

Al₂O₃-ZrO₂ nanocomposites produced by solution combustion synthesis followed by ultrasonic milling

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Zirconia toughened alumina materials (ZTA) have been produced by solution combustion synthesis (SCS). SCS has proved to be a rather rapid and simple method to produce nano-structured ceramic oxides powders. Its main drawback is a limited sinterability of the powder due to aggregation of the nanometric grains into larger particles characterized by irregular shapes. It was found out that when coupling the preparation of ZTA nanocomposites by SCS with ultrasonic milling it is possible to improve the powder sinterability. The effect of ultrasonic irradiation on the powders was observed by BET and SEM analyses, and by its effect on the final density.

Keywords: nano-structures, powder processing, sintering, combustion synthesis.

Introduction

Tetragonal zirconia in an alumina matrix (ZTA) is nowadays a well known material, used for its improved toughness over standard oxide ceramics. Its good fracture strength is due to the presence of tetragonal zirconia particles that transform into the stable monoclinic zirconia upon loading. Since this transformation is accompanied by a volume increase, the effect is to cause a compressive stress in the crack tip zone, opposing its opening [1-3]. Particularly interesting are ZTA materials where both phases are of nanometric size. Several methods of preparing ZTA composites have been reported in the literature like conventional dry milling [4] or wet milling [5] of the mixture of zirconia and alumina but these traditional methods of mixing and milling tend not to yield ideal phase distributions. Coprecipitation [6] and sol-gel [3] synthesis methods have emerged as the front runners for preparation of nanocomposites, however, these techniques are quite complicated and need high temperatures and long processing times. By contrast, solution combustion synthesis (SCS) has emerged (in the last 10-15 years) as a simple, fast and economically viable method to prepare pure and ultrafine powders of oxides, solid solutions or composites for a variety of applications. The idea at the base of SCS is to prepare a solution containing cations of the metals needed, an oxidiser and a fuel, and let them react in order to cause a self-sustaining reaction. Often, the metal cations derive from nitrates, that are very soluble salts in water, and allow

to obtain highly homogeneous solutions. The redox reaction occurs between the nitrates, that are oxidisers, and a convenient reducing fuel. Urea, carbonylhydrazide, glycine, hydrazine, etc. have been used as fuels, providing a strong reaction with the nitrates. Urea is largely used as a fuel since it is cheap, easily available and safe for the health [7].

By SCS the final oxide composition can be tailored carefully and also metastable structures can be formed, thanks to the very fast heating and cooling rate typical of the SCS reactions. 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 [8-11].

Its main drawback is a limited sinterability of the powder due to aggregation of the nanometric grains to form micrometre-sized agglomerates characterized by an irregular shape. Nowadays, the synthesis of nanomaterials in powder form has been successfully demonstrated in a large number of materials and the methods for forming nanopowders are several and varied; by contrast the sintering of nanopowders to full or nearly full density without appreciable grain growth continues to present a significant practical challenge [12]. In particular the processing of nano-structured powders to produce dense pieces retaining the nanometric microstructure (< 100 nm) by traditional forming techniques followed by pressureless sintering has not proven easy [13].

To improve sinterability, we coupled the SCS method for the synthesis of nanostructured zirconia-toughened alumina with an ultrasonic milling technique.

Ultrasound is being used more and more in the preparation of materials due to its interesting properties linked to the phenomenon of acoustic cavitation. Cavitation is the formation, growth and implosive collapse of a bubble

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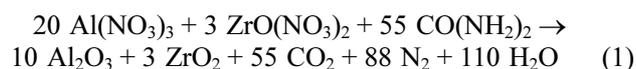
in a liquid. This phenomenon generates localized hot spots through adiabatic compression or shock wave formation within the gas phase of the collapsing bubble. The so formed hot spots can have a transient temperature of about 6000 K, a pressure of 2000 bar and cooling rates in excess of 10^9 K s^{-1} [14, 15].

