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Sol–gel processing of alumina–zirconia minispheres

J. Chandradass, M. Balasubramanian*

Department of Metallurgical and Materials Engineering & Composites Technology Center,
Indian Institute of Technology, Madras, Chennai 600036, India

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Abstract

Alumina–zirconia minispheres were prepared by the sol–gel method. The starting material used for the preparation of alumina sol was aluminium-tri-isopropoxide. Zirconia sol was prepared from zirconium oxychloride. Required quantity of zirconia sol was added to alumina sol, so that the final composite contains 5, 10, 15, and 20 wt.% zirconia. A suitable binder was added to the mixed sol and aged at room temperature for some gelation to occur. At the appropriate viscosity, spheres were formed in ammonia solution. The spheres were dried at room temperature and then sintered at 1300 °C for 2 h. X-ray diffraction (XRD) analysis shows the presence of α-Al_2O_3 in alumina spheres and α-Al_2O_3 and t-ZrO_2 in spheres containing 5 wt.% zirconia. Monoclinic ZrO_2 is also present in spheres containing higher amount of ZrO_2. Thermogravimetric analysis indicated the removal of most of the volatile up to 600 °C. Differential thermal analysis shows, that the α-Al_2O_3 phase transformation temperature is higher for sample containing zirconia. Fourier transform infrared spectroscopy (FTIR) indicated the phase transition to α-Al_2O_3 in corroboration with X-ray studies. The density of the sintered spheres was found to be highest for spheres containing 10 wt.% zirconia.

Keywords: A. Sol–gel process; A. Sintering; D. Al_2O_3; D. ZrO_2

1. Introduction

Conventionally ceramic-grinding media was produced using powder compaction method. This has certain limitation on the fabrication of high quality, fine grinding media, since slight change in processing parameter leads to variety of size, density and non-uniformity in shape. In order to overcome this difficulty, sol–gel technique has been developed [1]. Sol–gel method is used for the preparation of gels of various shapes, that is, monoliths, fibers, coating films, spheres, etc. It is well known that the composition of the starting alkoxide solution including the kind of catalyst, water content and presence or absence of any additives and the reaction condition affects the rate of hydrolysis, the rate of condensation, the shape of polymer particles produced in the solution and the state of aggregation of particles, and thus the characteristics of the sols and gels produced in the reaction. The flow property of the sol is important in obtaining information on the structure of sol as well as in making shaped gels [2]. Various methods used for preparing spheres, such as drop generation technique, spray pyrolysis, emulsion evaporation technique, emulsion water extraction, emulsion-ion extraction technique have been developed [3].

The discovery of the stress-induced transformation toughening of zirconia [4] has led to the development of new class of tough ceramics. Among these tough ceramics zirconia toughened alumina is widely studied because of its high strength, toughness, and good stability in humid environment [5–9]. Alumina with dispersed zirconia can be expected to combine the high modulus and strength of alumina with toughening by zirconia particle to give good mechanical property [10]. The present work aims at the preparation of alumina–zirconia spheres by the sol–gel technique and the characterization of spheres.

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* Corresponding author. Tel.: +91 44 2257 8609;
fax: +91 44 2257 0039/0545.
E-mail address: mbala@iitm.ac.in (M. Balasubramanian).

