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Microwave synthesis of yttria stabilized zirconia

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Abstract

Yttria stabilised zirconia (YSZ) nanocrystals, with a mean size between 5 and 10 nm, were prepared by microwave flash synthesis. Flash synthesis was performed in alcoholic solutions of yttrium, zirconium chloride and sodium ethoxide (EtONa) using a microwave autoclave (RAMO system) specially designed by authors. Energy dispersive X-ray analysis (EDX), X-ray powder diffraction (XRD), BET adsorption technique, photon correlation spectroscopy (PCS) transmission and scanning electron microscopy (TEM and SEM) are used to characterized these nanoparticles. Compared with conventional synthesis, nanopowders can be produced in a short period (e.g. 10 s), both high purity and stoechiometric control are obtained. Nevertheless, this mean of production is more cheaper and much faster than the ones commonly used to produce yttria stabilized zirconia (YSZ) by conventional sol–gel techniques.
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1. Introduction

Yttria stabilized zirconia (YSZ) is usually used as electrolyte in the technology of solid oxide fuel cell (SOFC). It exhibits an appropriate ionic conductivity [1], has a good chemical stability in oxidizing or reducing environment [2] and is not reactive to electrode materials for SOFC applications [3,4].

Various techniques have been used to synthesize this compound: solid state reaction [5], hydrothermal route [6], polymerization route [2] and sol–gel method [7]. Advantages and limitations of these

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techniques have been discussed in literature [8]. Typical drawbacks of conventional methods of preparation are inhomogeneity, varied particle size distribution and poor reactivity when fine spherical particles, with narrow size distribution, are desirable for producing ceramics with enhanced reliability. As a common point, morphology of nanocrystals and control of chemical composition appear to be crucial for industrial applications.

Microwave-assisted synthesis is a new way to produce inorganic compounds because microwave heating is an in situ mode of energy conversion very attractive for chemists. The RAMO system (french acronym of Reacteur Autoclave MicroOnde) is an original microwave device designed by our research team [9]. This device is able to produce rapid bulk heating. Due to strong thermal gradients induced by microwave heating, strong stirring occurs for liquids leading to thermal uniformity of heated medium. Hence, it combines advantages of forced hydrolysis (homogeneous precipitation) and very fast heating rate. RAMO system has allowed production of various nanomaterials [10–17].

Only a few publications reported microwave synthesis of zirconia [12,18–21]. Nanosized monoclinic zirconia has been produced by flash-synthesis with RAMO System [12]. These operating conditions using acidic aqueous solutions of zirconium chloride had tremendous drawback. It is not possible to associate other metal as yttrium or cerium with zirconium in order to obtain solid solutions. Consequently, the purpose of this work is to synthesize YSZ powders with narrow size distribution close to 10 nm. Starting materials are zirconium and yttrium chloride with sodium ethoxide (EtONa). The use of sodium ethoxide as mineralizer is based on our previous works upon iron metal/oxide nanocomposites [13,16]. The nominal composition chosen for the present study is $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}O_2$ leading to cubic phase of zirconia. This flash-synthesis process is called microwave forced hydrolysis.

2. Experimental

2.1. Operating conditions

All the chemicals products, anhydrous zirconium chloride ($ZrCl_4$, Acros Organics, purity >98%), yttrium chloride ($YCl_3{\cdot}6H_2O$, Acros Organics, purity >99,9%), sodium ethoxide (EtONa, Aldrich, 96%) and ethanol (Prolabo, Normapur, 96%) were reagents grade used without further purification. Initial concentrations were chosen to obtain a yttrium(III) to zirconium(IV) ratio chosen in relation to crystallographic phase expected: tetragonal (down to 7 mol% of Y_2O_3) and cubic (from 7 mol%). The general flowchart of the operating conditions is described by the Fig. 1. The solution 1 was prepared by mixing appropriate amounts of zirconium and yttrium chloride in ethanol. The zirconium and yttrium concentration are fixed at 0.25 M (22.8 g l^{-1}) and 0.04 M (3.6 g l^{-1}) respectively in order to obtain cubic phase: ratio Y_2O_3 to ZrO_2 close to 15% in weight. The concentration of the sodium ethanoate solution (solution 2) is equal to 1M (68 g l^{-1}). These solutions 1 and 2 were vigorously mixed and stirred in the RAMO system (Fig. 2) whereas a precipitate appears.

