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Alumina–zirconia–yttria nanocomposites prepared by solution combustion synthesis

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Abstract

Nanostructured zirconia toughened alumina composite has been prepared by solution combustion synthesis. Urea has been used as sacrificial fuel and metal nitrates as precursor reagents. A traditional composition for the final ceramic–ceramic composite has been chosen: 20 vol.% of t-zirconia partially stabilized with 3 mol% of yttria dispersed in alumina matrix. TEM characterization on composite powders as obtained by the combustion synthesis process revealed that nanosized particles of both alumina and zirconia can be obtained with a homogeneous dispersion of zirconia nanoparticles in the alumina matrix. Successively, the behaviour of composite powders during pressureless sintering was evaluated. SEM characterization on sintered body was done thus showing that the nanostructured character and the homogeneous dispersion of zirconia particles obtained by solution combustion synthesis were retained also after the thermal treatments necessary for sintering.

Keywords: A. Powders: chemical preparation; B. Nanocomposites; Combustion synthesis; Alumina–zirconia composite

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].

It is well known that both the fracture toughness and the strength of alumina ceramics are improved significantly by the dispersion of 10–20 vol.% of metastable tetragonal (t) zirconia particles which transform into the stable monoclinic phase (m) under loading. As a crack grows through the ceramic, the zirconia particles in the region of the crack change from t- to m-phase with a martensitic transformation which is accompanied by a volume expansion of 3%. This volume expansion generates compressive stresses in the alumina matrix thus contrasting the opening of the advancing crack and acting as an energy barrier to further crack growth. This is the reason why the retention of t-ZrO_2, until the composite is used for service, has to be considered carefully. To this purpose, the zirconia dispersed into the fine alumina powder may either be pure, un-stabilized ZrO_2 particles or better tetragonal partially stabilized ZrO_2 particles, usually using 3 mol% yttria to partially stabilize the tetragonal phase. In addition to the transformation toughening associated with the t–m transformation around advancing cracks, other mechanisms, such as crack deflection, crack bridging and the presence of microcracks, may also enhance the toughness [2–5].

Several methods of preparing ZTA composites have been reported in the literature such as dry milling [6], or wet milling [7] of the mixture of zirconia and alumina, sol–gel [8], liquid precursor methods [9], etc. However, all these techniques are quite involved and need high temperatures and/or long processing times. On the contrary solution combustion synthesis has emerged as a simple, fast and economically viable method to prepare pure and ultrafine

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powders of more or less complex oxides, solid solutions or composites for a variety of applications. Accordingly, today, this method is being used all over the world to prepare oxide materials with interesting magnetic, dielectric, electrical, mechanical, luminescent and/or optical properties [10,11].

This work is focused on the synthesis of nanostructured ZTA composite powders by solution combustion synthesis and the evaluation of the advantages that this process may introduce. In order to do that, a traditional composition for the final composite has been chosen: 20 vol.% of t-zirconia partially stabilized with 3 mol% of yttria dispersed in alumina matrix. In order to face the complexity of the three-component system, the binary alumina–zirconia and zirconia–yttria mixtures were formerly synthesized for comparison. Special attention was paid to characterize the resulting materials in terms of retention of t-ZrO_2 at room temperature, dispersion of ZrO_2 particles in Al_2O_3 matrix, powder granulometry and morphology as well as sintering behaviour.

2. Experimental

2.1. Solution combustion synthesis

Solution combustion synthesis process involves an aqueous mixture containing suitable metal salts which are the precursors of the final desired oxide and a proper sacrificial organic fuel which acts as reagent reducer. In particular, among salts, hydrate nitrates are generally preferred because their good solubility in water allows to obtain an highly homogeneous solution, while urea seems to be the most convenient fuel to be employed, given that it is cheap and readily available commercially as well as its employment is more safe if compared to carcinogenic hydrazine-based hydrazide fuels. In particular, the starting chemicals used in this study were: aluminium nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$), zirconyl nitrate hexahydrate ($ZrO(NO_3)_2 \cdot 6H_2O$) and yttrium nitrate hexahydrate ($Y(NO_3)_3 \cdot 6H_2O$) from Aldrich and urea ($CO(NH_2)_2$) from Alfa.

