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Properties of magnesia-stabilized zirconia powders prepared by a combustion route

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Zirconia is known [1] to undergo a series of destructive phase changes as follows:

$$\text{monoclinic} \xleftrightarrow{950-1150\,^{\circ}\text{C}} \text{tetragonal} \xleftrightarrow{2370\,^{\circ}\text{C}} \text{cubic}$$

The monoclinic-to-tetragonal phase transformation is likely to be martensitic in nature, and it has generated great interest since it contributes to the toughening of ceramics [2]. In stress-induced phase transformations [3], metastable tetragonal (t) zirconia can transform spontaneously into monoclinic (m) zirconia by absorbing fracture stresses. Retention of metastable tetragonal zirconia is accomplished either by altering the chemistry (adding CeO_2, Y_2O_3, MgO and CaO) [4] or by controlling the particle size (≤ 30 nm) [5]. Stabilization of the high-temperature polymorphs is conventionally achieved [3] by heating a binary mixture in a high-temperature-phase region, equilibrating, and then cooling to room temperature. The inherent problem in ZrO_2–MgO binary systems is the decomposition of tetragonal and cubic (c) zirconia to monoclinic zirconia and magnesia at higher temperatures. The fabrication of high-performance ceramics with high bulk densities and uniform microstructures requires sinteractive powders with spherical shapes, a small size and a narrow size distribution.

During the last decade, attention has focused on the low-temperature synthesis of sinteractive submicrometre zirconia powders with desirable properties using innovative preparative techniques [6–8]. Combustion methods are such a technique, developed in our laboratory and used for the preparation of various oxide materials [9, 10]. This letter describes the preparation and properties of magnesia-stabilized zirconia by a novel combustion method. The process involves combustion of a saturated aqueous solution containing stoichiometric quantities of zirconyl nitrate, magnesium nitrate and carbohydrazide, CH_6N_4O (CH), redox mixtures at 350 °C. The fuel, carbohydrazide ($N_2H_3CON_2H_3$) was prepared by the hydrazinolysis of diethylcarbonate as reported in [11]. Stoichiometric compositions of zirconyl nitrate (ZON), magnesium nitrate (MGN) and CH for combustion were calculated using the total oxidizing and reducing valencies of the components, which serve as the numerical coefficients for stoichiometric balance, so that the equivalence ratio, Φ_e, was unity and the energy released by combustion was a maximum [12]. According to the concepts used in propellant chemistry [12], the total oxidizing valency of ZON and MGN are both -10 (considering $\mathrm{Zr} = +4$, $\mathrm{Mg} = +2$, $\mathrm{O} = -2$ and $\mathrm{N} = 0$). Similarly, the total reducing valency of CH ($\mathrm{C} = +4$, $\mathrm{H} = +1$ and $\mathrm{O} = -2$) becomes $+8$. Therefore, the equivalence ratio, Φ_e, for ZON/MGN:CH was 1:1.25.

Magnesia-stabilized zirconia powders (7, 9 and 14 mol MgO) were obtained by the combustion of aqueous solutions containing stoichiometric amounts of zirconyl nitrate, carbohydrazide and the desired amount of magnesium nitrate in a cylindrical Pyrex dish (vensil, capacity 300 cm^3). The solution when heated rapidly at 350 °C boils, foams and ignites to burn with a flame (temperature 1100 ± 100 °C, as measured by an optical pyrometer) to yield voluminous, foamy, zirconia powders in less than 5 min. The flame persisted for about 1 min. Theoretical equations assuming complete combustion of the redox mixture may be written as:

$$4ZrO(NO_3)_2 + 5CH_6N_4O \xrightarrow{350\,^{\circ}\mathrm{C}} 4ZrO_2(s) + 5CO_2(g) + 15H_2O(g) + 14N_2(g) \quad (1)$$

(with 8.5 mol of gases/ZrO_2). During combustion, magnesium nitrate added to the redox mixture decomposed to MgO and stabilized the high-temperature ZrO_2 phase.

