SPHERICAL CALCIA STABILIZED ZIRCONIA POWDERS OBTAINED BY SPRAY PYROLYSIS

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Abstract

Physical and chemical properties of ceramic powders are highly dependent on the morphology and chemical composition of the precursor powders. Therefore, properties of ceramic powders are expecting to be improved by controlling the most important parameters of morphology such as composition of precursors, temperature and airflow. Promising techniques to produce ceramic powders with controlled morphology are sol-gel, coprecipitation, and pyrolysis. Among these techniques, spray pyrolysis is one of the most suitable to control the morphology and the chemical composition of the particles, because the spray pyrolysis technique integrates the evaporation, precipitation, decomposition and sintering stage of powder synthesis into a single continuous process. Spherical powders were prepared from acetylacetonate of zirconium and acetate calcium hydrated solutions by pneumatic spray pyrolysis. The morphology and size of the powders change with variation of airflow, temperature, and solution concentration.

Keywords: Spray pyrolysis technique, ultrafine powders, precursor ceramics, zirconia and calcia.

1. Introduction

In the past twenty years, a considerable interest has arisen in zirconia-based (ZrO2-based) solid electrolyte materials for numerous high-temperature technology applications. High oxygen-ion conductivity combined with high thermochemical stability are responsible for the use of stabilized zirconia materials, for example in oxygen sensor or fuel cells [1, 2]. More applications as: knives and scissors, precision ball valve balls and seats, high-density ball and pebble mill-grinding media. Rollers and guides for metal tube forming, thread and wire guides, hot metal extrusion dies, deep well downhole valves and seats, powder compacting dies, marine pump seals and shaft guides, oxygen sensors, high temperature induction furnace susceptors, fuel cell membranes, electric furnace heaters over 2000°C in oxidizing atmospheres[3].

Zirconia exists in three crystal phases at different temperatures. At very high temperatures (>2370°C) the material has a cubic structure. At intermediate temperatures (1170 to 2370°C) it has a tetragonal structure. At low temperatures (below 1170°C) the material transforms to the monoclinic structure. The transformation from tetragonal to monoclinic is rapid and is accompanied by a 3 to 5 percent volume increase that causes extensive cracking in the material. This behavior destroys the mechanical properties of fabricated components during cooling and makes pure zirconia useless for any structural or mechanical application. Several oxides dissolve in the zirconia crystal structure can eliminate these crystal structure changes. Commonly used effective additives are MgO, CaO, and Y2O3. With sufficient amounts
2.2. Powder characterization

The crystalline structure of the zirconia-based powders was analysed by X-ray diffraction (XRD) in a D5000 X-ray diffractometer, using Cu Ka radiation, at 40kV and 30 mA. The 2θ angle were swept in a range from 5 to 80°, with a 2θ step size of 0.1° and step time of 5 s. Particle composition was analysed by electron microscopy, using a JSM 5800LV scanning and a CM200 transmission electron microscopes, both equipped with a DX prime energy dispersive X-ray spectrometer (EDS). In addition, crystalline structures were studied by selected area electron diffraction patterns (SAED), and compared with XRD results.

Additionally, particle size, morphology and microstructure were evaluated as functions of the experimental conditions. For the determination of the average particle sizes (APS) of each sample, around 200 particles were measured directly from several bright field transmission electron micrographs, using a digital imaging analyser IMAGE-PRO PLUS 4.1.

