Materials Science-Poland, Vol. 27, No. 2, 2009

Preparation and characterization of yttria stabilized zirconia minispheres by the sol-gel drop generation method

J. JUDES*, V. KAMARAJ

Department of Ceramic Technology, Anna University, Chennai – 600025, India

Near-net-shaped zirconia minispheres were prepared by a novel processing technique based on the sol-gel method. Yttrium was used as a stabilizing agent. Formation of minispheres was achieved in a setting solution by drop generation. The impact of the stabilizing agent on sintering conditions was analysed in detail. The spheres were crystallized into tetragonal phase at 472 °C, and the tetragonal phase was retained up to 900 °C. Maximum theoretical density (97%) was achieved for spheres sintered at 900 °C. Sintering temperatures higher than 900 °C led to the formation of monoclinic phase and reduction in density. The grain size and crystallite size were identified as 0.8 μm and 24 nm, respectively. The phase identification, density variation, chemical decomposition, functional group specification and microstructural features of the dried and sintered final product were also studied

Key words*: sol-gel method; zirconia minispheres; sintering; X-ray diffraction; thermal analysis*

1. Introduction

Ball milling is the most common and effective method for commutation into a range of finer particle sizes. The comminution occurs by compression, impact and shear (friction) between the moving grinding media and the particles. The rate of grinding increases inversely with the radius of the ball. However, grinding media should have high density in addition to uniformity in shape and size, in order to perform the effective particle fracture. The conventional powder compaction method has its limitations in the production of fine milling media, such as the variety of sizes, density and non-uniformity in shape, since slight change in processing parameter leads to structural changes. In order to overcome these limitations, in the present study, a novel processing technique based on the sol-gel method was adapted to produce near-net-shaped prototype zirconia minispheres.

---

*Corresponding author, e-mail: taj_judes@yahoo.com

Among various monolithic ceramics, yttria stabilized tetragonal zirconia polycrystalline ceramics (Y-TZP) have been regarded as a potential structural material. Its unique combination of high strength, fracture toughness and chemical inertness makes it indispensable for a use as milling media [1]. Small grain structure is required to produce a high strength zirconia minispheres that can be obtained by the addition of yttria with 5 mol %, which also sets the crystal structure in tetragonal phase [2]. The stabilization of tetragonal zirconia has been attributed to structural similarity of the larger yttrium ion radius, compared with the zirconium ion radius, and based on the formation of oxygen vacancies resulting from the presence of these trivalent cations [3]. Crystalline structures and catalytic properties of zirconia are generally dependent on the synthesis and thermal treatment. Thus, the sol-gel method was chosen to control the process at the molecular level: it produces nanocrystalline zirconia and also avoids impurities. Various methods had been attempted for preparing spheres, such as drop generation, spray pyrolysis, emulsion evaporation, emulsion water extraction, emulsion ion extraction. Among the above methods, drop generation is found to be very economical and effective. The paper describes the preparation of yttria stabilized zirconia minispheres by the sol-gel drop generation route. The characterization studies reveal the structural and physical properties of yttria stabilized zirconia minispheres.

2. Experimental

Various potential sol precursors were investigated and characterised for the preparation of zirconia minispheres, the optimum being an aqueous sol made from hydrolysed zirconium oxalate ($ZrO(COO)_2$) [4]. The starting material used for the preparation of zirconium oxalate sol was zirconium oxy-chloride octahydrate ($ZrOCl_2\cdot 8H_2O$). 1 M concentration of zirconium-oxy chloride and oxalic acid ($(COOH)_2.2H_2O$) taken in 1: 0.7 vol. ratio to obtain a transparent sol. The stabilizing (sintering) agent yttrium nitrate hexahydrate ($Y(NO_3)_3\cdot 6H_2O$) of 5 mol % was added. The concentration was chosen based on the formation of spheres in the setting solution and the retention of shape after sintering. The formation of zirconium oxalate can be expressed as

$$ZrOCl_2\cdot 8H_2O + (COOH)_2\cdot 2H_2O \rightarrow ZrO(COO)_2 + 2HCl + 10H_2O \qquad (1)$$

