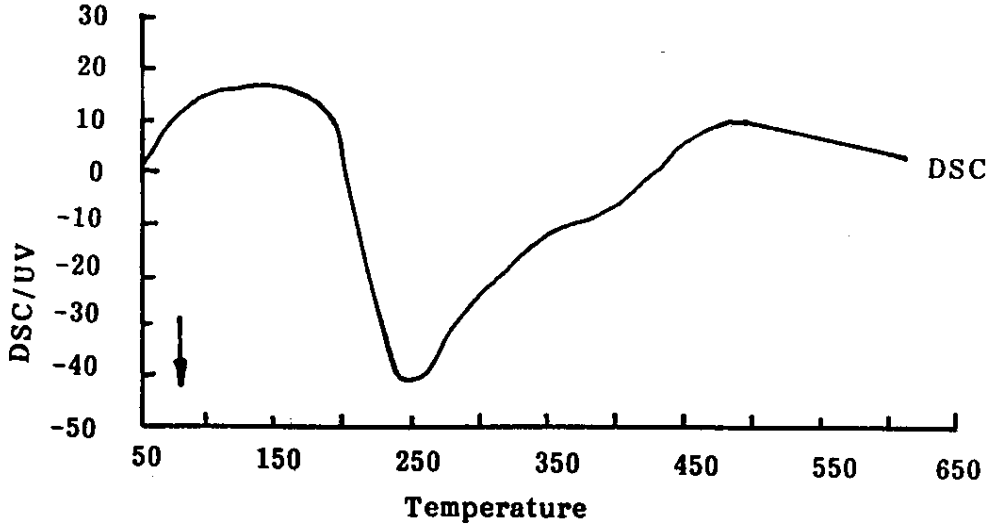

Fig. 12: Differential scanning calorimeteric (DSC) analysis of magnesia partially stabilized zirconia binded with polyvinyl alcohol.

~5.61 and 5.52% centred around 80°C, represent the removal of physically adsorbed water for MC and PVA respectively. The second, at 250°C represents the dehydroxylation reaction and pyrolysis degradation of organics and an additional weight loss of ~72% was observed. Above 350°C further oxidative degradation, producing 99 to 100% weight loss took place indicating combustion of the carbon residues to carbon dioxide. DTA curves for MC and PVA has one main endothermic effect, at 283°C and 265°C respectively, corresponding the total weight loss on TG i.e., 5.78% for MC and 5.67% for PVA. The results were found to be similar with literature data [23]. The DSC traces of MgO-ZrO_2 ceramic using PVA and MC as binder materials are shown in Figures 12-13. It was observed that the endothermic peaks, which commenced at 176-344°C and T_{max} = 248°C

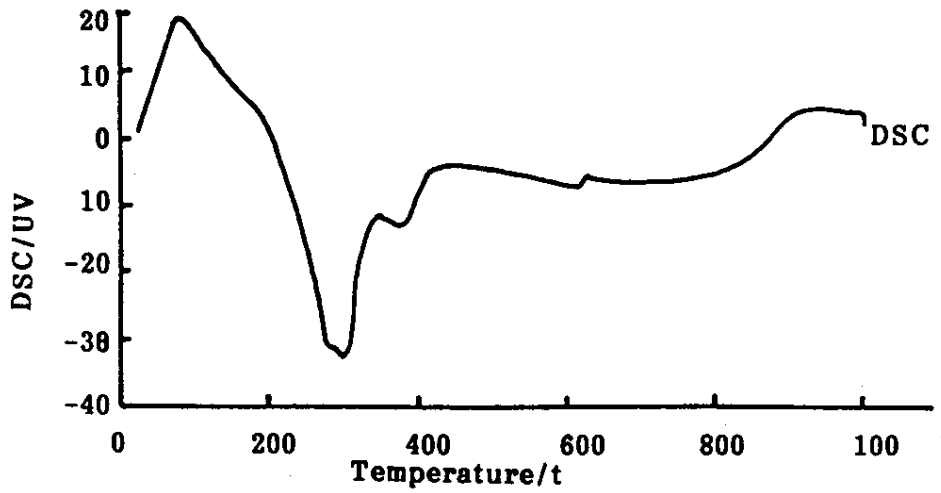

Fig. 13: Differential scanning calorimeteric (DSC) analysis of magnesia partially stabilized zirconia binded with methylcellulose.