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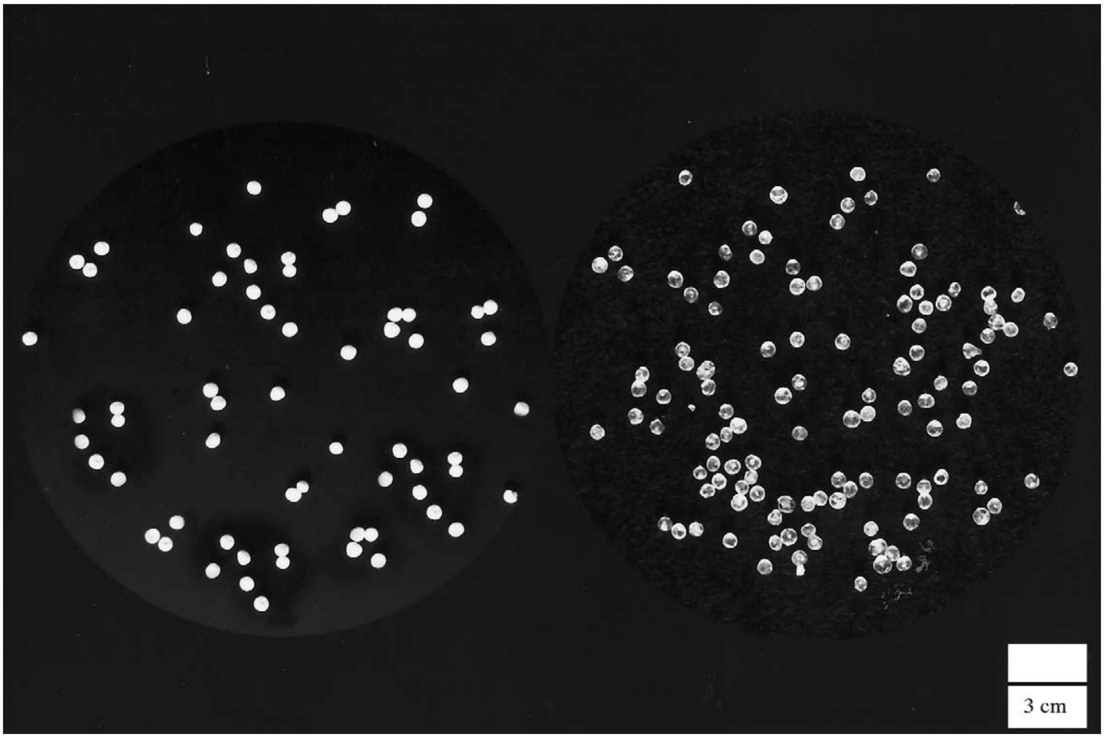

Fig. 1. Photograph of sintered and as-dried alumina–5 wt.% ZrO_2 minispheres.

2. Experimental procedure

Alumina sol was prepared according to the procedure described by Yoldas [11]. Aluminium-tri-isopropoxide (CDH, New Delhi) was dissolved in distilled water to 1M concentration and refluxed at 80 °C for 3 h in the presence of acid catalyst (0.07 mol nitric acid) and then cooled. Zirconium oxychloride (Otto Kemi, Mumbai) was dissolved in distilled water taken in a beaker to 1M concentration.

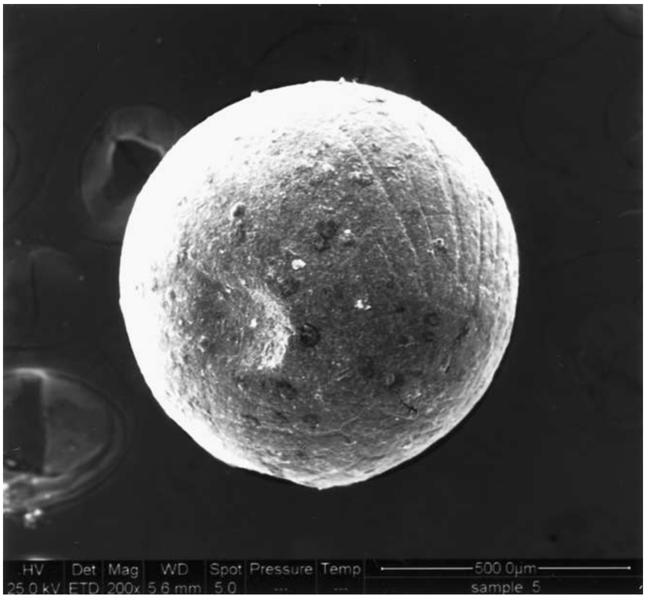

Fig. 2. SEM micrograph of sintered Al_2O_3–5 wt.% ZrO_2.