In this study we aimed at overcoming one of the main limitation of the SCS, i.e. the poor sintering behavior of the powders produced. Due to hard agglomeration, these powders sinter with difficulty, however ultrasonic milling allows the break up of the agglomerates, producing finer and more dispersed powders.

Experimental

In this study Al_2O_3 toughened by 20% of partially stabilised zirconia (3%mol Y_2O_3) has been produced by SCS. Details of the preparation of alumina-zirconia-yttria nanocomposites by solution combustion synthesis have been described in a previous paper [8].

In this study, nitrates have been used as a cationic source for the final oxide and urea ($\text{CO}(\text{NH}_2)_2$) has been used as sacrificial fuel. The SCS reaction, ignoring the yttrium contribution, may be described as:



A water solution of the reagents is inserted into an oven kept at 600°C and, in a few minutes, an exothermic reaction takes place resulting in a very high local temperature for very short times, leading to the formation of crystalline or amorphous structures of the desired composition. Due to the large amount of gases evolved during the reactions, the products are very porous, with a spongy structure [16].

The powders obtained by combustion synthesis were subjected to different ultrasonic milling experiments. Two types of treatment were studied, direct and indirect milling. In the first case water was used as a dispersing agent and an ultrasonic transducer (Vibra-Cell VCX, maximum power 750 W, frequency 20 kHz) with a 12.7 mm diameter titanium probe was dipped in the powder-containing solution for times ranging from 30 seconds to 30 minutes. In a second experimental set, indirect milling was realised. The powder was inserted in a glass vessel using isopropyl alcohol as a dispersing medium. The glass vessel was put in a beaker full of water that was then irradiated by the transducer for times ranging from 5 to 60 minutes.

Both the powders as-obtained and the ultrasonically milled ones were characterized by X-ray diffraction using a X-Pert Philips diffractometer (Cu K_α radiation), in order to verify their purity and the retention of t-ZrO_2 . The specific surface area of the powders was measured before and after the ultrasonic milling by the BET method, using a Micro-metrics ASAP2010 instrument; the nitrogen adsorption-desorption isotherms were measured at 77 K after degassing the samples at 150°C for 5 h. The morphology and the

microstructure of the products were examined by means of scanning electron microscopy, energy dispersion spectroscopy (FESEM-EDS) and transmission electron microscopy (TEM).

Finally, the powders were pressed into discs (approximately 10 mm in diameter and 2 mm thick) in order to evaluate their sintering behavior. Conventional sintering of the nano-composite powders was performed at temperatures between 1550°C and 1700°C in air. The final bulk density of the sintered samples was measured by measuring the weight and dimensions, and the apparent density by the Archimede's method.

Results and Discussion

By tailoring the amount of sacrificial fuel into the reagent water solution it is possible to tailor the final oxide properties as described in several reports about SCS [17-20]. When the stoichiometric amount of fuel is used, a crystalline powder characterized by a low specific surface area is obtained ($5\text{-}10 \text{ m}^2/\text{g}$). By contrast, when a fuel lean solution (i.e. fuel amount inferior than the stoichiometric one) is used, an amorphous powder characterized by a high specific surface area (over $200 \text{ m}^2/\text{g}$) is obtained. Surface area measurements are reported in table 1 as well as XRD spectra in Fig. 1.

By varying the fuel-to-nitrate ratio, typically addressed as ϕ , it is possible to produce two types of ZTA nano-composite powders. The parameter $\phi = 1$ represents the stoichiometric amount of fuel according to reaction (1), while $\phi < 1$ means lean fuel mixtures. By controlling ϕ it is possible to affect the local temperature of the reaction, the amount of gaseous species evolved as well as the reaction rate. In particular, when using a fuel lean mixture with $\phi = 0.5$, a lower local temperature is reached by the reacting mass which is not sufficient for the crystallization of the final product thus resulting in an amorphous powder (see Fig. 1) characterized by a higher surface area. Instead, when a stoichiometric amount of fuel ($\phi = 1$) is used a higher local temperature is reached. This allows the crystallization of the powder accompanied by a reduction of the surface area because of a partial sintering of the grains