3. Results

3.1 Parameters in powder preparation by spray pyrolysis

It is well established, for conventional pneumatic spraying, that the droplet sizes decrease when the airflow increases [2]. If the sprayed droplets are focussed directly towards the reaction chamber, the droplets size corresponds to that mentioned above. However, if the atomizer sprays down to the solution container and the mist of solution is carried out in an upward direction by the airflow; the droplet size selection occurs due to the combined effect of gravitational and Stokes' force [1]. When these forces reach equilibrium the droplet travels with a constant terminal velocity, which is function of the particle size. Therefore, only the droplets smaller than certain critical sizes can be carried out to the reaction chamber. This critical size (d_c) is airflow dependent, and for low and medium airflow (0 < G_A < 8 dm^3 min^-1) in fact reverse the reliance between droplet size and airflow, i.e. average droplet size increase with the increase of airflow just to certain limit flow. Only if the gas carrier flow increases further (G_A > 8 dm^3 min^-1) the average droplet size can decrease. The real residence time (τ) of the droplets is in the region of high the temperatures of the cylindrical furnace, it also was estimated as a function of the gas carrier flow rate (G_A), taking into account the geometry of the reactor. Gas expansion correction was estimated by this factor, since the work of Milosevic et al. [2]. Subsequently, at a fixed furnace temperature the residence time decreased when airflow increased. In addition, the rate of droplet heating (R) has been estimated considering furnace temperature distribution,
airflow rate and geometry of the reaction chamber. It can be concluded that, under the experimental conditions utilized in this work, very high increases of the heating rate (several thousand \( \text{°C} \text{s}^{-1} \)) happens when the airflow increases.

### 3.2 Composition and crystalline structure of ZrO2-CaO Fine Powders

Figure 2 shows characteristic EDS spectrum of CaSZ powders. The average Zr:Ca molar proportion in the powders is almost the same as in the precursor solution; i.e. Zr:Ca and is approximately equal to 0.86:0.14.

![Characteristic EDS spectra of CaSZ powder](image)

Fig. 2. Characteristic EDS spectra of CaSZ powder.

Figure 3 shows the XRD spectrum of the calcia stabilized zirconia (CaSZ) powder. It is observed that diffraction peaks corresponding to the cubic and tetragonal phases, indicating that a partially stabilized structure has been formed. SAED results also confirm this finding. Table 1 shows interplanar distance calculated from SAED patterns of CaSZ powders. It can be concluded, the presence of Cubic and Tetragonal phases. A preliminary estimation using the Rietveld method reports a proportion of 5 weight percent for the tetragonal phase. An exhaustive study is in course.

![XRD spectrum of CaSZ powder obtained at 900°C](image)

Fig. 3. XRD spectrum of CaSZ powder obtained at 900°C.

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#### 3.3 Particle size of CaSZ powders

In general, the growth and characteristics of the powders prepared by spray pyrolysis are determined by the combined effect of the droplet size generated in the sprayer, the size of those effectively transported (de) to the reaction chamber, the residence time (t) and the rate of droplet heating (RH) in the chamber. These parameters are, as well, dependent on the geometry of the system, principally spraying and reaction chambers, solution composition and concentration, airflow and to the reactor temperature.

First of all, it is worthwhile to consider that the average particle size (APS) measured in all the samples of this work are nano-metric (40 to 350 nm), they were considerably smaller than those calculated from the average droplet size using a well known approach [2]. This result can be explained by two possible mechanisms considering that each droplet did not convert to a unique particle. The first one, due to the occurrence of an important droplet broke down [2] or explosive boiling [6]. These events probably take place when the droplets travel into the nozzle, before they have been injected into the reaction chamber. At this stage the residence time (~10^-3 s) is shorter than the drying time (~0.1 s [5]) and the heating rate is very high (>10^5 °C s^-1), in these conditions a vigorous boil of the droplets can happen, given as a consequence, their broke down.

The second additional mechanism can occur after dehydration of the droplet/particle, at the beginning of their travel in the quartz tube. Due to the high temperature and very large surface area of the precursor salt particles, the total evaporation rate can be extremely high, given as a consequence, the loose of the precursor material or the formation of many ultra fine particles. This mechanism was also suggested for ZnO powders by Liu et al. [7]. It is expected that precursor evaporation was more intense at low airflow, i.e. when the residence time in the reaction chamber was high. Moreover, at high solution concentration the droplets tended to evaporate the solvent more quickly, thus, they formed precursor salt particles more easily and consequently the precursor evaporation rate increased. The experimental
results are consistent with these two considerations. The APS was a bimodal distribution of sizes, small sizes (»40 nm) at low 6 dm3 min⁻¹ and large size distribution (350 nm) at higher flows (see figure 4); additionally, the APS increased with the increase of solution concentration (see figure 5).