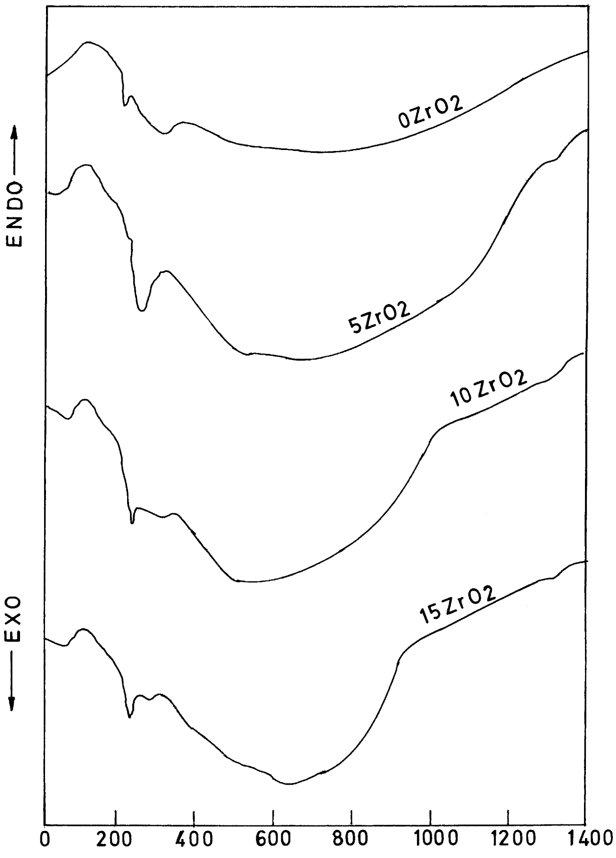

Fig. 3. Differential thermal analysis of alumina and alumina–zirconia minispheres.

Oxalic acid was taken in another beaker and dissolved in distilled water to 1M concentration. Both the solutions were mixed and stirred continuously until the solution becomes transparent [5]. Required amount of zirconia sol (5, 10, 15, or 20 wt.% zirconia in the final composition) was mixed with alumina sol. Polyvinyl alcohol (PVA) was added as binder to the sol to impart green strength and plasticity. Then the mixed sol was kept at room temperature for some gelation to occur. At the appropriate viscosity, the sol was added dropwise to a gelation container (250 ml beaker filled with 150 ml of ammonia solution). Gelation time is very short requiring only 1–2 min. The spheres were immediately transferred into a drying pan and then dried at room temperature for 24 h. After drying, the minispheres had sufficient strength. Minispheres were then sintered at 1300 °C for 2 h with a heating rate of 5 °C/min.

The spheres were characterized using X-ray diffractometer with Cu Kα radiation (SHIMADZU XD-DI), Thermal analyser (NETZSH STA 409PC) and Fourier transform infrared spectrometer by the KBr method (PERKIN-ELMER RXI). Density of spheres was determined using specific gravity bottle.

3. Results and discussions

The ordinary photograph and scanning electron micrograph of sintered Al_2O_3–5 wt.% ZrO_2 spheres are shown in Figs. 1 and 2.

Differential thermal analaysis of alumina minispheres and alumina–zirconia minispheres are shown in Fig. 3. The exothermic peak corresponding to α-phase crystallization was not observed in alumina minispheres. The reason for this is that crystallization takes place at a much lower temperature (the region where thermal change(s) took place due to loss of water), consequently crystallization temperature could not be identified from the respective DTA curve [12]. The exothermic peak was not apparent in alumina–zirconia minispheres, so a first order derivative was taken for 5, 10, and 15 wt.% zirconia curve. It was found that, the α-Al_2O_3 phase crystallization temperature was about 1290 °C, which was higher, compared to the crystallization temperature reported by Yoldas [11]. The reason for this is that,