Various phases of combustion-derived ZrO–MgO powders were characterized by powder X-ray diffraction (XRD) (Fig. 1), recorded using a Philips

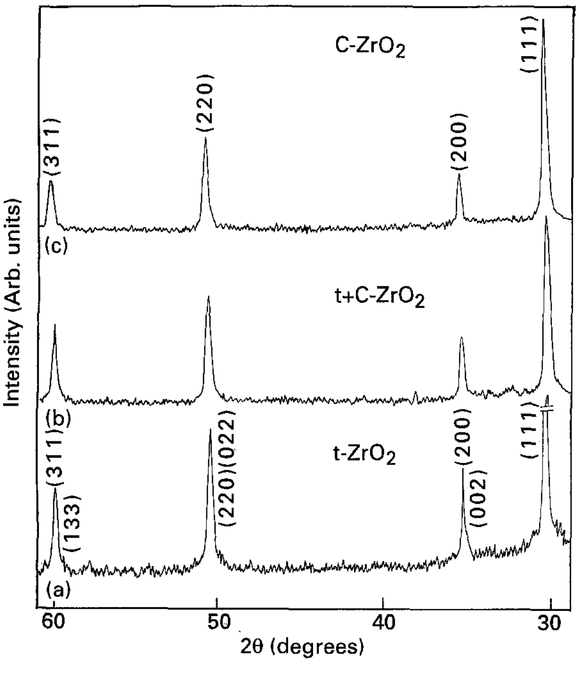

Figure 1 XRD patterns of (as-formed): (a) ZrO_2–7 mol % MgO, (b) ZrO_2–9 mol % MgO, and (c) ZrO_2–14 mol % MgO.

PW 1050/70 X-ray diffractometer with CuK_α radiation and a Ni filter. The combustion residues showed the fully crystalline nature of zirconia powders. On heating, ZrO_2–MgO partitioned into two/three-phase mixtures. As shown in Fig. 2, ZrO_2–7 mol% MgO partitioned into equilibrium phases at higher temperatures, following the sequence t-$ZrO_2 \rightarrow$ t-ZrO_2 + m-ZrO_2 + MgO $\rightarrow$ m-ZrO_2 + MgO. As the calcination temperature increased the concentration of the monoclinic phase also increased. The tetragonal phase disappeared only after the specimen was heated to 1500 °C. This was expected from the ZrO_2–MgO binary equilibrium phase diagram [13]. According to this phase diagram, 4 to 7 mol% of MgO stabilizes the t-phase, 8–12 mol% of MgO stabilizes the partially stabilized zirconia (PSZ, t + c), and more than 13 mol% of MgO stabilizes the cubic-zirconia phase. Thermal decomposition of magnesia-stabilized zirconia to pure MgO and monoclinic zirconia can be represented as:

$$Zr_{(1-x)}Mg_xO_{(2-x)} \rightarrow (1-x)ZrO_2 + x\text{MgO} \qquad (2)$$

The precipitation of MgO in the ZrO_2–MgO binary system could be due to the smaller ionic radius of Mg^{2+} (0.078 nm) compared with Zr^{4+} (0.086 nm) and it could also be due to the lower free energy of m-ZrO_2 and MgO (the most stable equilibrium phase) in the ZrO_2–MgO binary system [7]. The presence of MgO was manifested by a (400) diffraction peak at $2\theta \approx 44.90°$. All three compositions of ZrO_2–MgO showed high-temperature-phase precipitation, indicating the metastable nature of the combustion products. Because of the large temperature gradients and the extremely high heating (unquenched) and cooling rates experienced by the material during combustion, high defect concentrations and non-equilibrium phases are likely to be present in the products [9, 10]. The presence of metastable phases and high defect concentrations facilitates the sinteractivity of the combustion products.

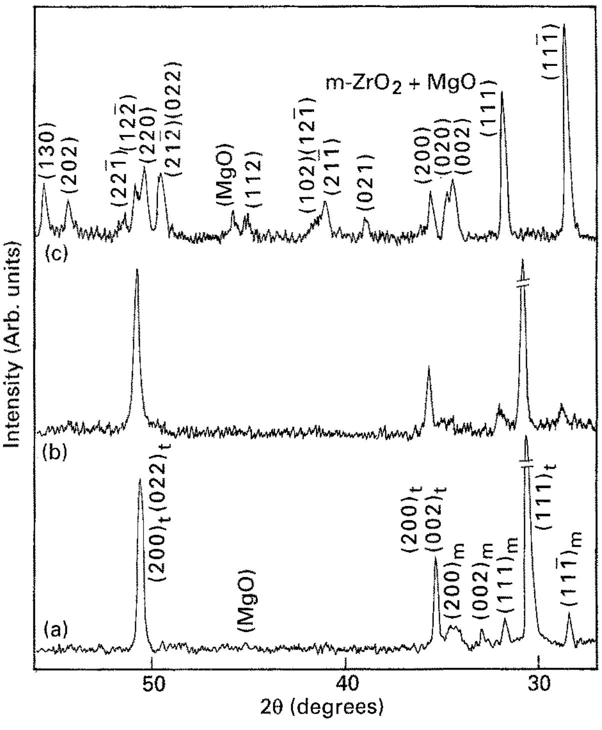

Figure 2 XRD patterns of calcined ZrO_2–7 mol% MgO: (a) 950 °C, (b) 1150 °C, and (c) 1500 °C.