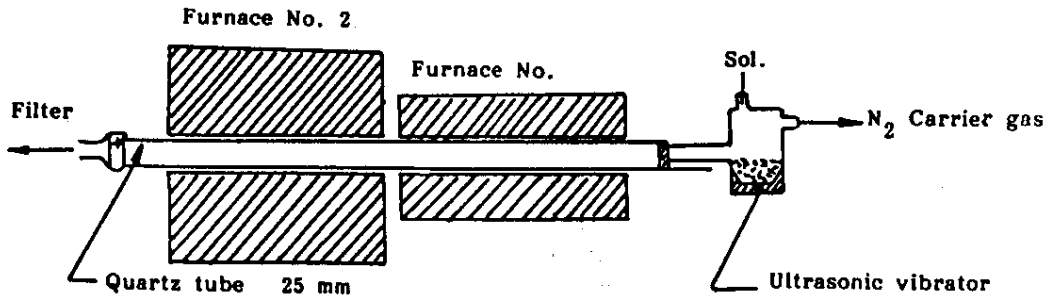

Fig. 14: Schematic diagram of the apparatus for spray pyrolysis.

for PVA and at 229-342°C with T_{max} = 300°C for MC corresponded to the tightly bound water loss and desorption of organic materials. This endothermic peaks were due to the thermal decomposition of the organic as shown on the TG-DTA trace. The Table-3 showed the calculated values of ΔH for the polyvinyl alcohol and methylcellulose polymers.

Experimental

Powder synthesis

Preparation of spherical fine zirconia has been described somewhere else [24]. In a typical preparation of 9mol% magnesia doped zirconia ($MgO-ZrO_2$), 1 M $ZrO(NO_3)_2$ solution was autoclaved in a teflon lined stainless steel autoclave for 5 hrs at 200°C. The resulting slurry was centrifuged and the clear supernate was poured off. Distilled water was added to the cake to produce a ~ 1.5 M slurry. The later was centrifuged, and slightly cloudy supernate was decanted. The milky-white sol was obtained by the addition of more water. A calculated amount of magnesium nitrate was added to get the magnesia doped zirconia milky-white gel, which was put in the ultrasonic nebulizer (Heyer, ORION-I Germany) to produce small droplets of uniform size. The droplets were first introduced into the furnace-1 heated at 400°C and then passed into the next furnce (Figure 14) maintained at 700°C in nitrogen medium (flow rate of 4.0 $L.min^{-1}$). Magnesia doped zirconia powder was collected on filter paper and calcined at 900°C for 1 hr.

Fabrication of sintered ceramic

The green pellets (dia = 18 mm, thickness = 3.1 mm) of calcined powder of $MgO-ZrO_2$ was

prepared by uniaxial pressing (23 MPa) using the MC and PVA polymers as binders (2 to 7.5% w/w). PVA was dissolved in hot water whereas MC in cold water prior to ceramic powder mixing for uniform distribution of binder. The green pellets were sintered at 1200°C for 5 hrs in a resistance heating tube furnace.

Physico-chemical analysis

The elemental analysis of ZrO_2 and MgO-ZrO_2 samples were quantitatively performed by Inductive Coupled Plasma (ICP) emission technique using the ARL 3580 ICP-OES. Brunauer-Emmett-Tellet (BET) [25] specific surface area determinations were carried out using Quantasorb Sorption System (Quantachrom, USA). Crystallinity of ZrO_2 and MgO-ZrO_2 were determined by XRD on a Rigaku Geigerflux instrument using Cukα radiation. The step-scans were performed with a step size of 0.5° (2θ), the time of counting at each step was 10 seconds. The scanning range was 25-130° (2θ). The morphology of samples was observed using a JEOL JSM-35CF scanning electron microscope. The porosity and bulk density were examined by Hg-porosimetry using the Penetrometer 08-0709. The particle size and particle size distribution were measured by means of a laser particle sizer (SK-Laser Micron PRO-7000S, USA). Isothermal shrinkage experiments were performed on computer-controlled dilatometer. The burn-out temperature and enthalpy (ΔH) of methylcellulose and polyvinyl alcohol polymers occluded in the sintered MgO-ZrO_2 were studied using a Netzsch DSC-404 microcalorimeter in air at flow rate of 200 ml min^{-1} and the heating rate was 10°C min^{-1}. Weight of the sample was 50 mg for DSC and TG/DTA. Combined TG-DTA analysis was performed using a Netzsch STA-409 thermoanalyzer.

Conclusions

Spray pyrolysis technique can produce quite dense, fine spherical zirconia and magnesia doped zirconia ceramic powder (diameter of ~0.2mm) from the zirconium sol and magnesium nitrate mixture. The synthesized powder of zirconia and magnesia doped zirconia can be sintered into uniform and fine grained ceramic at quite lower temperature than the required sintering temperature. Polyvinyl alcohol and methylcellulose polymers were found good binder materials for zirconia and magnesia doped zirconia ceramic powders.

Acknowledgement

Thanks are due to PINSTECH Scientists/Engineers Mr. Khalid Saeed for XRD, Mr. Nazar Hussain and Mr. Mohammad Arif for TG/DSC, Mr. Waqar Ahmed for SEM and Dr. Bashir Mohammad for the chemical analysis work.

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