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Effect of the fuel type on the synthesis of yttria stabilized zirconia by combustion method

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Abstract

Nano-sized 8 mol% yttria stabilized zirconia (YSZ) powders were synthesized by the combustion method using two different fuels (urea and glycine). The effect of the nature and amount of the fuel was investigated on the phase structure, particle size and microstructure of the resulted YSZ ceramics. The results showed that YSZ powders synthesized using urea presented larger crystallite size and lower specific surface area than those derived from glycine route. This behavior is closely related to the combustion flame temperature. The elevated temperature during combustion synthesis with urea favored the formation of large aggregates, instead of loose and porous particles as observed for glycine route. As a consequence, the best result in terms of densification was obtained for the pellets prepared by sintering of powders synthesized through glycine route.

Keywords: A: Powders: chemical preparation; B: X-ray methods; D: ZrO_2; E: Fuel cells

1. Introduction

Yttria stabilized zirconia (YSZ) exhibits high oxygen ionic conductivity and good mechanical properties at elevated temperatures making its use ideal for various applications, such as oxygen sensors, oxygen separation membranes and electrolyte materials in solid oxide fuel cells (SOFC). The ionic conductivity of the YSZ electrolyte is related to processing technology of the powders, particle sizes and sintered density [1].

For YSZ electrolytes, the electrical and mechanical properties can be enhanced by preparing a fully dense ceramic after sintering, which requires ultrafine powders with a narrow size distribution [2]. The conventional solid-state reaction for preparation of YSZ powders usually yields large particle sizes, inhomogeneity and poor reactivity [3]. A distinct advantage of using nano-crystalline YSZ powders in the fabrication of sintered compacts is the lower sintering temperature needed [4]. Thus, different processing methods have been developed for production of nano-crystalline YSZ, such as co-precipitation technique [5], sol–gel preparation [6,7], hydrothermal synthesis [8], sonochemical process [9], and Pechini method [10]. However, these methods are generally complicated, require multi-step reaction routes and/or long processes.

Combustion synthesis is an attractive method for preparing multicomponent oxide powders that are crystalline, homogeneous, with high-purity and a narrow particle size distribution [11]. The combustion technique consists of a self-propagating high-temperature synthesis (SHS), discovered by Merzhanov and co-workers, which involves a wide variety of chemical routes and products [12]. The main feature of SHS is a very short time required for attaining high combustion temperatures due to heat released during exothermic reactions [12]. This paper deals with solution combustion synthesis that is based on the principle of thermal decomposition of metal nitrate and fuel gel to produce a spontaneous flame with no controlled temperature leading to a foamy but well crystallized single-phase powder [13]. The stability of the gel depends essentially on the nature of the fuel; different fuels have been used in combustion synthesis, such as urea, glycine, citric acid, sucrose, carbohydrazide, among others [14,15]. The combustion method does not require special igniting equipment and the operation is simple and easy as well [16].

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The present work reports the synthesis of nano-crystalline 8 mol% YSZ powder by combustion method using two different fuels (urea and glycine). This study focuses on the effects of the nature and amount of the fuel on the structural and morphological properties of YSZ materials and assessing the microstructural densification of bulk YSZ.

2. Experimental

2.1. YSZ preparation

The starting materials for the combustion synthesis of 8 mol% Y_2O_3-stabilized zirconia (YSZ) were zirconyl nitrate hydrate ($ZrO(NO_3)_2{\cdot}6H_2O$, Acros Organics, 99.5%), yttrium nitrate ($Y(NO_3)_3{\cdot}6H_2O$, Acros Organics, 99,9%) and glycine (Vetec) or urea (Vetec). The amount of fuel was calculated based on the valencies of oxidizing and reducing elements, according to the propellant chemistry [17].