The variation with the calcination temperature of the lattice parameters and the percentage of monoclinic ZrO_2 (calculated using the formula given by Garvie and Nicholson [14]) in ZrO_2–7 mol% MgO are given in Table I. The data reveal that the cell-parameter values decrease as the calcination temperature of the combustion residue increases. With an increase in the calcination temperature, the tetragonality (c/a) initially increases and then it decreases as the percentage of monoclinic-ZrO_2 content increases. The initial increase in tetragonality with temperature may be due to relieving of diffusional constraints at higher temperatures [7]. The sample calcined at 950 °C had 14% of the monoclinic phase, and as the calcination temperature increased the percentage of monoclinic zirconia content increased to 17%.

The properties of ZrO_2–MgO powders are summarized in Table II. The powder densities (measured using a pycnometer with xylene liquid) of ZrO_2 were in the range 50–60% of the theoretical density and the Brunauer–Emmet–Teller (BET) surface areas (determined by using nitrogen as the adsorbate, Model 2100E Accusorb, Micromeritics Instrument Corp., Norcross, GA) were in the range 8–14 $m^2\,g^{-1}$. As the magnesia content in

TABLE I Variation of the lattice parameters of ZrO_2–7 mol% MgO with temperature (for a holding time of 3 h)

Temperature (°C)	Lattice parameter			Monoclinic phase (%)
	a (nm)	c (nm)	c/a	
As-formed	0.51331	0.51558	1.006	–
950	0.50974	0.51420	1.009	14
1150	0.50953	0.51350	1.007	15
1250	0.50935	0.51280	1.006	17

TABLE II Properties of combustion-derived magnesia-stabilized zirconia powders

Number	Material	Phases[a] by XRD	Crystallite size[b] (nm)	Powder density ($kg\,m^{-3}$)	Surface area ($m^2\,g^{-1}$)	Average agglomerate size (μm)
1	ZrO_2–7 mol% MgO	t	29.0	3200	8	1.8
2	ZrO_2–9 mol% MgO	t + c	26.0	3300	10	2.3
3	ZrO_2–14 mol% MgO	c	24.0	3400	14	2.5

[a] t, tetragonal; and c, cubic.

[b] From X-ray-line broadening.

ZrO_2–MgO increased a slight increase in surface area was observed. The average agglomerated particle size (measured using a light-scattering principle by a sedimentation method, Model SKC 2000 Photosizer, Micron) was 1.8 to 3 μm. A typical particle-size distribution (histogram) of ZrO_2–7 mol % MgO is shown in Fig. 3. It can be seen that 50% of the particles are below 2 μm, with an average agglomerate size of 1.8 μm. The crystallite sizes of ZrO_2 (calculated using the Debye–Scherrer formula [15] from the XRD line broadening with a scan speed of 0.5° min^{-1}) were below 300 nm. As the MgO content increased, the crystallite size decreased (more X-ray line broadening) possibly due to the increase in the defect concentration indicating the single-phase $(Zr_{(1-x)}Mg_xO_{(2-x)})$ nature of the combustion residue. The transmission electron microscopy (TEM, model EM 301, Philips Electronic Instruments, Inc., Mahwah, NJ) micrograph of ZrO_2–7 mol % MgO shown in Fig. 4 shows the agglomerated nature of the zirconia particles. Almost all particles have a platelet morphology with roughly a 30.0 nm particle size.

Recently, we reported the preparation of m-ZrO_2 and yttria-stabilized zirconia powders by a combustion method [10]. The yttria-stabilized zirconia powders are highly reactive and sinter at 1250 °C to achieve ≈ 99% of the theoretical density with a fine-grained structure. In magnesia-stabilized zirconia, the phase separation (MgO and m-ZrO_2) at high temperature reduces the densification. Conventionally, ZrO_2–MgO was sintered at a high temperature (1700 °C) and aged below 1100 °C and rapidly cooled to room temperature to retain the tetragonal phase. The cold-pressed-combustion-derived ZrO_2–MgO powder was heated at 1300 °C for 3 h and rapidly cooled to room temperature to achieve more than 98% of the theoretical density (the bulk density of the sintered pellet was measured using Archimedes method) with a fine-grained microstructure. A scanning electron microscopy (SEM, model S-150 Sterocan, Cambridge Physical Sciences, Cambridge, UK) micrograph of sintered ZrO_2–7 mol % MgO is shown in Fig. 5. The sample sintered at 1250 °C for 3 h (Fig. 5a) had a fine-grained nature with prismatic morphology. The pellet sintered at 1300 °C for 3 h revealed the uniform grain growth, with grains less than 2 μm in size, and dense nature (> 98% of the theoretical density) of the sintered body.