This original experimental device is constituted of a microwave applicator associated with an autoclave. Compared to a domestic oven or commercial device (CEM or Millestone), our microwave oven allows a higher electric field strength for the heated sample. The microwave generator used is a continuous wave system with a power up to 2 kW (2.45 GHz). The autoclave is made with polymer materials which are microwave transparent, chemically inert and sufficiently strong to accommodate the pressure induced. The reactants are placed in a Teflon flask inserted within a polyetherimide flask. A fiber-optic thermometry

Captions

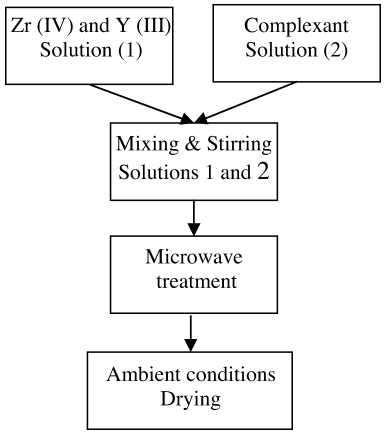

Fig. 1. Flowsheet of the YSZ powder preparation by the microwave process.

system, a pressure transducer and a manometer allow to measure simultaneously the temperature and the pressure within the reactor. Temperature measurements under microwave heating are very difficult and non-perturbing temperature sensor could be used. The system is controlled by pressure. The microwave power is adjusted in order to allow constant pressure within the vessel. A pressure release valve incorporated permits to use this experimental device routinely and safely. Furthermore, we can introduce an inert gas such as argon within the reactor to avoid sparking risk with flammable solvents as ethanol. This experimental device is able to raise the temperature from ambient to 200 °C in less than 20 s (the pressure is close to 1.2 MPa and the heating rate is close to 5 °C/s). More details about microwave devices, microwave heating and non-perturbing temperature sensors could be found in [9].

This reactor was quickly sealed and an argon pressure introduced (0.4 MPa). Microwave treatments were performed with RAMO. The treatment was decomposed in two steps. During the first step, the

Fig. 2. Presentation of microwave autoclave reactor RAMO.

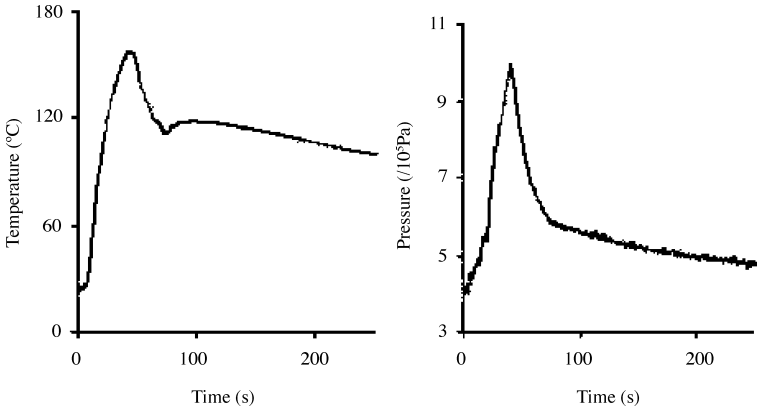

Fig. 3. Evolution of temperature and pressure vs. time. Initial power: 1 kW.

microwave power (1 kW) is applied until the pressure reaches a threshold value of 1 MPa. This pressure corresponds to a temperature close to 160 °C. During the second step, this pressure threshold was kept by monitoring the microwave power. The heating rate is close to 10 °C/s. The Fig. 3 illustrates the relationship between temperature and pressure generated within the reactor for ethanol and the reactive medium used: ethanol reaches a temperature of 160 °C and a pressure of 1.0 MPa in 40 s for a microwave power of 1 kW. The reactive medium leads to a higher heating rate since metallic salts and sodium ethoxide increase the dielectric losses.