Metal nitrates were taken in the required ratio, according to the formula $Zr_{0.85}Y_{0.15}O_{1.93}$, and dissolved in water, together with the fuel (urea or glycine). The molar ratios of fuel to metal nitrates (F/M) were 1:1 or 2:1. The homogeneous mixture was heated on a hot plate at 150 °C and it was converted to a viscous gel due to evaporation of water. The mixture was then heated in a muffle furnace at 600 °C until self-ignition. The resulting fine powders were calcined at 900 °C for 6 h using heating rate of 10 °C min^{-1}, with air flow of 60 mL min^{-1}.

The combustion temperature was measured with a K type thermocouple placed on the muffle furnace. The temperature falls below 600 °C when the muffle door was opened to introduce the basin and the thermocouple was inserted into the reagent mixture (150 °C). Temperatures were collected by Hydra Data Logger (Fluke).

The powder was uniaxially pressed at 200 MPa into pellets of 12.4 mm in diameter and 2.1 mm in thickness, followed by isostatic pressing at 150 MPa. The green pellets were sintered at 1600 °C for 3 h with a heating rate of 10 °C min^{-1}.

The samples studied are denoted as YSZ.G1, YSZ.G2, YSZ.U1 and YSZ.U2, where G and U represent glycine and urea, respectively, and the numbers represent the F/M ratio.

2.2. Powder characterization

Crystalline phases were identified by X-ray diffraction (XRD) analysis with a PANalytical X'Pert PRO diffractometer using Cu Kα radiation (λ = 1.5418 Å) with Ni filter and the data were collected from $2\theta = 5^\circ$ to 100°. The crystallite sizes (D_{XRD}) and microstrain (ε) were calculated using the model proposed by Williamson and Hall [18], by means of the following formula:

$$\beta\cos\theta/\lambda = 1/D_{XRD} + 4\varepsilon\sin\theta/\lambda \quad (1)$$

where θ is the diffraction angle, λ is the wavelength of incident radiation and β is the full width at half maximum (FWHM) of the peak. Plotting the $\beta\cos\theta/\lambda$ versus $4\sin\theta/\lambda$ straight line yields the crystallite size from interception with the ordinate and microstrain from the slope.

The specific surface area (S_{BET}) of the powders was measured with a Micromeritics Tristar equipment by the BET method. The average particle size (D_{BET}) was calculated assuming the presence of spherical particles, by means of the equation:

$$D_{BET} = 6/\rho S_{BET} \quad (2)$$

where ρ is 5.96 g/cm^3, the theoretical density of YSZ (JCPDS 030-1468).

Thermogravimetric analysis (TGA) of the as-prepared powders (before calcination) was carried out using a TA thermal analyzer (SDT Q600 model). The thermal analyses were conducted at a heating rate of 10 °C min^{-1} from 25 to 1200 °C in air flow.

The microstructure of the powders and sintered pellets was examined by scanning electron microscopy (SEM, Jeol JSM-64602 LV). For sintered pellets, cross-sectional areas were polished and thermally etched at 1550 °C for 30 min, to reveal grain boundaries. The density of the sintered pellets was measured by the Archimedes method (Mettler AE-200 analytical balance) with distilled water as the immersion medium.

3. Results and discussions

3.1. Powder characterization

Fig. 1 shows the X-ray diffraction patterns of YSZ powders synthesized by the combustion process. For both the fuels, single-phase cubic YSZ (JCPDS 030-1468) has been obtained after calcination. The presence of other phases, such as Y_2O_3, monoclinic or tetragonal ZrO_2, was not observed. Thus it can be assumed that homogeneous solid solution between Y_2O_3 and ZrO_2 was formed, which is required in order to obtain the cubic crystal structure.