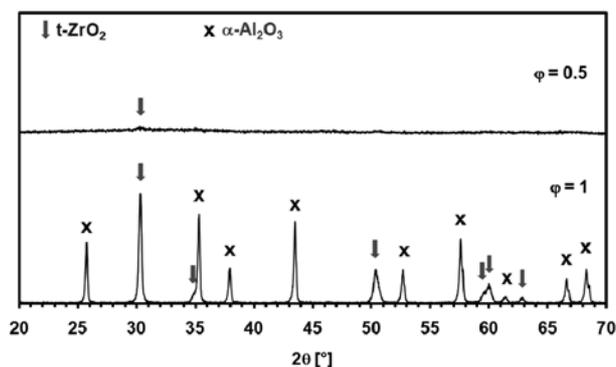


Fig. 1. XRD spectra of as-obtained powders with stoichiometric fuel condition ($\phi = 1$) and lean fuel condition ($\phi = 0.5$).

constituting the powder. In Fig. 1 it is possible to observe that when the stoichiometric amount of urea is used, the resulting powder is made of well crystallized α -Al₂O₃ and tetragonal ZrO₂ phases. No traces of monoclinic ZrO₂ can be detected.

In Fig. 2(a) detailed comparison between the two types of powders, as produced by SCS, is given in terms of SEM and TEM characterization. The particles are micrometric agglomerates of nanometric particles. In particular SEM images at low magnification (Fig. 2(a) and 2(b)) allow the observation that both the powders are made of aggregates with a comparable size in the micrometre range. The powders obtained with a lean fuel solution at high magnification do not exhibit a clear phase differentiation between Al₂O₃ and ZrO₂ because of their amorphous character (Fig. 2(c)). By contrast, for the well crystallized powders obtained with a stoichiometric mixture (Fig. 2(d)), the phase differentiation between Al₂O₃ matrix (dark phase) and the nanostructured ZrO₂ particles (light phase) is evident. Also TEM characterization confirms that phase differentiation is observed only in the sample obtained with $\phi = 1$, as shown in Fig. 2(e) and 2(f) (where Al₂O₃ is the light phase and ZrO₂ the dark one). In addition TEM characterization pointed out that the agglomerates appear to be more compact when stoichiometric fuel solutions are used while less compact aggregates exhibiting high nanoporosity (responsible for

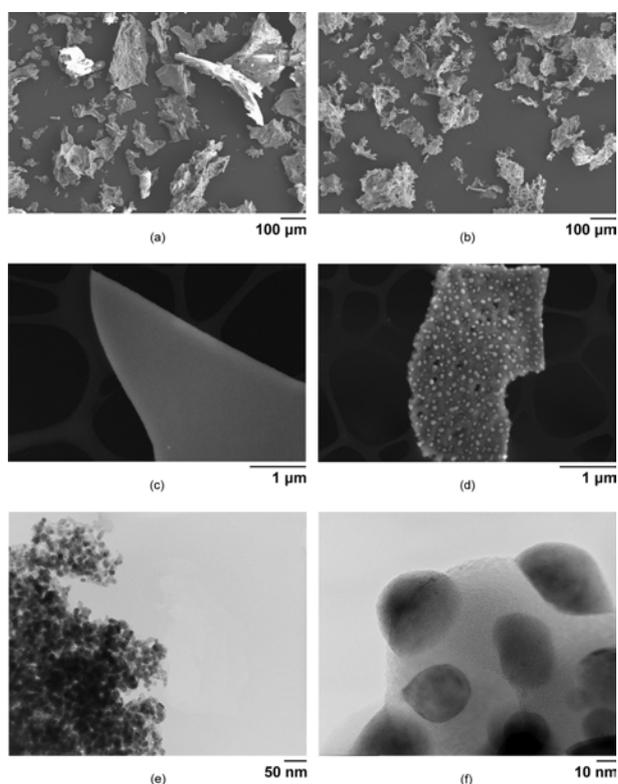


Fig. 2. SEM and TEM images of the as-prepared powders: (a) low magnification SEM for $\phi = 0.5$ powders, (b) low magnification SEM for $\phi = 1$ powders, (c) high magnification SEM for $\phi = 0.5$ powders, (d) high magnification SEM for $\phi = 1$ powders (Al₂O₃ is dark phase and ZrO₂ is light phase), (e) TEM image for $\phi = 0.5$ powders, (f) TEM image for $\phi = 1$ powders (Al₂O₃ is light phase and ZrO₂ is dark phase).

the high surface area) form in the cases of lean fuel mixtures.