Microwave treatment time chosen is equal to 2 min. After this microwave treatment, powders were centrifuged and washed with distilled water in order to eliminate sodium and chloride ions. They were dried at room temperature. Finally, annealing treatment at 300 °C, 600 °C, 800 °C and 1200 °C was made to induce growing of crystals in order to reveal cubic phase. Typically, 350 mg of nanosized YSZ is obtained in one step.

2.2. Characterization

The X-ray powder diffraction (XRD) patterns of the samples, as prepared or heated at different temperatures, were recorded using a SIEMENS D-5000 diffractometer with Cu-Kα radiation source for phase identification. The standard BET technique was employed to measure the specific surface area, of YSZ powder as prepared, using an AUTOSORB 1 QUANTA CHROME device and nitrogen as adsorption gas. Chemical analysis was done by using OXFORD INSTRUMENT EDX. Granulometric distributions was measured by photon correlation spectroscopy (PCS) with the spectrometer 7032 MALVERN INSTRUMENTS. Finally, scanning electron microscopy (JEOL JSM 6400) and transmission electron microscopy (JEOL 2010 F) were used to estimate particle size, nature of agglomerates and morphology of the final YSZ powder.

3. Results

Table 1 compares Y_2O_3 and ZrO_2 mol% between initial mixture, raw powder and after annealing at 800 °C for 2 h. Powders composition is determined by EDX analysis. Despite microwave and annealing

Table 1
Percentage by mol of zirconia and yttria in the initial solution and in YSZ powders after microwave treatment and subsequent thermal treatment in air at 800 °C

	ZrO_2	Y_2O_3
Initial reactants in solution 1 (mol%)	92.5 ± 0.2	7.4 ± 0.2
YSZ powder after microwave treatment (mol%)	92.2 ± 0.9	7.7 ± 0.7
YSZ powder after heat treatment at 800 °C in air for 2 h (mol%)	92.0 ± 0.9	8.0 ± 0.6

treatments, the ratio yttrium to zirconium of the initial mixture is kept within solid solution of zirconia and yttria. Hence, these operating conditions allow composition control of powder produced in relation to chloride precursor ratio of within initial solution. EDX analysis shows that no sodium or chlorine is present in the powders.

To determine the morphology powder have been, firstly, analyzed by X-ray diffraction. The XRD patterns are shown, Fig. 4, for microwave raw powder and after annealing treatment at 300 °C, 600 °C, 800 °C and 1200 °C. If the initial mixture of solutions 1 and 2 is not microwave treated, yield precipitation is very slight (<5%) and a mixture of zirconium and yttrium oxides are obtained. The nanometric size of the particles leads to strong broadening of X-ray lines and despite careful analysis of XRD patterns of raw powder, it is difficult to conclude about nature of the crystallographic phase produced. However, Bragg reflections intensities of cubic phase are observed after annealing treatment. The XRD pattern after heat treatment at 300 °C shows a slight increase of crystallinity as compared to the raw microwave powder and X-ray lines become thinner and thinner with temperature increasing (up to 600 °C) due to strong growing of crystal size. Crystallinity of raw microwave powder was found to be poor compared to those obtained after annealing treatment. Absences of either monoclinic zirconia or segregated yttrium compounds demonstrate homogeneous dispersion of yttrium within powder.