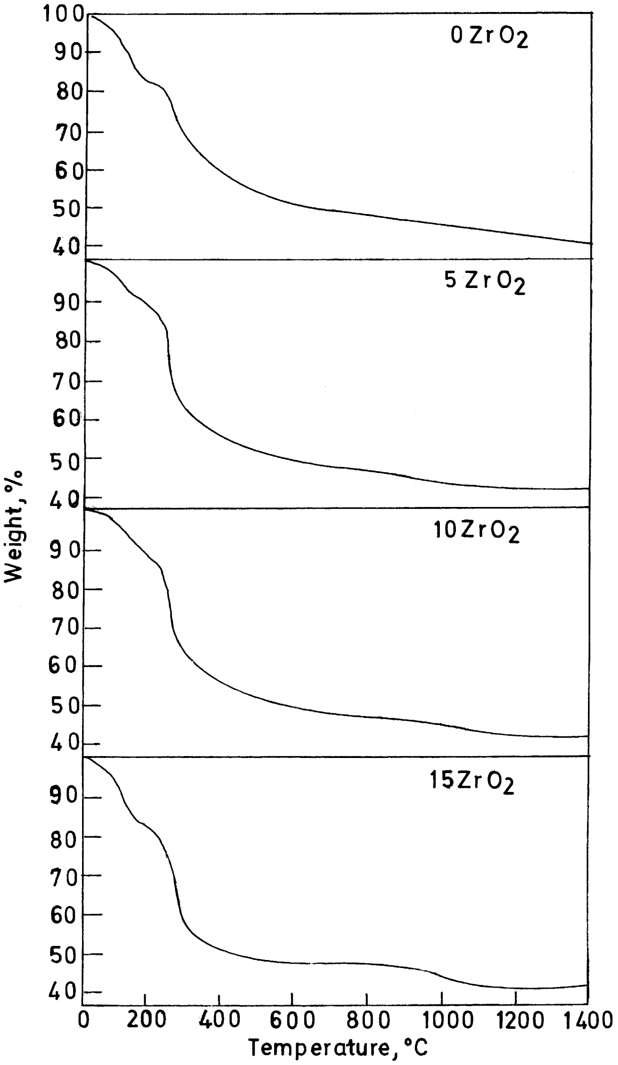

Fig. 4. Thermogravimetric analysis of alumina and alumina–zirconia minispheres.

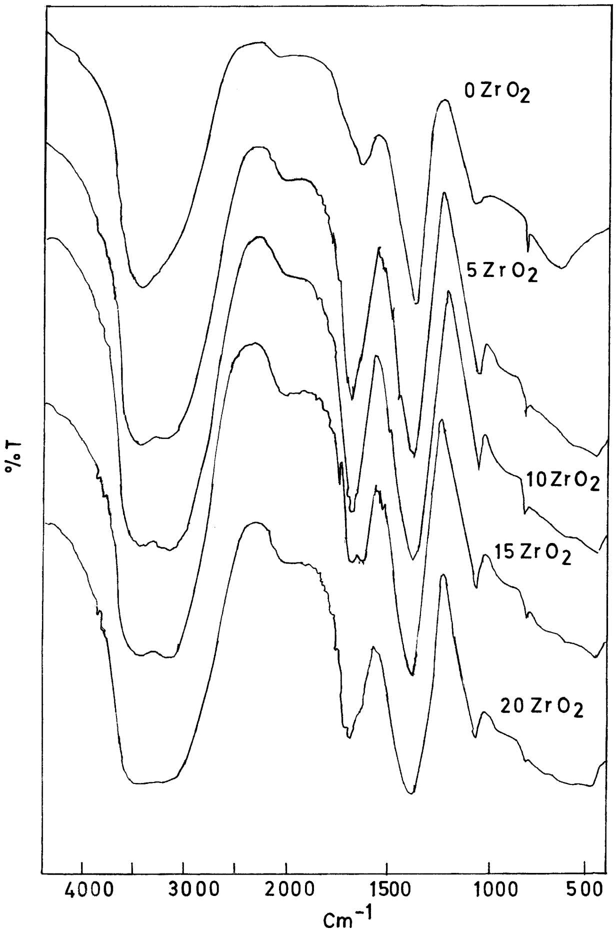

Fig. 5. FTIR curves of as-dried alumina and alumina–zirconia minispheres.

during the transformation to α-Al_2O_3, the zirconium atoms come out of the cubic lattice sites and enter the interstitial and vacant sites causing expansion of the lattice along the *a*-axis. The zirconium atoms probably exert a dragging force on the diffusion of aluminium ions [13,14]. Because of these reasons, the transformation to α-Al_2O_3 occurs at higher temperature in the presence of zirconia.

The TGA curves of alumina and alumina–zirconia minispheres containing 5, 10, and 15 wt.% zirconia show a total weight loss of 58, 57, 58.6, and 58.2%, respectively (Fig. 4). The curve for alumina minispheres and alumina–zirconia spheres shows three stages of weight loss. The first stage corresponds to loss due to adsorbed water. The second stage corresponds to loss due to binder burn out. The third stage may be attributable to loss of structural water (decomposition of structural –OH groups).