The effect of ultrasonic milling on the sinterability of the low and high surface area powders was then investigated and analysed by BET and SEM characterization of the powders after different times of ultrasonic milling.

In Table 1, the effect of the time of ultrasonic milling on the specific surface areas of the powders are given. It can be seen that 1 minute of direct ultrasonic milling is sufficient to almost double the specific surface area of crystalline low surface area powders ($\phi = 1$). With higher milling times (5 minutes) a maximum in the surface area is reached suggesting the effectiveness of the method for a certain de-agglomeration of the powder. This is confirmed by SEM characterization where a mean inferior size of the agglomerates is observed (Fig. 3(a)). The above mentioned maximum in surface area is followed by a slight surface area diminution probably due to a partial occlusion of porosity.

In the case of the high surface area powder, obtained by solution combustion synthesis with a lean fuel mixture, ultrasonic milling did bring about a small decrease in the specific surface area. This is probably due to pore occlusion during ultrasonic milling and subsequent solvent evaporation without any de-agglomeration effect. In Fig. 3(b) it is shown however that the size of agglomerates is much reduced thanks to the ultrasonic treatment.

XRD characterization of the powders after ultrasonic milling showed that it does not induce either crystallization or a phase transformation.

Concerning the indirect milling, it proved to be ineffective with regard to surface area modification. It seems that the

Table 1. Specific surface areas of powders as prepared by solution combustion synthesis (SCS) and after the ultrasonic milling (US) ($\Phi = 1$, stoichiometric fuel; $\Phi = 0.5$, lean fuel).

Powder description	Specific surface area [m ² /g]	
	$\phi = 1$	$\phi = 0.5$
As prepared by SCS	6.5	265.3
0.5 minute direct US	9.4	217.0
1 minute direct US	10.3	212.4
5 minute direct US	12.9	-
10 minute direct US	12.7	193.8
15 minute direct US	11.0	-
15 minute indirect US	2.4	201.4

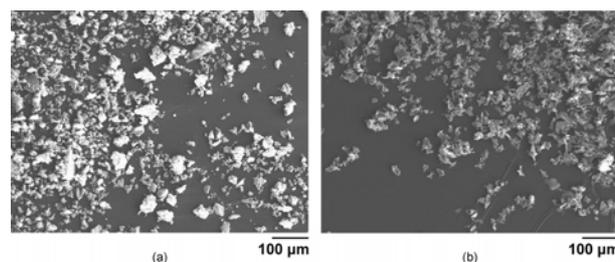


Fig. 3. SEM images of the powders after 5 minutes of direct ultrasonic milling: (a) low magnification SEM for $\phi = 0.5$ powders, (b) low magnification SEM for $\phi = 1$ powders.

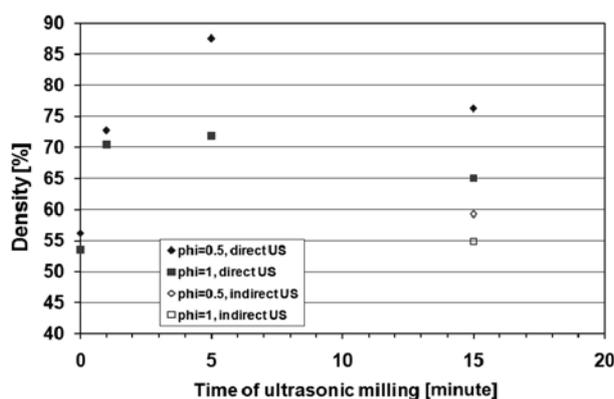


Fig. 4. Density of composite samples after a sintering treatment at 1700 °C for 2 h in air with respect to time of ultrasonic milling (US).

surface area of indirectly-milled powders decrease, probably due to pore occlusion by the smaller fragments without any de-agglomeration effect.