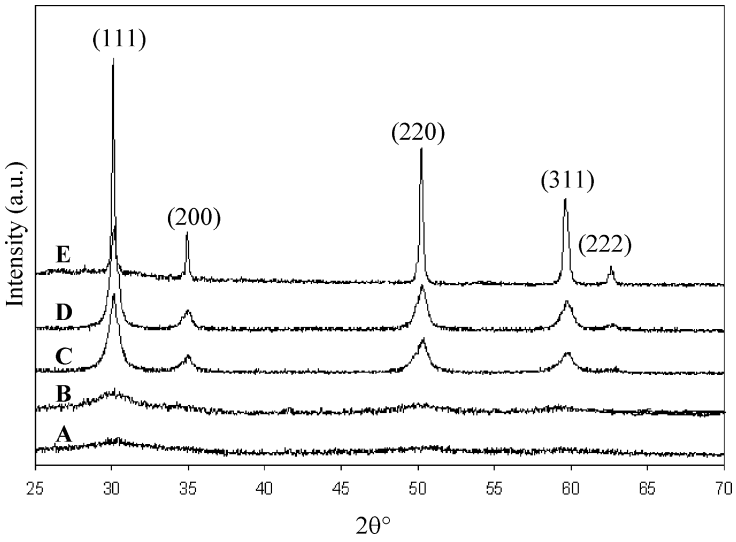

Fig. 4. X-ray patterns of YSZ powders calcinated at various temperatures for 2 h in air. A = 25 °C (before heat treatment); B = 300 °C, C = 600 °C, D = 800 °C E = 1200 °C.

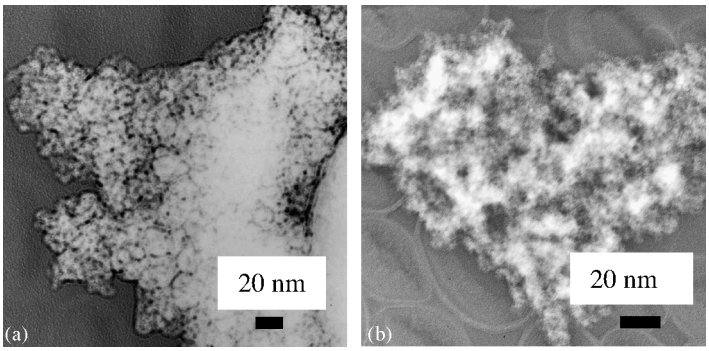

Fig. 5. (a) TEM micrograph in dark field (b) TEM micrograph in bright field.

The surface area of raw microwave powder was measured by BET technique, after bakeout at 40 °C for 72 h. The nitrogen adsorption at 77 K leads to a relatively high value (228 $m^2\ g^{-1}$). Assuming spheroids particles, a mean value of diameter close to 5 nm can be estimated using Eq. (1). TEM micrographs displayed by the Fig. 5 confirm the nanostructured features of samples produced. The crystallites exhibit mean size lower than 20 nm (a) whereas submicronic aggregates which look like snowflakes are observed (b). The mean size of these aggregates is close to 150 nm. These results corroborate the strong broadening of X-ray lines observed.

$$D = \frac{6}{\rho S} \tag{1}$$

where D is the diameter in μm, ρ the volumic mass in g cm^{-3} and S is the specific area in $m^2\ g^{-1}$.

To corroborate the size of these agglomerates, measurements by photon correlation spectroscopy (PCS) were carried out. A piece of powder was dispersed into water under ultrasonic device during 30 min. A narrow size distribution, Fig. 6, centered at 120 nm was obtained.

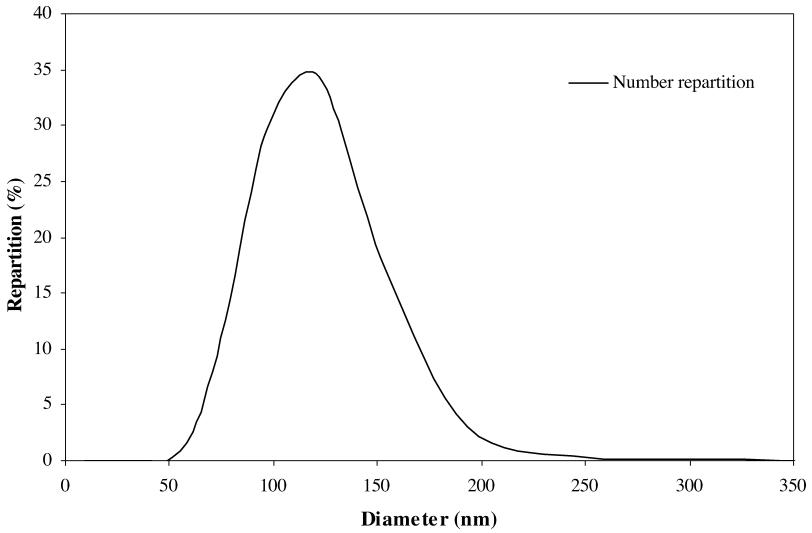

Fig. 6. PCS size distribution of the Microwave YSZ powder in dispersion in water.

