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Effect of Calcination Temperature on the Alumina-Zirconia Nanostructures Prepared by Combustion Synthesis

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Abstract

In this research, a sol gel autocaombustion route has been proposed to synthesize alumina-zirconia composite powders, using ammonium bicarbonate as a new fuel. Then the effect of calcination temperature on phase transformation and crystallite sizes was investigated. To characterize the products XRD, TEM and BET analyses were used. XRD patterns of as-synthesized powder and calcined powders at 1100 °C and 1200 °C showed $t\text{-}ZrO_2$ phase with small crystallite sizes (<14 nm). As-synthesized powders were also sintered at 1300 °C and the particle sizes after calcination were 14.90 nm and 50 nm for ZrO_2 and Al_2O_3 phases, respectively as calculated from XRD and the transformation of $t\text{-}ZrO_2$ to $m\text{-}ZrO_2$ started at 1300 °C. TEM micrograph of as-synthesized powder revealed nanosize spherical particles of about 8 nm.

1. Introduction

Rapid developments in the micro-structure of basic ceramics have introduced ceramic-ceramic composites for many engineering applications. In particular, according to its good mechanical properties, zirconia toughened alumina (ZTA) has widened the scope of application of oxide ceramics and is effectively used in manufacture of cutting tools, dies or prosthesis components [1].

Sevral methods of preparing ZTA nanocomposite powders have been reported in the literatures such as dry milling [2], or wet milling [3] of the mixture of zirconia and alumina, sol-gel [4] and liquid precursor methods [5]. However, all these techniques are quite involved and need high temperatures and/or long processing times.

Sol-gel combustion is a novel method, with a unique combination of the chemical sol gel process and the combustion process, based on the gelling and subsequent combustion of aqueous solution containing salts of the desired metals (usually nitrates) and fuel, giving a voluminous and fluffy

products with large surface area. This method has the advantages of low processing cost, energy efficiency and high production rate [6].
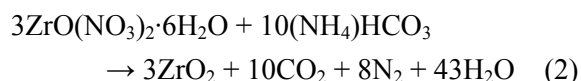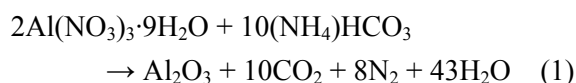
Bae et al. [6] have prepared zirconia dispersed alumina powders in homogenous condition by sol gel autocombustion technique using different fuels (citric acid, acetylaceton, oxalic acid and urea) with particle sizes in the range of 50-95 nm. Bhaduri et al. [7] and Deb et al. [8] have prepared Al_2O_3-ZrO_2 nanopowders by solution combustion synthesis using urea as a fuel and particles with 35 nm and 65 nm sizes were obtained, respectively. They have also studied the phase stability of ZrO_2. Aruna et al. [9] also prepared alumina-zirconia nanocomposite by solution combustion synthesis using mixture of fuels approach (urea, ammonium acetate, ammonium nitrate and glycin). In optimized condition, for 100% urea as fuel, nanopowders with specific surface area of about 2.6 m^2g^{-1} and particle sizes 40 nm (Al_2O_3) and 9 nm (ZrO_2) were obtained and for mixture of fuels (75% urea and 25% ammonium acetate) nanopowders with specific surface area of about 7.7 m^2g^{-1} and particle sizes 34 nm (Al_2O_3) and 9 nm (ZrO_2) were obtained. Thay have also investigated the phase stability of ZrO_2.

Since there is no report on the combustion synthesis of alumina-zirconia nanopowders using mineral fuels, ammonium bicarbonate has been used as a new mineral fuel to produce ZTA nanopowders by sol-gel autocombustion technique and investigate the effect of calcination temperature on crystallite sizes and the phases stability of Al_2O_3 and ZrO_2. Ammonium bicarbonate has lower price compared to often organic fuels and it can be used in combustion synthesis to produce nanomaterials with high surface area because of releasing vigorous enormous amount of gas during combustion reaction.

2. Experimental procedure

Aluminum nitrate nanohydrate $Al(NO_3)_3.9H_2O$ (Merck) and zirconyle nitrate hexahydrate $ZrO(NO_3)_3.6H_2O$ (Sigma-Aldrich) were used as the metallic precursors for the powder. Ammonium bicarbonate $NH_4(HCO_3)$ (Merck) was used as a new mineral fuel, too. The theoretical stoichiometric reactions for the formation of ZTA involved in the present work and the preparation procedure are detailed as follow:

$$2Al(NO_3)_3 \cdot 9H_2O + 10(NH_4)HCO_3$$
$$\rightarrow Al_2O_3 + 10CO_2 + 8N_2 + 43H_2O \quad (1)$$
$$3ZrO(NO_3)_2 \cdot 6H_2O + 10(NH_4)HCO_3$$
$$\rightarrow 3ZrO_2 + 10CO_2 + 8N_2 + 43H_2O \quad (2)$$