The calculated 'd' values match with the reported yttria stabilized cubic zirconia having a composition of $Zr_{0.85}Y_{0.15}O_{1.93}$ or $92ZrO_2{\cdot}8Y_2O_3$, and the lattice parameter

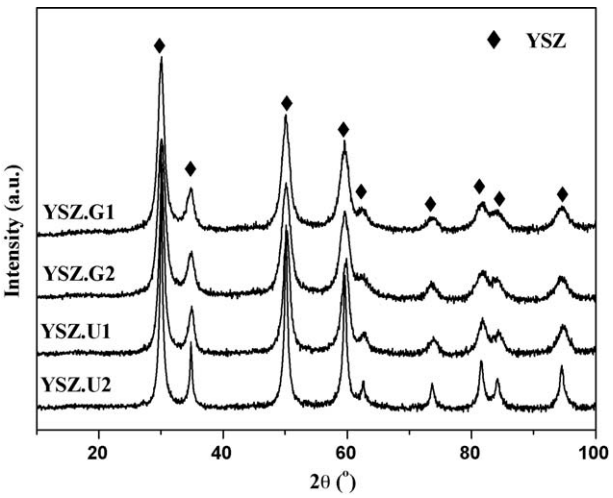

Fig. 1. X-ray diffraction patterns of YSZ powders after calcination.

Table 1
Microstrain (ε), average crystallite size (D_{XRD}), specific surface area (S_{BET}), average particle size (D_{BET}) and D_{BET}/D_{XRD} ratio of the YSZ samples.

Sample	ε (%)	D_{XRD} (nm)	S_{BET} (m^2/g)	D_{BET} (nm)	D_{BET}/D_{XRD}
YSZ.G1	0.32	5.8	21.6	46.7	8.0
YSZ.G2	0.30	4.4	19.2	52.6	11.9
YSZ.U1	0.31	7.2	1.3	773.4	107.4
YSZ.U2	0.16	13.1	1.9	524.3	40.0

'a' was estimated to be 5.139 Å, in agreement with JCPDS standard.

The microstrain, average crystallite size, specific surface area, average particle size and D_{BET}/D_{XRD} ratio for each sample are given in Table 1. Results confirmed that YSZ powders obtained are nanocrystalline, with crystallite sizes varying from 4.4 to 13.1 nm. Broad XRD peaks indicate the nanocrystalline nature of the synthesized powders and not lattice distortions caused by non-uniform distribution of admixtures, since the values of microstrain are very low.

It can be seen that the crystallite size slightly decreases with the glycine amount, which is in accordance with the results of He et al. [3]. Moreover, YSZ powders presented larger crystallite sizes when urea was used in the synthesis. This behavior can be associated with the combustion temperature, which is higher for urea, as will be shown in Fig. 2.

The textural characteristics of the resulting oxide are strongly influenced by the gas evolution during combustion reaction, which causes the dissipation of the combustion heat and decreases the temperature in the reagent mixture. The samples synthesized with glycine presented specific surface area considerably higher than those derived from urea which is consistent with the lower temperatures involved during combustion with glycine. High temperatures lead to further crystalline growth, thus high D_{XRD} and low S_{BET} [16].

Fig. 2 shows the evolution of the combustion temperature as a function of time for the studied systems. For the samples prepared from urea it was observed higher flame temperatures, leading to crystalline growth. Comparing the flame temperature of the combustion reaction using urea and glycine, it can be observed from Fig. 2 that the combustion process with urea is much more violent, with considerably shorter times for self-ignition of the reagent mixture. The higher temperature for the initiation of combustion reaction using urea fuel may be due to the lower value of heat of combustion [19].

The elevated D_{BET}/D_{XRD} ratio for urea samples indicates a high agglomeration degree caused by elevated temperature during the combustion reaction, with partial sintering of material accompanied by loss of surface area.