4. Discussion, conclusion

According to these data, nanosized YSZ could be produced by microwave flash synthesis with RAMO system. Powders with high specific surface are produced at low temperature (160 °C) and short heating time (2 min). Grain size and crystallinity could be increase by further thermal annealing. Moreover, the stability of cubic phase is maintained up to 1200 °C. Operating conditions use zirconium and yttrium chlorides alcoholic solutions associated with sodium ethoxide. These conditions are cheaper and more rustic comparing to classical sol–gel conditions using other alkoxides. Nevertheless, they allow the control of yttrium to zirconium ratio within powder produced.

Among papers reported microwave synthesis of zirconia, Komarneni et al. [18] have produced zirconia submicron powder (monoclinic) from aqueous zirconyl nitrate solutions at 164 °C for 2 h using KOH as mineralizer. Among crystalline unary oxide produced by these authors, zirconia do not show evidence of precipitation kinetic enhancement. According to their results, crystallization time for pure zirconia is around 2 h for both microwave and conventional methods. Bellon et al. [12] contrary to these results have observed very fast microwave forced hydrolysis of zirconium tetrachloride aqueous solutions. Operating conditions using RAMO system and acidic aqueous solutions leads to monodisperse zirconia nanoparticles (monoclinic). The induction period of 20 h usually observe for conventional heating mode is reduce to few seconds. According to Khollan et al. [21] using aqueous solutions of zirconyl nitrate and yttrium chloride and operating conditions close to ours (200 °C, microwave heating time close to 5 min), crystallization kinetics was faster for YSZ because yttrium might enhance crystallization of YSZ phase. Homogeneous dispersion of yttrium in YSZ powder is also observed. It seems that microwave core heating allows volumetric nucleation in relation to temperature superior to 100 °C. In our case, sodium ethoxide used instead of potassium hydroxide enhance crystallization kinetic and surface area (228 compare to 125 $m^2 g^{-1}$). This value of surface area seems the higher obtained whatever the method of preparation: conventional or microwave heating [8]. Due to this high surface area and high temperature stability of cubic phase, powder produced with RAMO system could have catalytic properties enhanced compared to conventional powder. This point should be tested in future. Aggregation during precipitation from a supersaturated solution is the general mechanism for particles growth. Despite nanosized crystals, powders are systematically composed of several aggregation levels overlapped and typical size of lumps is close to micrometer (Fig. 7). According to value of surface area, it seems that aggregation level of microwave powder is quite different comparing to conventional powders. This second point could be also examined in the future.

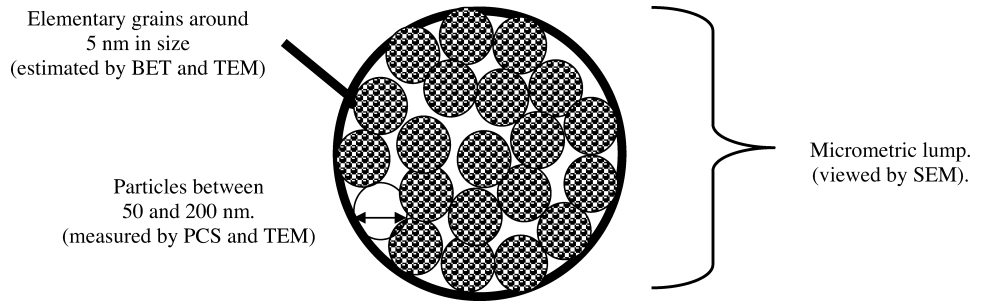

Fig. 7. Schematic morphology of YSZ powder synthesized by microwave technique.

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