The sol thus obtained was kept at room temperature for a very short time to achieve gelation. The viscosity of the gel increases with time. The required viscosity and fluidity were obtained by adding polyvinyl alcohol (PVA) of 35 wt. %. At the suitable viscosity, the mixed sol was added drop by drop to the sphere container (a 500 ml beaker filled with 400 ml of ammonia solution) for the formation of uniform minispheres. The spheres were dried at 40 °C and then sintered in stages from 300 °C to 1500 °C in steps of 200 °C for 5 h at the heating rate of 10 °C/min. Vasylkiv [5] observed that the crystallization stage was shifted to higher temperatures as the heating rate was increased, and a slow heating rate delivers a much better final density of zirconia spheres [5]. In contrast with earlier studies Wang [4] found that the weight loss was almost the same for all heating rates. Zirconium oxalate ($ZrO(COO)_2$) was decomposed to zirconia when the sintering temperature was increased

$$ZrO(COO)_2 \longrightarrow ZrO_2 + CO + CO_2 \tag{2}$$

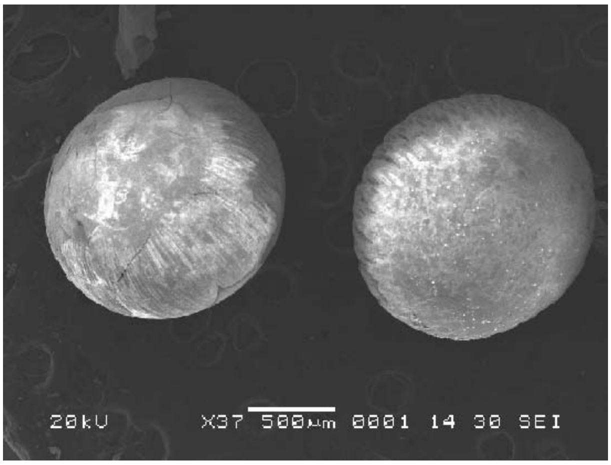

Fig. 1. SEM micrograph of zirconia minispheres sintered at: 1500 °C (left) and 900 °C (right)

Figure 1 shows the SEM micrograph of zirconia spheres sintered at 1500 °C and 900 °C. Microcracks are evident on the surface of spheres sintered at 1500 °C. pH during the sol-gel processing of ZrO_2 had no influence on the thermal stability of t-ZrO_2 product [6].

3. Results and discussion

3.1. Thermal analysis

Thermogravimetric analysis (TGA, Perkin Elmer) and differential thermal analysis (DTA, Netzsch STA409PC) studies (Fig. 2) were carried out to analyse the weight loss and phase transitions of dried spheres (heating rate was 10 $°C\cdot min^{-1}$ in air). TGA shows three major stages of weight losses. The first stage weight loss of around 11.54% up to 150 °C corresponds to the loss due to residual ammonia and dehydration of the samples. The second stage of weight loss of around 6.88% is observed between 150 °C and 230 °C, and corresponds to the release of nitrates. The third weight loss of 12.77% is due to: (i) the decomposition of oxalate with the simultaneous binder removal process; and (ii) the elimination of CO and CO_2 molecules in the 260–428 °C temperature range. The liberation of chlorine may take place at around 512 °C.