In Fig. 4 the density after sintering in air for 2 hours at 1700 °C versus the time of ultrasonic milling is shown for both types of powders ($\phi = 1$ and $\phi = 0.5$). Due to the poor sinterability of the powders, only the highest sintering temperature was chosen to be reported in this paper, which allows to obtain the highest relative density.

The first information deduced from Fig. 4 is that the as-obtained powders have indeed a very low final density (about 50% after sintering for both the two types of powders). In addition, it is interesting to note how the direct ultrasonic milling improves, in a very significant manner, the sinterability of both the two types of powders.

In the case of stoichiometric synthesis conditions ($\phi = 1$), the increase in relative density reflects the specific surface area improvement. There is a strong improvement in the final density after 1 minute of direct ultrasonic milling, while augmenting the milling time has a smaller effect or it is even counter-productive. Our hypothesis is that this type of powder has both a soft agglomeration and a hard one. The former is quickly reduced by the ultrasonic treatment, while the latter is not affected by the process, not even for prolonged time of ultrasonic milling.

In the case of samples obtained by a lean fuel mixture ($\phi = 0.5$), by contrast, the increase of density is progressively continuous from the unmilled sample to those milled for 1 or 5 minutes. In this case the surface area is already very high at the beginning, with large soft aggregates. The increase in final density seems due to a reduction of the size of the aggregates, which leads to a better compaction. The very high surface area then results in a significant driving force for sintering. The effect is very significant, 5 minutes of direct ultrasonic milling are sufficient to increase the final density after sintering from 56% to 87%.

By contrast, the indirect ultrasonic milling did not lead to any sintering improvement. It is evident that in this case only the pore occlusion effect is present, without the reduction of the size of agglomerates. Thus surface area decreases without an effect on the sinterability.

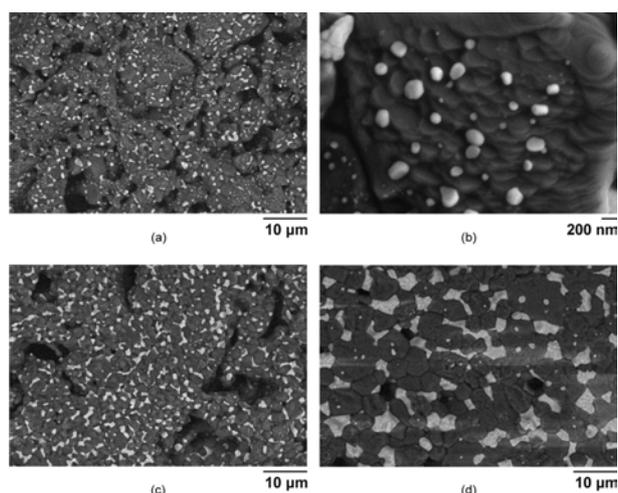


Fig. 5. BS-SEM images of sintered (1700 °C, 2 h in air) specimens obtained with a lean fuel mixture (Al_2O_3 is dark phase and ZrO_2 is light phase): (a) low magnification without ultrasonic milling, (b) high magnification detail without ultrasonic milling (c) low magnification 1 minute direct ultrasonic milling, (d) low magnification 5 minutes direct ultrasonic milling.

In every case, lean fuel aqueous solutions allow one to obtain samples that sinter to higher relative density with respect to stoichiometric fuel ones. A similar behavior has been observed by Jayaseelan *et al.* [2] and the explanation that can be given is twofold. On one side the higher surface area increases the driving force for sintering. On the other side, with amorphous powder crystallization occurs contemporary to the sintering process and probably this convergence simultaneously of the phase transformation and sintering provides a better opportunity for densification.