Fourier transform infrared spectroscopy (FTIR) analysis was performed for both the gel and oxide minispheres in the wavenumber region 4000–400 cm^{-1}. The spectra of different absorption bands are shown in Fig. 5 for dried minispheres. The absorption due to OH stretching vibration peak is observed around 3480 cm^{-1} [1,15] indicates the presence of molecular water. The absorption band in the region 2066 cm^{-1} [16] indicates the presence hydrogen bonded OH. The absorption band around 1630 cm^{-1} [16] corresponds to OH bending vibration mode confirming the presence of free water. The absorption around 1380 cm^{-1} [1] and 1070 cm^{-1} [5,16] corresponds to Al–OH bending mode. A small absorption band was observed at 827 cm^{-1} [17] corresponds to four coordination of aluminium ions. A broad band around 520 cm^{-1} [18] corresponds to Al–O vibration for alumina spheres and a broad band around 474 cm^{-1} [19] containing 5, 10, 15, and 20 wt.% zirconia corresponds to Zr–O vibration. The spectra of different absorption band for sintered minispheres are shown in Fig. 6. The entire absorption band observed for dried sphere is observed in sintered minispheres also. The absorption band of free water molecule with reduced intensity may be due to the moisture absorption during testing. In addition to that, an absorption band around 620 cm^{-1} [5] is observed, that corresponds to six coordination of aluminium ions and a well-defined characteristic absorption band is observed around 450 cm^{-1} [1] indicates the presence of α-Al_2O_3.

X-ray diffraction patterns of the dried alumina and alumina–zirconia minispheres are shown in Fig. 7. Very broad peaks of the as-dried alumina and alumina–zirconia

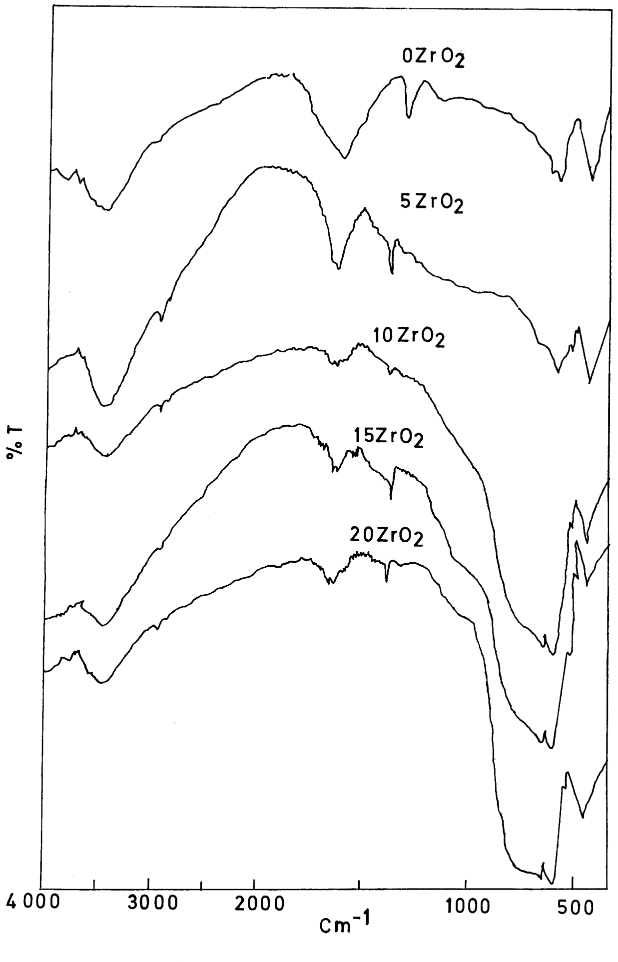

Fig. 6. FTIR curves of sintered alumina and alumina–zirconia minispheres.