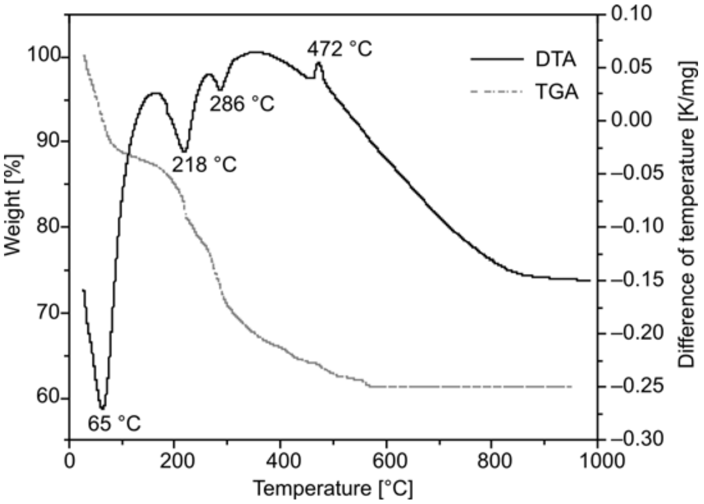

Fig. 2. TGA/DTA curves for the zirconia minispheres dried at 40 °C

A residue weight of 59.13% was found for the spheres sintered at 1500 °C. The porosity details were estimated from the shrinkage data, assuming that there was no further shrinkage above 1500 °C. However, it is quite possible that some porosity remained at this temperature and that these porosity values were underestimated [7, 8]. Variations in percentage weight loss, shrinkage and porosity with the gradual increase in temperature have been studied in detail (Table 1).

Table 1. Weight losses, linear shrinkage, estimated porosities, densities and average crystallite sizes of minispheres with the sintering temperature

Temperature [°C]	Shrinkage [%]	Weight loss [%]	Porosity [%]	Density of sintered spheres [g/cm^{-3}]	Percentage of theoretical density [%]	Average crystallite size [nm]
300	29.79	29.87	67.62	n/a	n/a	n/a
500	38.69	34.32	51.35	5.01	82.13	09.87
700	44.73	37.34	33.63	5.72	93.77	17.32
900	47.99	38.97	20.36	5.89	96.56	24.17
1100	49.01	39.48	15.48	5.85	95.90	30.19
1300	51.33	40.64	2.81	5.82	95.41	49.62
1500	51.79	40.87	~0.0	5.81	95.25	54.32

The DTA showed one exothermic and three distinct endothermic peaks. The endothermic peak around 64 °C is due to the dehydration of the sample and loss of residual ammonia: as observed in the TGA curve. The second endothermic peak around 216 °C is due to the decomposition of nitrate. The endothermic peak around 288 °C is attributed to the decomposition of oxalate. The liberation of chlorides was not observed in the DTA curve, which may be due to smooth release of the same. The exothermic peak around 472 °C is due to the crystallization of zirconia in tetragonal phase, which is connected with the phase change from amorphous zirconia to a metastable tetragonal phase [9, 10]. It is believed that the dopants are uniformly distributed on the pore surface of the zirconyl oxalate gel structure. During sintering, the dopant ions are substituted for zirconium ions in the crystal structure, which favours the formation of tetragonal phase (t phase) and subsequently facilitates transformation toughening. Gradual elevation in the DTA curve beyond 900 °C indicates a possible tetragonal to monoclinic phase transformation.

3.2. X-ray powder diffraction analysis

X-ray diffraction studies (XRD, Philips PW-1730 X-ray unit, CuK$_\alpha$ radiation) were carried out in order to determine the crystal structure and phase identification of spheres sintered in the range 300–1500 °C (Fig. 3).