Even if combustion synthesis mechanism [12], in terms of occurring reactions, has proved to be very complex because it involves not only fuel-nitrates reaction but also reagent thermal decomposition as well as reactions between decomposition products, the global process may by schematized as complete combustion. The theoretical reactions involved in the present work and the preparation procedure are detailed in the following.

$$2Al(NO_3)_3 \cdot 9H_2O + 5CO(NH_2)_2 \rightarrow Al_2O_3 + 5CO_2 + 8N_2 + 28H_2O \tag{1}$$

$$3ZrO(NO_3)_2 \cdot 6H_2O + 5CO(NH_2)_2 \rightarrow 3ZrO_2 + 5CO_2 + 16N_2 + 28H_2O \tag{2}$$

$$2Y(NO_3)_3 \cdot 6H_2O + 5CO(NH_2)_2 \rightarrow Y_2O_3 + 5CO_2 + 8N_2 + 22H_2O \tag{3}$$

Few minutes stirring on a heating plate are sufficient to ensure proper homogeneity of the aqueous solutions containing the precursor metal nitrates and the fuel. The as prepared solutions are transferred in ceramic dishes, which are placed into an oven preheated and kept at 600 °C. First the aqueous solutions undergo dehydration, then at a certain stage the mixtures froth and swell, until very fast reactions take off and large amount gases is evolved.

The whole process proves to be self-sustaining after the ignition. It is over and the final product is available in a few minutes, but the time between the actual ignition and the end of the reaction is few seconds only. The resulting solid product has a foamy structure and it is very easily crumbled to give a fine powder.

2.2. Characterization

The powders were characterized by X-ray diffraction (XRD) in order to verify their purity and the retention of t-ZrO_2. The average crystallite sizes were estimated using the Scherrer and Warren equation:

$$D_{SW} = \frac{0.9\lambda}{(B^2 - b^2)^{1/2} \cos\theta} \tag{4}$$

where λ is the wavelength of the radiation, θ the Bragg's angle while B and b are the full width at half maximum (FWHM) for the sample and a standard silicon sample, respectively.

The specific surface area of the powders was measured by BET method.

The morphology and the microstructure of the products were examined by means of scanning electron microscopy, energy dispersion spectroscopy (SEM–EDS) and transmission electron microscopy (TEM).

Finally, the powders were wet with isopropilic alcohol, used as a lubricant, and pressed into pellets (approximately 10 mm in diameter and 2 mm thick) in order to evaluate their sintering behaviour. Several sintering processes (starting from 3 h at 1530 °C up to 7 h at 1600 °C) were tested and final bulk density of the sintered samples was measured by Archimede's method.

3. Results and discussion

During the present investigation, binary alumina–zirconia and zirconia–yttria mixtures were firstly considered, as a preliminary step, in order to progressively increase the complexity of the system. In particular 20 vol.% t-ZrO_2–Al_2O_3 (AZ) was produced by solution combustion synthesis starting from a solution containing aluminum nitrate, zirconyl nitrate and urea (according reactions (1) and

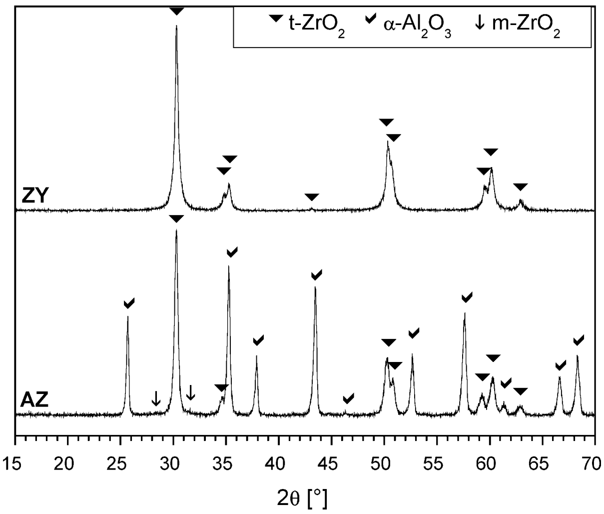

Fig. 1. XRD spectra of preliminary binary mixtures: (AZ) 20 vol.% t-ZrO_2–Al_2O_3 and (ZY) 3 mol% Y_2O_3–ZrO_2.

(2)), as well as 3 mol% Y_2O_3–ZrO_2 (ZY) from a solution containing zirconyl nitrate, yttrium nitrate and urea (according reactions (2) and (3)). As produced AZ and ZY powders as produced were characterized by X-ray diffraction. Their XRD pattern are shown in Fig. 1 and proved the suitability of solution combustion synthesis to contemporary synthesize two different oxides both if the two oxides do not react together and form a mixture (as AZ case) both if one of the two oxides as the role to stabilize a particular phase of the other (as ZY case).