![Graph](image)

Fig. 4. APS as a function of the airflow.

![Graph](image)

Fig. 5. APS as a function of the solution concentration.

3.4. Morphology and inner structure of the CaSZ particles.

Secondary electron SEM micrograph representative of CaSZ powder is shown in figure 6.

![SEM Image](image)

Fig. 6. Secondary electron SEM micrograph of powders CaSZ.

![TEM Images](image)

Fig. 7. Bright field TEM micrographs of calcia stabilized zirconia obtained at airflow: a) 4, b) 6, c) 8 and d) 10 dm³ min⁻¹. The solution concentration was 0.05 mol dm⁻³, furnace temperature 900 °C and voltage of electrostatic precipitator 4.6 kV.
For this sample obtained at 900 °C, 0.05 mol dm⁻³, 4.6 kV, 5 dm³ min⁻¹, it can be observed that spherical particles are the predominant morphology; only a small number of them show a hollow or irregular shape.

Airflow has also a noticeable effect on the morphology of the particles. It is shown in figure 7, that the number of irregular hollow shaped particles increases as the airflow increases. The formation of hollow particles is related to the localized super-saturation of the solute with the consequent formation of a crust on the droplet surface [1]; which depends on the evaporation rate of the solvent, and on the strength and permeability of the crust. When the concentration of precursor solution is high enough, the crust is formed earlier on the droplet surface. The internal solvent, encapsulated by the forming crust, expands when heated and increases the particle size of the powder; rose after the complete evaporation of the solvent of hollow particles that can break into irregular particles. It is expected that the influence of the residence time is higher when it is shorter than the time needed for complete evaporation of the solvent. In this case, with high enough airflow, the particle size tends to grow, because the formation of a crust occurs earlier by the cooperative effect of low t and high RH. This proposal is in concordance with the particle size (as discussed before) and porosity of the particles (see below), and with the results of other works [2, 7, 8, 1].

Figure 8 shows the variation of particles porosity as a function of the airflow. It is observed as a decrease of the porosity, hence the permeability, of the particles as the airflow increases. The logical consequences are the increase of irregular hollow particles and particle sizes with the increase of airflow, as described above.

In addition, TEM analysis demonstrates that the spherical particles contain inner small crystallites. Figure 9 shows that inner crystallite size growth as furnace temperature increases and airflow decreases. Figures 9a and 9b show bright field TEM micrographs of powders obtained at 900 °C and 1000 °C respectively. (6 dm³ min⁻¹, 4.6 kV, 0.1 mol dm⁻³). In this case, it can be noted as a slight increment of crystallite size, from 2 - 6 nm to 3 - 8 nm approximately. In contrast, for samples obtained at 900 °C and an airflow of 2 dm³ min⁻¹ the crystallite size increases to 24 - 41 nm (see figure 9c).

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Fig. 8. Bright field TEM micrographs of calcia stabilized zirconia obtained at airflow: a) 4, b) 6, c) 8 and d) 10 dm³ min⁻¹.
The solution concentration was 0.05 mol dm⁻³, furnace temperature 900 °C and voltage of electrostatic precipitator 4.6 kV.
4. Conclusions

The feasibility of produces Zirconia and Calcia stabilized zirconia nanopowders without post-heat treatment by spray pyrolysis has been demonstrated. Compared with the traditional method the powders are obtained in a step, saving time and energy.

The size, morphology, and structural characteristics of zirconia and CaSZ nanopowders depend principally on the source solution concentration, reaction chamber temperature, and airflow. Average particle size range between 40 to 350 nm.

Each particle is composed by many small crystallites of sizes varying between 2 to 40 nm.

In spite of porous or dense ceramic powder production, an appropriate precursor solution concentration is needed to fit the requirements.

Acknowledgment

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References.