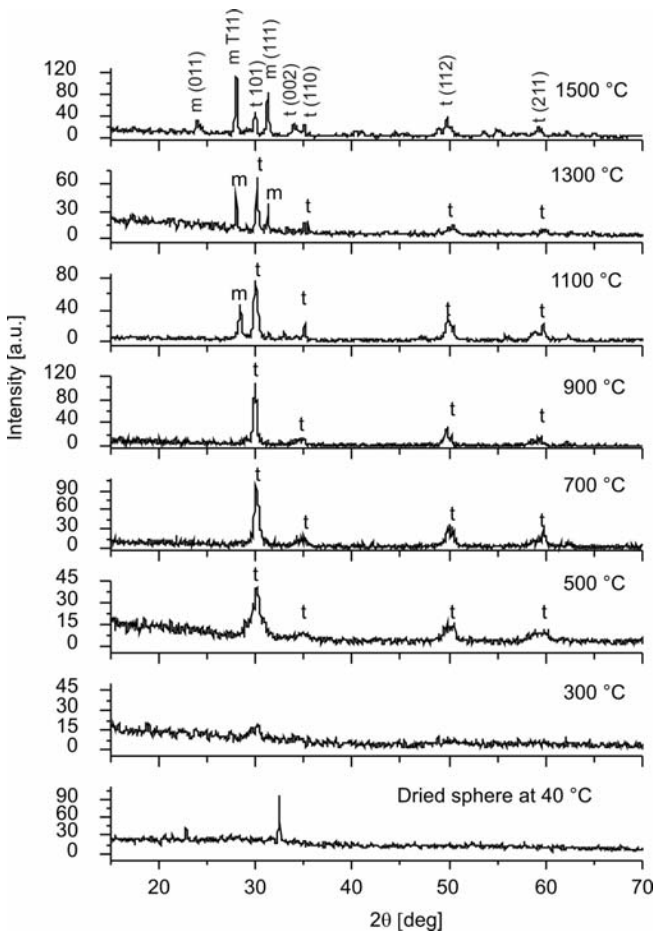

Fig. 3. XRD patterns of zirconia minispheres after heat treatment at various temperatures (t – tetragonal, m – monoclinic)

It was observed that the spheres sintered at 300 °C were amorphous in nature. The metastable zirconia spheres crystallized into tetragonal phase at 470 °C and retained the tetragonal phase up to 900 °C. The intensities of the tetragonal diffraction peaks were found to vary with the sintering temperature. Transformation toughening depends directly on the t phase content and therefore materials containing 100% of the tetragonal phase can be extremely tough. The role of stabilization of the t phase of zirconia by yttrium ions shows that the presence of these ions reduce the overcrowding of the oxygen around the zirconium ions, and hence relieve the strain energy associated with it. On further rise in temperature, tetragonal to monoclinic phase transformation occurs at 1100 °C. The fraction of monoclinic phase (m-ZrO_2) in zirconia is only 0.29 at 1300 °C. Srinivasan et al. observed that the tetragonal phase forms first from the amorphous phase and that the tetragonal crystals grow subsequently [11–13]. The sphere sintered at 1500 °C is dominated by the monoclinic phase with 0.41 fractions. The decrease in the t-phase content on increase of sintering temperature may indicate the sluggishness of the diffusion of yttria into zirconia.

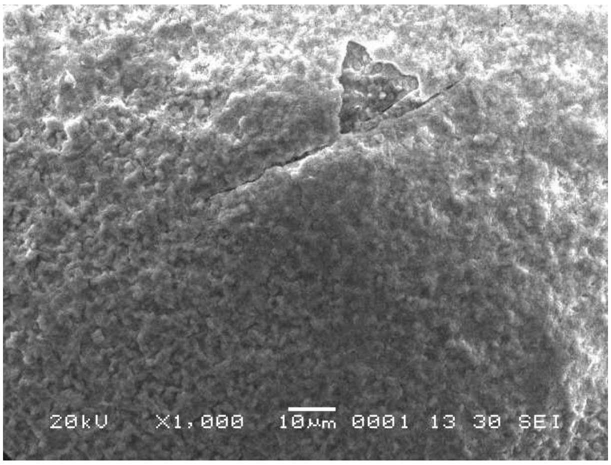

Fig. 4. SEM micrograph of zirconia minispheres sintered at 1500 ° C with a microcrack

From the earlier investigations [14, 15], it is evident that partially stabilized zirconia with a mixture of m and t phases was observed for the compositions with up to 11 mol % of yttria, even for firing temperatures of up to 1500 °C. The t-phase in yttria stabilized spheres is metastable and might be due to compressive stress developed during sintering. When the tetragonal material reverts back to the monoclinic phase, the transformation results in microcracking which weakens the strength of spheres [16]. The microcrack is evident from the SEM micrograph (Fig. 4) of yttria stabilized zirconia spheres sintered at 1500 °C. The grain size is found to be around 1.4 µm from the microstructural evidence. It has been observed that the average grain size increases from 0.8 to 1.4 µm with an increase in the sintering temperature from 900 °C to