3.2. Thermal analysis

Fig. 3 represents thermogravimetric analysis (TGA) of the as-prepared YSZ powders. All TGA profiles presented the same behavior, with three different stages of decomposition that may be described as follows. The first weight loss that occurred before 300 °C is associated with desorption of physisorbed water and

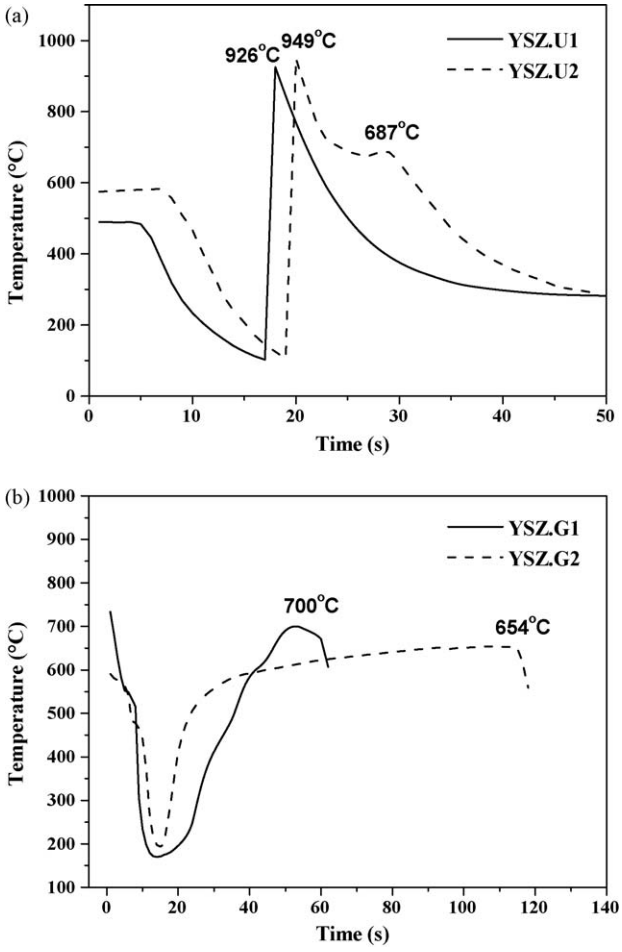

Fig. 2. Evolution of temperature as a function of time for combustion synthesis using (a) urea and (b) glycine as fuel.

the removal of chemisorbed hydroxyl groups; the second stage occurred over a temperature range of 300–600 °C, which can be attributed mainly to the oxidation process of the residual organic materials and the third stage above 600 °C is related to the decomposition of carbonate and nitrate residues [3].

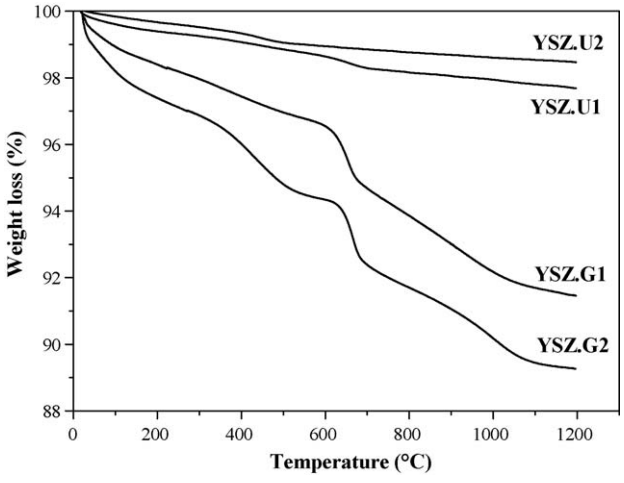

Fig. 3. TG curves of the as-synthesized YSZ powders prepared by the combustion method.

Table 2
Total weight loss, maximum combustion temperature and color of the as-synthesized powders and relative density of the YSZ pellets.

Samples	Total weight loss (%)	Maximum combustion temperature (°C)	As-synthesized powder color	Relative density (%)
YSZ.G1	8.5	700	Light brown	97.5
YSZ.G2	10.7	654	Dark brown	94.3
YSZ.U1	2.3	926	White	79.4
YSZ.U2	1.5	949 and 687	Light yellow	83.9

The total weight loss and maximum combustion temperature are summarized in Table 2. The carbon content of the products synthesized using glycine is higher than those using urea, since the heat released during combustion is relatively lower. This behavior is mainly attributed to the lower flame temperature, resulting in higher amount of residual carbon in the as-ignited products and consequently higher total weight loss. The higher carbon content of glycine samples can also be seen by the darker powder color (Table 2).