Suitable amount of stoichiometric starting materials were dissolved in distilled water separately. The Zr-containing solution was added to the Al-containing solution to produce 20wt.%ZrO_2-Al_2O_3 mixture solution. Then fuel solution was added to the Al-Zr mixture solution and stirred vigorously. By adding the fuel, solution gradually changed to gel. Gel was stirred for 2h and it was aged at room temperature for 2 days, then it dried at 39 °C for 5h and combusted in an electric furnace at 500 °C. The materials underwent foaming followed by decomposition generating large volume of gasses like CO_2, N_2, NO_2 and H_2O. Then spontaneous ignition eccurred and underwent smoldering combustion with enormous swelling producing a foamy and voluminous mass.

The crystallinity and phase identification of the powders were recorded by X-ray diffractometer (D4 Bruker) using Cu Kα as the radiation source and Ni as the filter. The strongest peaks in XRD patterns for ZrO_2 and Al_2O_3 were selected to calculate the cryatallite sizes by the Scherrer

equation (($d = 0.9 \lambda / \beta\cos\theta$) where d; crystal size, λ; wavelength of X-ray, θ; Bragg angle and β; peak broadening). BET surface area and pore size distribution of synthesized powders were determined by nitrogen adsorption at 77 K using BET and BJH methods respectively, by adsorption analyzer (BEL Japan, Inc). Transmission electron microscopy (JEM 2100F) was carried out to determine shape and average size of the particles.

3. Results and discussion

Fig. 1 shows the XRD pattern of the as-synthesized powder. Al_2O_3 was determined as the γ-phase and ZrO_2 as the t-phase. The crystallite size for the two phases were calculated to be 1.9 nm and 7.7 nm for Al_2O_3 and ZrO_2, respectively using the Scherrer equation. These values are lower than those values reported for production of ZTA powders by combustion synthesis using organic fuels and mixture of fuels [1-11]. The production of ZTA powders with crystallite sizes about 5 nm, 4 nm for Al_2O_3 and ZrO_2, respectively has been reported by S.T. Aruna [9] using 75% urea and 25% ammonium acetate as fuel, but in that report, low specific surface area (7.3 m^2g^{-1}) was obtained for ZTA powders.
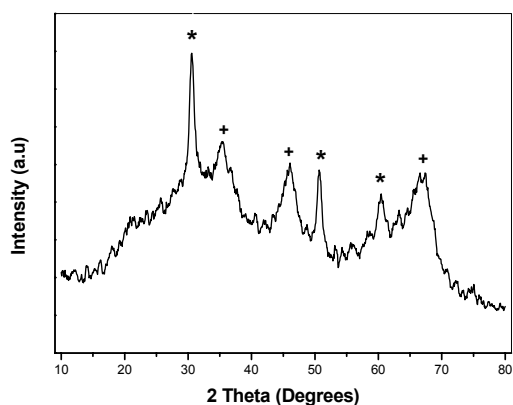

Fig. 1. XRD pattern of the as- synthesized powder **((+)** γ-Al_2O_3; **(*)** t-ZrO_2**)**

In most industries there are actual needs for powders with high surface area. So, the surface area of the as-synthesized powder was calculated according to the Brunnauer-Emmet-Teller (BET) procedure by using the data of adsorption of nitrogen on the sample at 77 K assuming the cross sectional area of o.16 nm^2 for the nitrogen molecules. The surface area, pore size and average pore volume data for sample were found to be 270.54 m^2g^{-1}, 1.6 nm and 0.185 cm^3g^{-1}, respectively. The BET surface area analysis data shows that ammonium bicarbonate as a new mineral fuel has a significant effect on the specific surface area of the products. This specific surface area value is much higher than those values reported for production of ZTA powders by combustion synthesis using organic fuels and mixture of fuels [1,9,10]. In fact, ammonium bicarbonate reduces thermal energy of the combustion reaction and prevents highly agglomeration of particles and increases the specific surface area. The surface area data was utilized to determine the particle size of the powders according to the following equation:

$$D_{BET} = \frac{6}{r * S_{BET}} \qquad (3)$$

Where D_{BET} (nm) is the particle size, S_{BET} is the specific surface area expressed in m^2g^{-1} and ρ is the theoretical density of the powder expressed in g/cm^3 [13]. Assuming the particles to be spherical in nature and the theoretical density of ZTA to be 4.28 gcm^{-3} the calculated particle size was found to be 5.2 nm which is close to the average crystallite sizes of alumina and zirconia in ZTA powders obtained from XRD analysis.