1500 °C. This influences the internal tensile stress produced, due to the thermal expansion of zirconia. When the grain size is above the critical level, the internal stress is equal to the stress required for transformation. Thus, zirconia grain growth and the internal tensile stress are responsible for tetragonal to monoclinic transformation at temperatures above 900 °C. The average crystallite size of 5 mol % yttria stabilized zirconia minispheres is determined by the diffraction line, using the Scherer and Warren equation [17]. The crystallite size increases from 10 to 54 nm when the sintering temperature is increased from 500 °C to 1500 °C (Table 1). The increased crystallite size of zirconia spheres is evident in the XRD spectrum by the decrease in width of the dominant tetragonal spectral lines. It was found that the reduction of the crystallite size to the nanometre regime can result in the stabilization of high-temperature phases.

3.3. FTIR characterization

The vibrational frequencies of all possible functional groups for the minispheres dried at 40 °C in the region 4000–400 cm^{-1} were studied by considering the FTIR spectrum (Fig. 5).

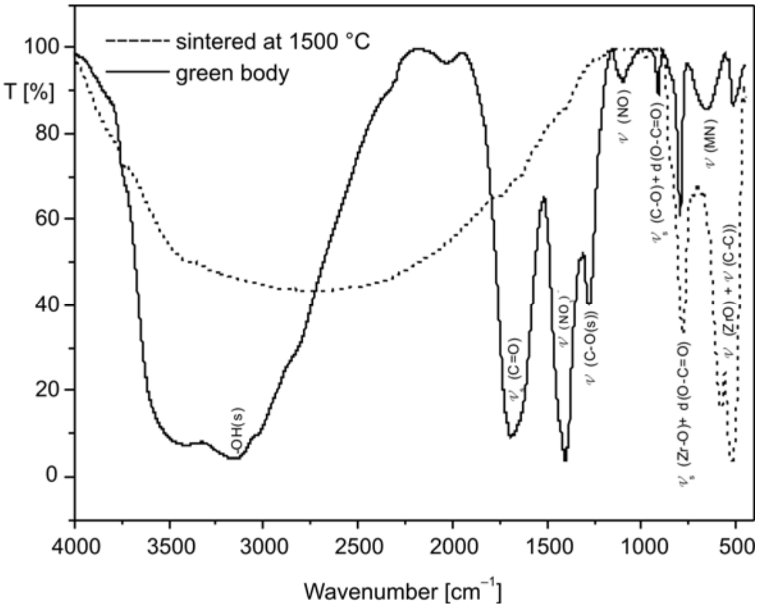

Fig. 5. FTIR spectrum of zirconia minispheres dried (40 °C) and sintered (1500 °C)

The peaks at 795 cm^{-1} and 517 cm^{-1} are prominent, which confirms the presence of Zr–O vibration. The appearance of the peak at 1402 cm^{-1} illustrates the presence of nitrates in the dried oxalate spheres. The peak at 3152 cm^{-1} shows the presence of OH stretching mode. The peaks at 910 cm^{-1}, 1096 cm^{-1}, 1279 cm^{-1} and 1689 cm^{-1} are related to the volatile compounds (O–C=O, NO, C–O and C=O groups). It has been reported that the oxalate ion has a quadridentate structure with the zirconium ion [18]. It is clear that the addition of yttrium ions does not affect the structure of the zirconyl oxalate. The results obtained in the present study are in good agreement with the results of previous reports [19, 20].

3.4. Density measurements

The density of spheres was determined by using a specific gravity bottle. The density variations with the sintering temperature are listed in Table 1. The theoretical density (TD) is calculated according to the theory of Ingel and Lewis [21]. The density of spheres increases with the sintering temperature. It reaches a maximum value of 5.89 gm/cm^3 (TD = 96.56%) for spheres sintered at 900 °C. On further increase in sintering temperature, the density of the spheres is found to be reduced, which may be due to the volume expansion that takes place during the phase transformation, from tetragonal to monoclinic phase, as well as the formation of microcracks.