Subsequently the preparation of the AZY composite containing 20 vol.% t-ZrO_2 partially stabilized with 3 mol% Y_2O_3 dispersed in Al_2O_3 matrix was investigated.

Solution combustion synthesis method offers two possibility to produce AZY composite. The first is a two-step process in which, at first, t-ZrO_2 powder is obtained by solution combustion synthesis and then, it is suspended in the solution containing aluminium nitrate and urea thus obtaining a slurry which leads to a second combustion synthesis step. The second method is a one-step process in which combustion synthesis reactions take place directly within a solution containing contemporary aluminum, zirconyl and yttrium nitrates and urea (according reactions (1)–(3)). Both the methods have been tested in this work and the final resulting powders were characterized by X-ray diffraction (see Fig. 2, patterns A and B, respectively). The one-step process seems to be more promising for several reasons. It guarantees a superior homogeneity of the zirconia dispersion in the alumina matrix (as successively confirmed by SEM characterization) if compared to the two-step process, where a slurry is kept in the oven without stirring till the ignition of the exothermal reactions, thus certainly determining a gravitational deposition of suspended zirconia particles. Above all, it allows for a higher retention of t-ZrO_2 at room temperature as shown in Fig. 2 (curve A and B) and it is also a more rapid and simple process.

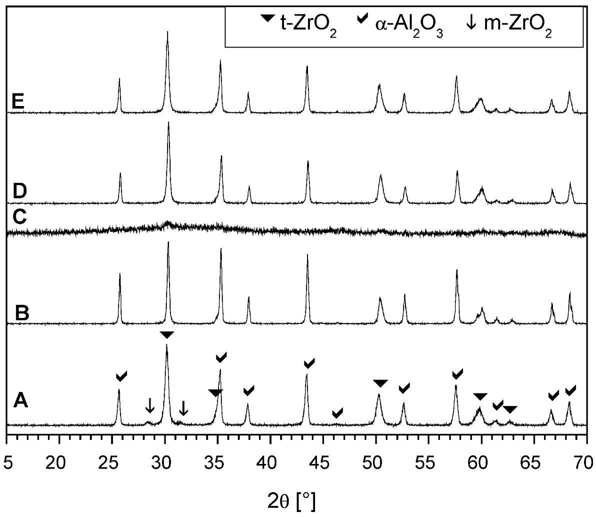

Fig. 2. XRD spectra of Al_2O_3–20 vol.% of t-ZrO_2 partially stabilized with 3 mol% of Y_2O_3 (AZY) composite synthesized: (A) two-step process with stoichiometric fuel; (B) one-step process with stoichiometric fuel; (C) one-step process with fuel-lean mixture; (D) one-step process with stoichiometric fuel-rich mixture and (E) one-step process with stoichiometric fuel and NH_4NO_3.

Then further experiments were performed adopting the one-step process. In particular, the role of the fuel-to-nitrates ratio on the properties of the final product as well as the effect of using ammonium nitrate (NH_4NO_3), in the role of combustion aid, were investigated. Three solutions were prepared using, respectively: a deficiency of urea with respect to reactions (1)–(3) which gives a fuel-to-nitrates ratio equal to 0.5 (fuel-lean mixture), an excess of urea which gives a fuel-to-nitrates ratio equal to 2 (fuel-rich mixture), a stoichiometric amount of urea coupled with one additional gram of NH_4NO_3 per gram of final AZY powder. The powders resulting from combustion synthesis were characterized by X-ray diffraction and the results are shown in Fig. 2, patterns C–E. Specific surface area and crystallite size according Eq. (4) of the five samples of AZY powders are compared in Table 1.

The comparison of powders B, D and E shows that the addition of an excess of urea or ammonium nitrate does not drastically change the properties of the final powder in terms

Table 1

Surface area and crystallite size of AZY composite synthesized: (A) two-step process with stoichiometric fuel; (B) one-step process with stoichiometric fuel; (C) one-step process with fuel-lean mixture; (D) one-step process with fuel-rich mixture and (E) one-step process with stoichiometric fuel and NH_4NO_3

Sample	Surface area (m^2/g)	Crystallite size from XRD (nm)	
		Al_2O_3	t-ZrO_2
A	7.66	30	18
B	3.39	60	33
C	182.94	–	–
D	5.83	44	24
E	5.97	37	19