Increase in glycine content results in slower decomposition of the salts and incomplete combustion, with higher amount of carbonaceous matter in the as-prepared powder. The effect for urea fuel is the opposite: increasing the fuel amount the exothermicity of the reaction increased, resulting in lower weight loss in TGA profile.

3.3. Microstructure and densification

Micrographs of the powder samples are displayed in Fig. 4. The morphology of YSZ particle is affected by the fuel type. The prevalence of high temperatures when urea is used as fuel promoted the formation of large aggregates instead of porous particles with a foamy aspect as presented in the micrographs for powders synthesized using glycine. The loose and porous

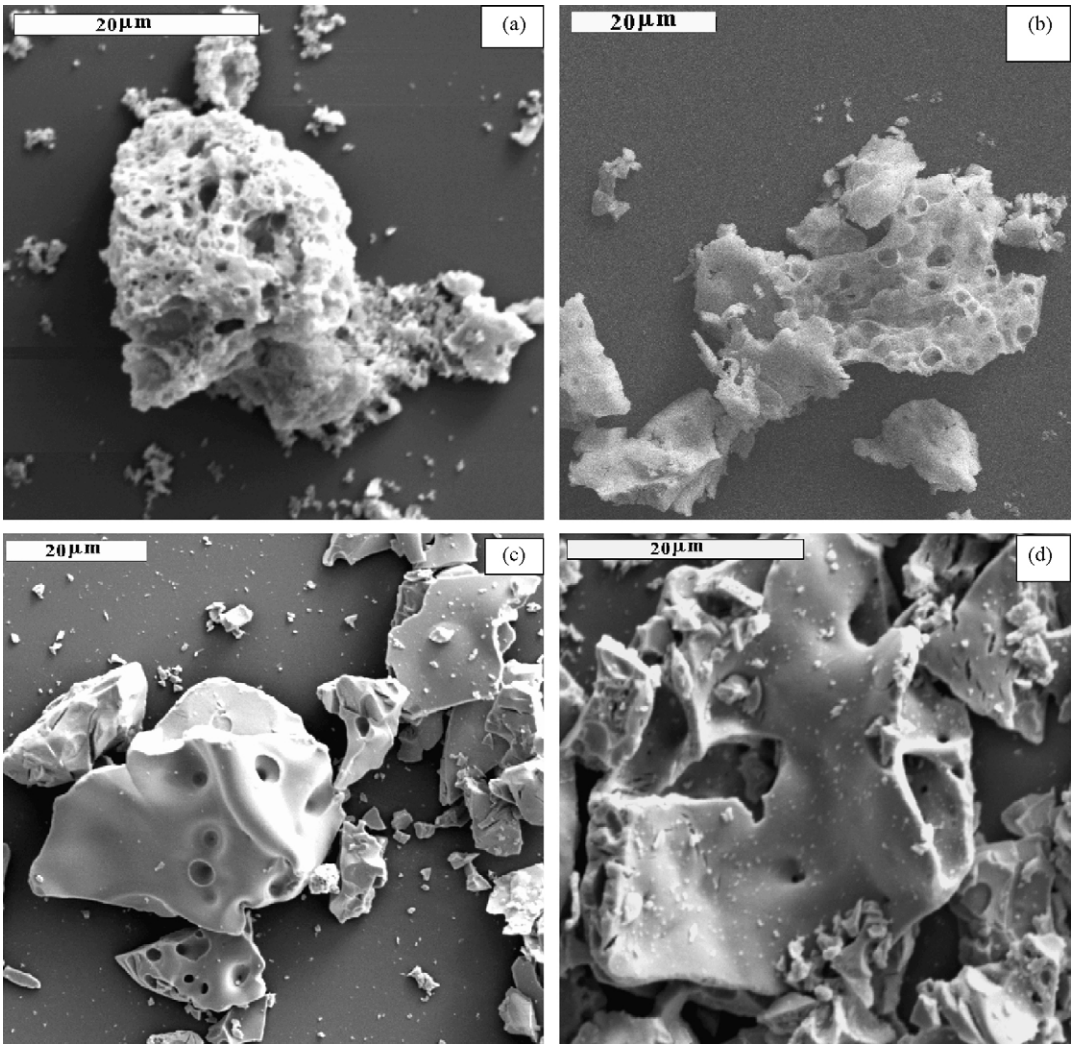

Fig. 4. SEM micrographs of (a) YSZ.G1, (b) YSZ.G2, (c) YSZ.U1 and (d) YSZ.U2 powders.

structure of glycine samples (Fig. 4(a) and (b)) can be attributed to the evolution of large amount of gases during combustion reaction and the formation of aggregate structure for urea samples (Fig. 4(c) and (d)) is associated with high combustion temperature resulting in partial sintering of particles.

As a consequence, the best result in terms of densification was obtained for the pellets prepared from powders derived from glycine route. Table 2 presents the results of densification analysis (relative density in percentage of the respective theoretical density). According to conventional sintering theory, the sinterability increases with decreasing particle size [20]. Thus, samples prepared using glycine