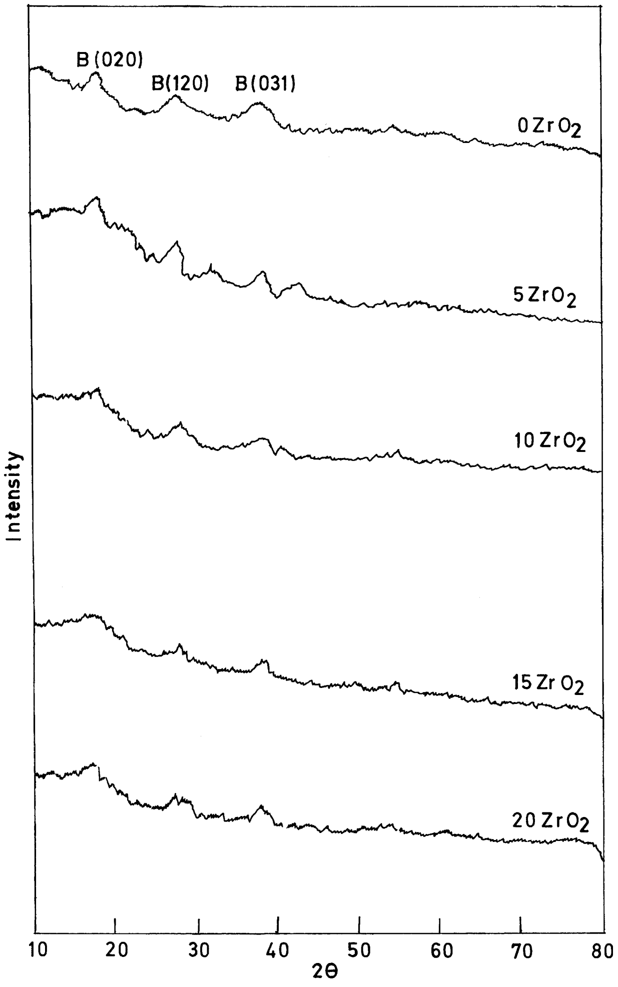

Fig. 7. X-ray diffraction patterns of as-dried alumina and alumina–zirconia minispheres.

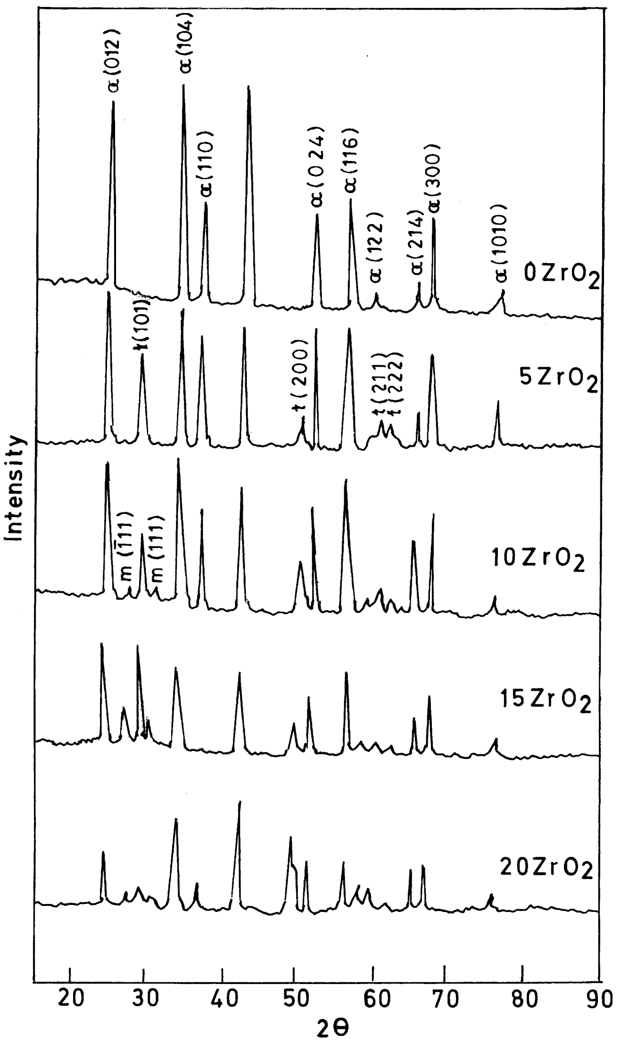

Fig. 8. X-ray diffraction patterns of sintered alumina and alumina–zirconia minispheres.