TEM analysis was carried out to determine the accurate particle size of the as-synthesized powder. Fig.2 shows a number of light and dark patches in the nanorange with average particle size of about

8 nm. The zirconia particles are uniformly and homogeneously distributed throughout the matrix as is evident from the micrograph. This result agrees well with the results of BET measurement in which the average particle size was calculated to be 5.2 nm.
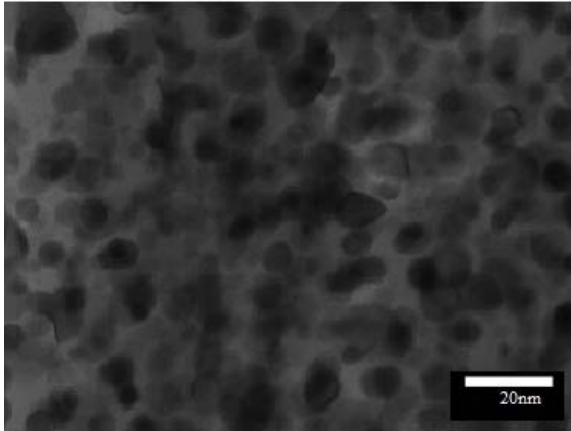

Fig. 2. TEM micrograph of the as-synthesized powder

In order to determine the maximum possible temperature where the nanocrystalline structure is stable, the as-synthesized powders were calcined for 2h at: (ZTA-1) 1100 °C, (ZTA-2) 1200 °C and (ZTA-3) 1300 °C. Fig.3 shows the XRD patterns of the calcined powders. It was observed that the phases present are γ-Al_2O_3 and t-ZrO_2 at 1100 °C. Increasing temperature to 1200 °C leads to retardation of α-Al_2O_3 phase while ZrO_2 is entirely in the tetragonal phase. Usually the tetragonal zirconia undergoes transformation to monoclinic zirconia at 1200 °C. But in case of ZTA-1 and ZTA-2, there was no phase transformation of tetragonal zirconia phase even after calcination at 1250 °C. This indicates that the nanosize alumina particles prevent the tetragonal to monoclinic transformation by matrix constraint and keeps the zirconia particles apart to avoid the growth of t-ZrO_2 [9]. As-synthesized powders were also sintered at 1300 °C for 2h and the transformation of

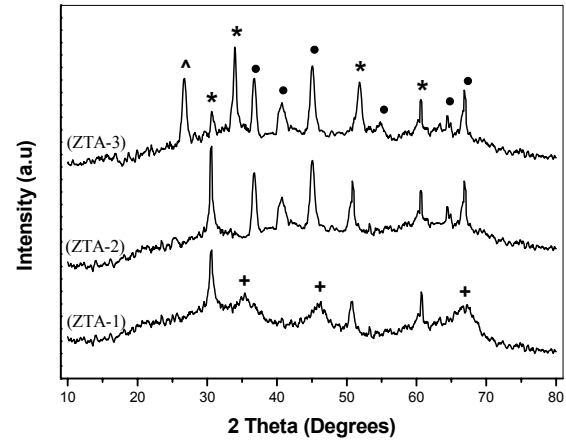tetragonal zirconia to monoclinic zirconia started at this temperature.

Fig. 3. XRD patterns of the calcined powders at: (ZTA-1) 1100 °C; (ZTA-2) 1200 °C; (ZTA-3) 1300 °C (**(+) γ-Al_2O_3; (•) α-Al_2O_3; (*) t-ZrO_2; (^) m-ZrO_2**)

The variation of alumina and zirconia crystallite size with change in calcination temperature is given in Table 1. As it can be seen the crystallite size increases with increasing the calcination temperature and obtained values are smaller than those values reported for production of ZTA powders synthesized by combustion technique using organic fuels and mixture of fuels [7-9].

Table 1. Variation of alumina and zirconia crystallite size with change in calcination temperature

Sample	Crystallite size (nm)	
	Al_2O_3	ZrO_2
ZTA-1	2.5	10.0
ZTA-2	4.7	13.8
ZTA-3	5.0	14.9

4. Conclusion

Sol-gel combustion synthesis has been successfully used to prepare nanostructured zirconia toughened alumina composite using

ammonium bicarbonate as a new mineral fuel and nanopowders obtained with particle size about 8 nm, fine agglomerates and large specific surface area (270.54 m^2g^{-1}). The specific surface area obtained in our study is higher than those values reported for production of ZTA powders by combustion synthesis using organic fuels. Then the effect of calcination temperature on phase transformation and crystallite sizes was investigated. Both alumina and zirconia were nanocrystalline as revealed by TEM and XRD. X-ray diffraction analysis showed that the crystallite size increases with increasing calcination temperature. It also indicated that even after sintering at 1250 $^\circ$C the phases present were α-Al_2O_3 and t-ZrO_2 and the transformation of tetragonal zirconia to monoclinic zirconia started at 1300 $^\circ$C.

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