4. Conclusion

Sol-gel derived yttria stabilized zirconia minispheres were successfully fabricated by the drop generation method. Formation of zirconium oxalate sol has been shown to be a good starting route for the preparation of yttria stabilized zirconia minispheres. Amorphous phase exists below 300 °C and the tetragonal phase is formed at 470 °C. The ideal sintering temperature for the production of sol-gel derived yttria doped zirconia minispheres was identified as 900 °C, which has the fully stabilized tetragonal phase with 97% of theoretical density. The minimum composition required for the fully tetragonal microstructure clearly depends on the sintering temperature and the grain size produced. Further increase in the sintering temperature above 900 °C leads to the phase transformation and a reduction in density. The presence and periodic removal of volatile compounds were observed by DTA and thermogravimetric analysis, which was confirmed by FTIR studies. Zirconia minispheres were extensively characterised in order to establish a correlation between physical and structural properties with the sintering temperature.

References

[1] RUIZ L., READEY M.J., J. Am. Ceram. Soc., 79 (1996), 2331.

[2] SETTU T., *Studies on preparation and characterization of tetragonal zirconia polycrystals by sol-gel method*, Ph. D. Thesis, Anna University, Chennai, India, 1995.

[3] PANDOFELLI V.C., RODRIGUES J.A., STEVENS R., J. Mater. Sci., 26 (1991), 5327.

[4] WANG J.A., VALENZUELA M.A., Catalysis Today, 68 (2001), 21.

[5] VASYLKIV O., SAKKA Y., J. Am. Ceram. Soc., 83 (2000), 2196.

[6] WANG H.C., LIN K.L., J. Mater. Sci., 26 (1991), 2501.

[7] PULLAR R.C., TAYLOR M.D., BHATTACHARYA A.K., J. Eur. Ceram. Soc., 21 (2001), 19.
[8] FULRATH R.M., PARK J.A., *Ceramic Microstructures*, Wiley, New York, 1968.
[9] KUNDA P., PAL D., SEN S., J. Mater. Sci., 23 (1988), 1539.
[10] MERCERA P.D.L., VAN OMMEN J.G., DOESBURG E.B.M., BURGGRAAF A.J., ROSS J.R.H., Appl. Catal., 57 (1990), 127.
[11] NAUER M., *Microstructure et superplasticite de Zircones Yittriées* These No. 996, Departement des Materiux, Ecole Polytechnique Fédérale de Lausanne, Switzerland, 1992.
[12] SRINIVASAN R., RICE L., DAVIS B.H., J. Am. Ceram. Soc., 73 (1990), 3528.
[13] SRINIVASAN R., DAVIS B.H., CAVIN O.B., HUBBARD R., J. Am. Ceram. Soc., 75 (1992), 1217.
[14] RAMADASS N., MOHAN S.C., RAVINDRA REDDY S., SRINIVASAN R., SAMDANI G., Mater Sci. Eng., 60 (1983), 65.
[15] SCOTT H.G., J. Mater. Sci., 10 (1975), 1527.
[16] GARVIE R.C., HANNINK R.H., PASCOE R.T., Nature, 258 (1975), 703.
[17] DING J., TSUZUKI T., MCCORMICK P. Nanostruct. Mater., 8 (1997), 75.
[18] ETIENNE J., LARBOT A., GRIZRAD C., COT.L., ALARY.I.A., J.Non-Cryst. Solids., 125 (1990), 224.
[19] KHARITONOV Y.Y., ZAITSEV L.M., BOCHKAREW G.S., EVSTAFEVA O.N., Russ. J. Inorg. Chem., 9 (1964), 876.
[20] GANGADEVI T., SUBBA RAO M., NARAYANAN KUTTY T.R., Ind. J. Chem., A19 (1980), 303.
[21] INGEL R.P., LEWIS III D., J. Am. Ceram. Soc., 69(4) (1986), 325.

Received 31 July 2008
Revised 16 November 2008