spheres correspond to γ-AlOOH (boehmite) phase. The boehmite phase changes to α-Al_2O_3 after heating at 1300 °C for 2 h. The phases present in alumina–zirconia spheres containing 5 wt.% zirconia are α-Al_2O_3 and t-ZrO_2, whereas m-ZrO_2 is also present for samples containing 10 wt.% or more zirconia (Fig. 8). Hence, 100% t-ZrO_2 is retained in the sample containing 5 wt.% ZrO_2. It was reported that for lower ZrO_2 contents, the ZrO_2 grain size always lies below the critical diameter [20]. When the Zirconia content is higher, the grain size increases and a part of the t-ZrO_2 is transformed into the monoclinic phase during cooling. Bechler [21] considered that there was critical volume fraction for a given particle size to cause transformation. It is based on the fact that an internal tensile stress is produced due to the thermal expansion mismatch of Al_2O_3 ($\alpha = 8.1 \times 10^{-6}\,K^{-1}$) and ZrO_2 ($\alpha = 10.5 \times 10^{-6}\,K^{-1}$). This internal tensile stress increases with increasing amount of ZrO_2. When the ZrO_2 content is above a critical level, the tensile stress is equal to the stress required for transformation. Thus, ZrO_2 grain growth and the internal tensile stress are responsible for t → m transformation in samples containing 10 wt.% zirconia or higher.

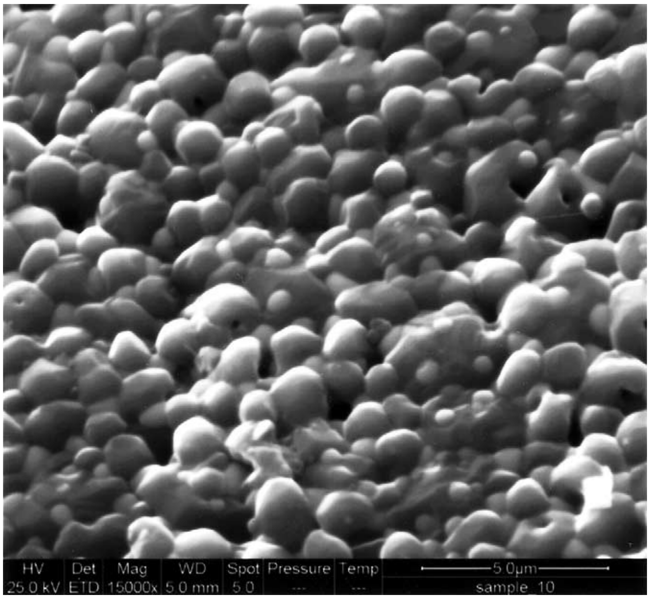

Fig. 9. SEM micrograph of Al_2O_3–10wt.% ZrO_2.

Fig. 9 shows the surface morphology of Al_2O_3–10 wt.% ZrO_2 sphere. The grain size of alumina is about 1–2 μm and the zirconia grains of size 0.6 μm embedded within the alumina grains.

The density measurement results are given in Table 1. The density was found to increase with increase in zirconia content up to 10 wt.% and decreases with zirconia content higher than 10 wt.%. This may be due to the volume expansion that takes place during the transformation from tetragonal to monoclinic and due to the formation of microcracks at higher volume fractions of zirconia.

Table 1
Density of spheres prepared by sol–gel process

Sample	Density of dried sphere (g/cm^3)	Percentage of theoretical density (%)	Density of sintered sphere (g/cm^3)	Percentage of theoretical density (%)
Al_2O_3	1.74	44.6	3.25	83.9
Al_2O_3–5ZrO_2	1.80	44.9	3.47	86.5
Al_2O_3–10ZrO_2	1.86	45.6	3.72	91.0
Al_2O_3–15ZrO_2	1.82	43.8	3.55	85.3
Al_2O_3–20ZrO_2	1.84	44.2	3.63	86.8

4. Conclusions

Formation of alumina and alumina–zirconia minispheres containing (5,10,15, and 20 wt.% zirconia) by sol–gel processing has been achieved. The phases present in sintered spheres are α-Al_2O_3 in alumina sphere, α-Al_2O_3 and t-ZrO_2 in alumina–zirconia sphere containing 5 wt.% zirconia, α-Al_2O_3, t-ZrO_2 and m-ZrO_2 in alumina–zirconia spheres containing more than 5 wt.% zirconia. The density was found to be the highest for Al_2O_3–10wt.% ZrO_2.

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