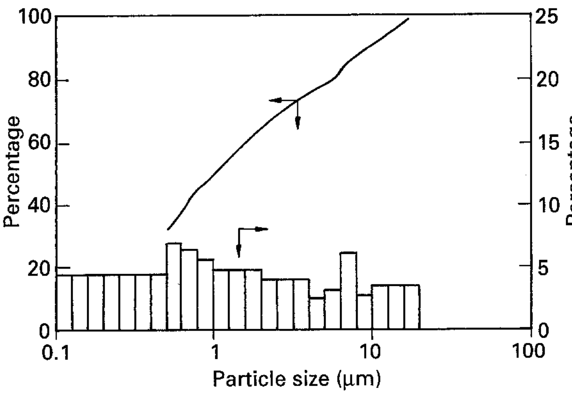

Figure 3 Particle-size distribution curve of ZrO_2–7 mol % MgO (50% average = 1.8 μm).

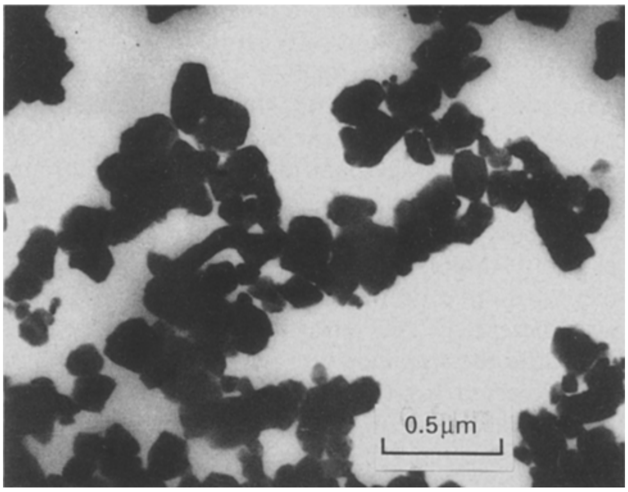

Figure 4 TEM micrograph of ZrO_2–7 mol % MgO.

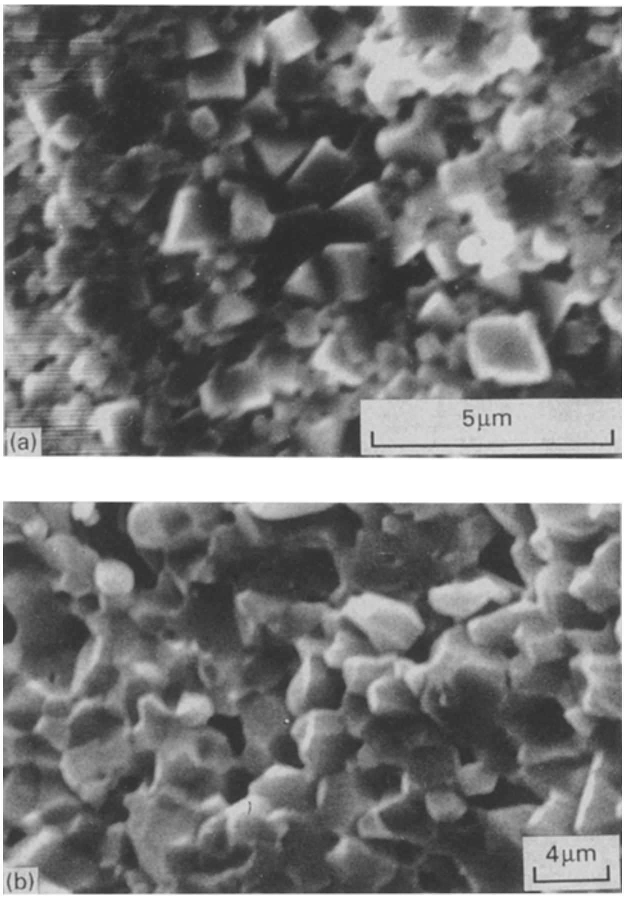

Figure 5 SEM micrographs of ZrO_2–7 mol % MgO sintered at: (a) 1250 °C, and (b) 1300 °C (cleaved surface).

In conclusion, magnesia-stabilized tetragonal zirconia was prepared using a simple, safe and instantaneous combustion process. Calcination of ZrO_2–7 mol % MgO precipitated MgO and m-ZrO_2, indicating the metastable nature of combustion-synthesized ZrO_2–MgO powders. The cold-pressed sample sintered at 1300 °C for 3 h gave a dense body (> 98% of the theoretical density) with a fine-grained morphology.

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