presented higher density than those derived from urea route. The relative density of YSZ.G1 sample (97.5%) is very close to that reported by He et al. [3] and Mazaheri et al. [21] for YSZ prepared by glycine–nitrate process. For glycine samples, the relative density decreased when more fuel was used because of coarsening of the particles, as observed by Wang et al. [16].

The lower density of the sintered pellet obtained using powders prepared by urea route is due to the presence of hard agglomerates which are difficult to break in compaction [19]. High densification is important because it leads to better electrical properties for the YSZ electrolyte.

Fig. 5 shows the microstructure of the fractured surface of YSZ pellets sintered at 1600 °C. The grain boundaries are straight, clear and thin, with smaller and more uniform grains for samples prepared using urea fuel. For glycine samples, there are pores inside the grains and others in the grain boundary, while urea samples show only intergranular porosity. However, large flaws can be seen in micrographs of urea samples (Fig. 5(c) and (d)), which show that agglomerates were not fully disintegrated by pressing, resulting in differential densification during sintering.

Average grain sizes, calculated by linear intercept method, were larger for samples synthesized using glycine (9.1 and 8.5 μm for YSZ.G1 and YSZ.G2, respectively) than for those derived from urea route (1.5 and 2.5 μm for YSZ.U1 and YSZ.U2, respectively). These results are in accordance with higher densification achieved by glycine samples.