In Fig. 5 back scattered SEM images made on thermally-etched sintered composites are shown and the increase in final density with the increase of time of direct ultrasonic milling is evident (Fig. 5(a), 5(c) and 5(d)). It is also interesting to observe the good and uniform distribution of zirconia between alumina grains as well as its location at the alumina grain junctions (intergranular zirconia location). The use of nanometric powders allows one to obtain, even after very high temperature sintering, submicrometric zirconia particles disposed between alumina grains of 1-2 micrometre size. Even smaller zirconia particles (nanometre sized) may be detected in intragranular locations, as shown in the back scattered SEM detail in Fig. 5(b). These particles are believed to be zirconia incorporated into the alumina during grain boundary migration.

By comparing Fig. 5(a), 5(c) and 5(d) a progressive increase in the microstructure size with the increase of time of direct ultrasonic milling is also evident.

If ultrasonic milling is carried on for too long times, it is possible to observe on the sintered sample an agglomeration of zirconia grains. The size of the microstructure increases, as shown in Fig. 6 for a sample milled for 15 minutes. It is probable that during ultrasonic milling small fragments form, and that zirconia and alumina tend to agglomerate

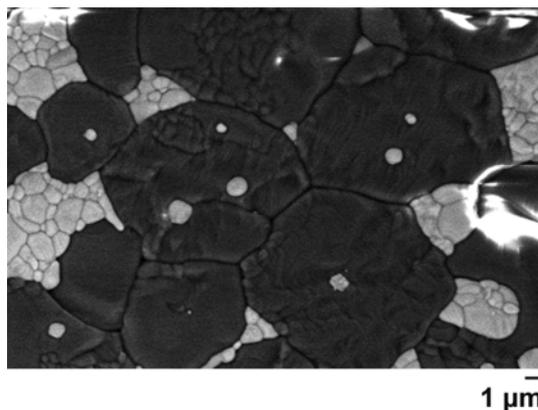


Fig. 6. BS-SEM image of a sintered (1700 °C, 2 h in air) specimen obtained from a powder after 15 minutes of direct ultrasonic milling.

each other separately. As a consequence, during sintering the dispersion of zirconia in the alumina matrix worsens significantly. Furthermore when XRD analysis is performed on sintered specimens two main features were characteristic only of the sample directly US milled for 15 minutes: the main peaks of monoclinic zirconia start to be detected as well as some foreign peaks compatible with a zirconium titanate phase. The appearance of monoclinic zirconia is in good agreement with the size increase of the zirconia particles by agglomeration, thus being no longer able to retain the tetragonal phase. Our hypothesis for the detection of a zirconium titanate impurity is that titanium comes from the ultrasonic transducer probe when direct ultrasonic milling is carried on for too long.

Conclusions

In this study composites in the Al₂O₃-Zr(Y)O₂ system have been realised by solution combustion synthesis. Two types of powders were prepared, a low surface area crystalline one (5-10 m²/g) obtained in stoichiometric conditions, and a high surface area amorphous one (> 200 m²/g) starting from a lean fuel solution. Both these powders were ultrasonically milled. The low surface area powder showed an improvement in specific surface area due to direct US milling, and the sintering behavior followed the same trend, increasing from 53% to 72% approximately. This suggested that direct ultrasound irradiation was sufficient to break the softer aggregates but not the stronger ones, thus limiting the final composite density. The high surface area powder presented a much more marked increase in final density after irradiation, reaching 87% of the theoretical value. SEM images showed two

size of zirconia grains, submicrometric and nanometric ones, in intergranular and intragranular position respectively. These grains are well dispersed into the alumina matrix, whose grain size is larger, being of the order of a micrometre. A too long ultrasonic milling lead to a reduction of the final density and to a growth of the alumina and zirconia grain size as well as to a titanium release by the ultrasonic transducer probe. An indirect US milling has been evaluated too in order to overcome the titanium release by the US probe but it exhibits too low energy not sufficient to affect powder sinterability.

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