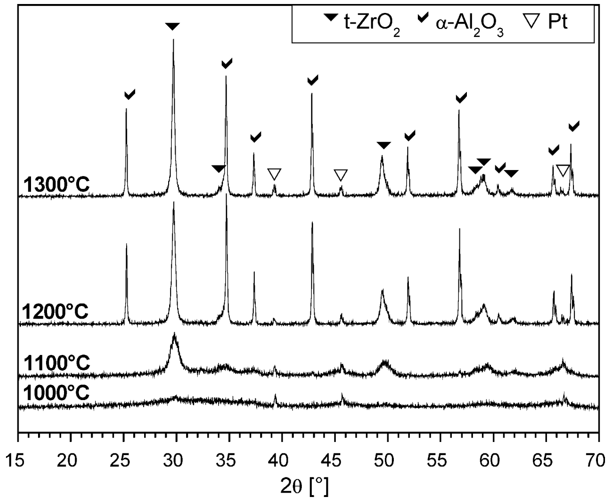

Fig. 3. Crystallization behaviour of powder C: hot stage XRD patterns at increasing temperature.

of crystallization, t-ZrO_2 retention, surface area and particle size. Thus demonstrating that a stoichiometric amount of fuel is sufficient to boost and sustain the reactions up to the completion of the process.

On the contrary the employment of a fuel amount inferior to the stoichiometric one is not sufficient to sustain the crystallization of the product which results amorphous.

Actually a fuel-lean solution reveals to be the most promising way of nanocomposites synthesis because it brings to the formation of powders which exhibit an amorphous character (see C XRD pattern) and a higher surface area (about 180 m^2/g) as well as a finer particle size.

The crystallization behaviour of the amorphous powder was investigated by means of hot stage XRD analyses performed in the range of temperature 500–1300 °C; XRD patterns were collected after conditioning the sample at increasing temperatures (steps of 100 °C). The most significant steps of the crystallization process are summarized in Fig. 3. The t-ZrO_2 phase crystallizes at lower temperature (about 1100 °C), while α-Al_2O_3 is completely crystallized only at about 1200 °C. The transformation to α-Al_2O_3 occurs at higher temperature than usual (1100 °C) in the presence of zirconia [3].

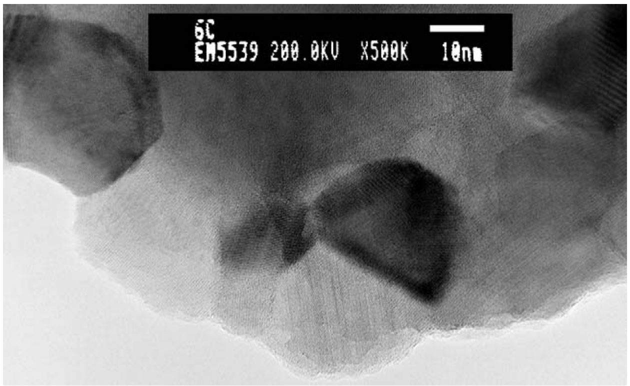

Fig. 5. TEM micrograph showing a detail of an agglomerate.

In Fig. 4A, a TEM micrograph demonstrates that the amorphous powder as obtained from the combustion synthesis process is made of particles which have approximately a mean diameter of 10 nm. At this point was not possible to distinguish between alumina and zirconia particles not even by mapping aluminium and zirconium in the sample. Fig. 4B shows the same powder after a treatment at 1200 °C for 3 h. After the heat treatment it was possible to discriminate between the two phase (zirconia particles are seen as the dark phase while alumina as the bright one) and the good dispersion of zirconia particles in the alumina matrix was confirmed as well as the nanometric size of its particles. It is particularly interesting to observe that if on one hand the permanence of the powder at high temperature determines a partial sintering of alumina particles which are in contact to each other being the prevailing phase, on the other hand alumina particles maintain their identity thus resulting only in a light agglomeration. In Fig. 5, a detail of an agglomerate is presented and it is possible to distinguish the different orientation of crystalline plane belonging to different particles which have a mean size of about 20 nm. As the transformation of zirconia from the tetragonal to the