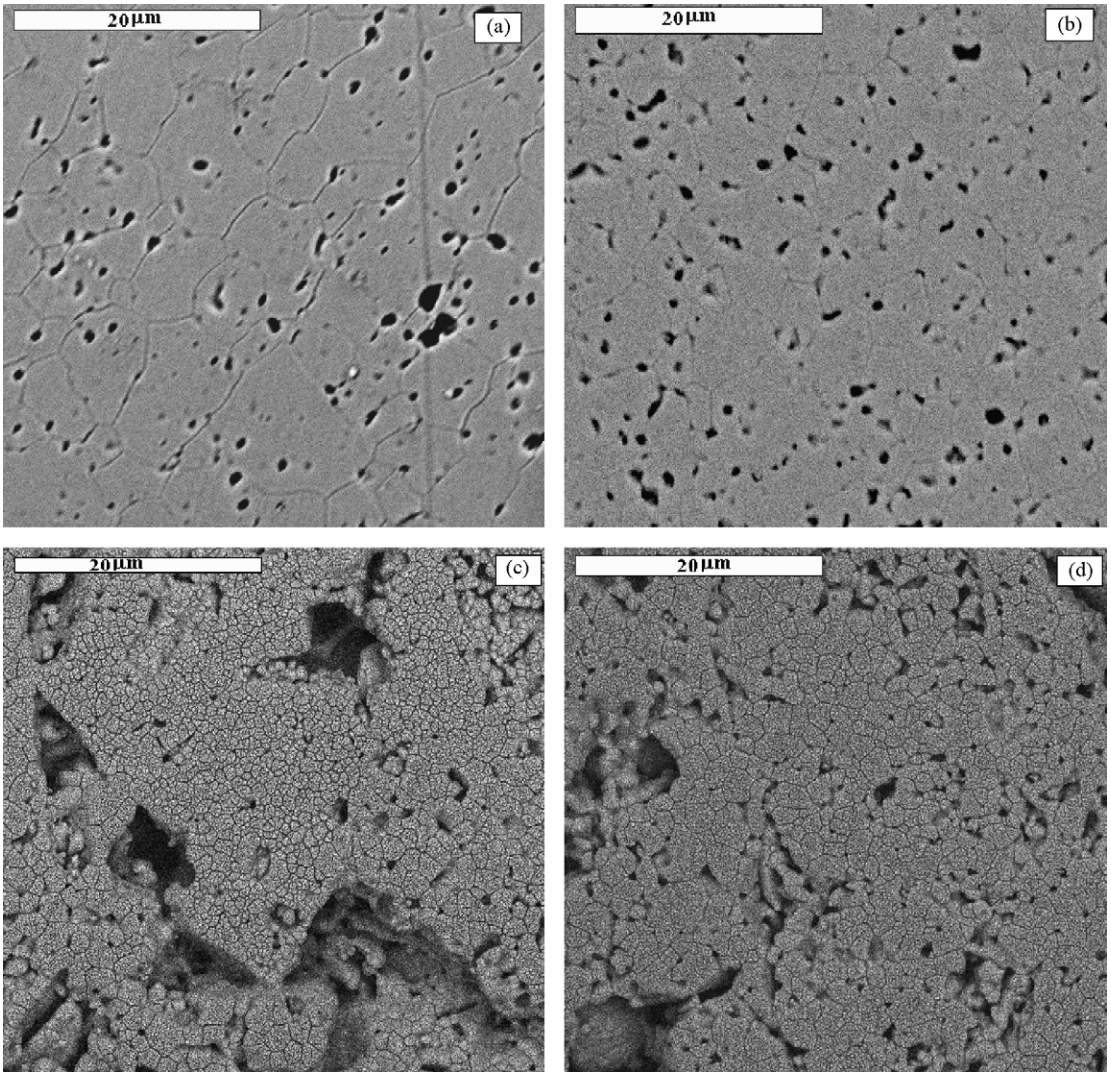

Fig. 5. SEM micrographs of fractured surface of the (a) YSZ.G1, (b) YSZ.G2, (c) YSZ.U1 and (d) YSZ.U2 pellets sintered at 1600 °C.

4. Conclusions

A combustion synthesis method from nitrate precursors has been successfully used to prepare nanocrystalline YSZ powders. All powders exhibited cubic structure when calcined at 900 °C. According to our results, crystallite size, thermal stability and microstructure are strongly dependent on the nature of the fuel (urea or glycine) and the fuel/metal nitrates ratio.

The combustion temperature is much higher when urea is used as fuel, which causes crystallite growth and decreases the specific surface area of YSZ powders synthesized from urea. As we have shown by thermal analysis, the carbon content of the products synthesized using glycine is higher than those using urea, since the heat released during combustion is relatively lower.

The elevated temperatures during combustion reaction caused high agglomeration degree of the YSZ powders synthesized from urea. As fine particles are easier to be densified, YSZ pellets prepared from glycine reached higher relative density (97.5% for 1:1 fuel/metal nitrates ratio) after sintering at 1600 °C. In this way, YSZ prepared by combustion process with glycine can be considered as potential candidate for application in SOFC electrolyte.

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