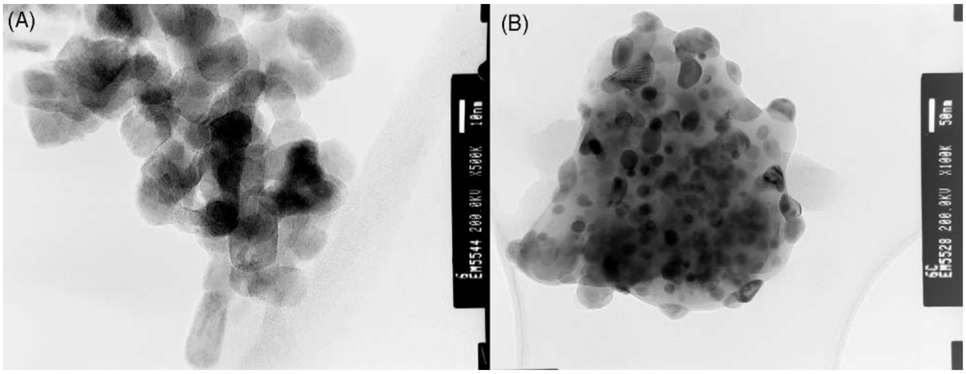

Fig. 4. TEM characterization of powder C: (A) amorphous powder resulting by combustion synthesis and (B) crystalline powder after 3 h at 1200 °C.

monoclinic phase becomes progressively more difficult with the particle size decrease, the fine granulometry obtained suggests the idea that yttria content, used to partially stabilise the tetragonal phase of zirconia, may be reduced. To this purpose future works will be focused on the evaluation of the effect of a progressive reduction of the yttrium nitrate content in the starting solution. The above mentioned agglomerates are characterized by a very irregular overall shape and a certain residual internal porosity.

Successively, the behavior of the five AZY powders during pressureless sintering was evaluated. Even if several sintering treatments were considered, all the five powders exhibits difficulty to reach high densification values (more than 92% of the theoretical density) without using any sintering aid. Probably this behavior may be strictly correlated to the irregular agglomerate shape and their residual internal porosity. Again, the better result, that is the highest density after sintering, was reached when the powder obtained using a fuel lean solution was used. Actually it is an amorphous powder so crystallizing and agglomeration processes have to occur contemporary to the sintering treatment. Probably, just the simultaneity of phase transformations and sintering provides a better opportunity for densification of AZY composite powder. Jayaseelan et al. [3] also observed this behaviour working with alumina–zirconia composites prepared by sol–gel technique.

SEM characterization on sintered body was done thus revealing that the nanostructured character of zirconia particles obtained by solution combustion synthesis was retained also after the thermal treatments necessary for sintering. Since the typical (according secondary electrons detection) SE-SEM observation did not allow to distinguish between alumina and zirconia particles, backscattered electrons (BSE-SEM) analysis were performed on polished samples thermally etched for 30 min at 1450 °C. The results are shown in Fig. 6 where zirconia particles appear as a bright phase, according to the higher atomic number of Zr with respect to Al, while alumina particles appear as a dark phase. Note the uniform and homogeneous distribution of zirconia throughout the alumina matrix as well as the typical intergranular location of the zirconia at the grain boundaries of alumina.

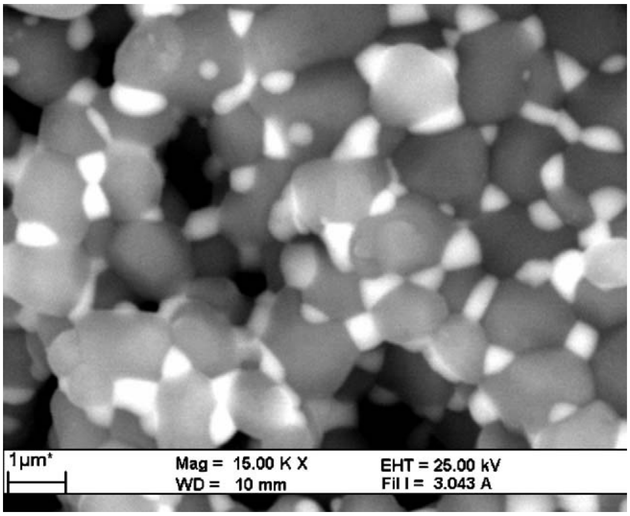

Fig. 6. Backscattered SEM image on a sintered body after polishing and thermal etching (30 min at 1450 °C).

4. Conclusions

Solution combustion synthesis process has been successfully used to prepare nanostructured zirconia toughened alumina composite. The employment of a starting solution with a fuel lean character turns up to be the best opportunity for the synthesis of a nanostructured AZY powder made of particles which have approximately a mean diameter of 10 nm. What is more important, the nanostructured character and the homogeneous dispersion of zirconia particles obtained by solution combustion synthesis were retained also after the thermal treatments necessary for sintering. Works are in progress both in order to improve the densification during the sintering process by means of sintering aid and to assess the more convenient content of yttria used as stabilizer.

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