The influence of sulphur on the processing of zirconia based ceramics

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Abstract

Yttria stabilized zirconia powders were synthesized by the coprecipitation route. Zirconium oxychloride containing sulphur as contamination and analytical grade yttrium chloride were used as raw materials. Powders were calcined at temperatures between 600 and 1100 °C and ground by ball and attrition milling. The ceramic bodies were sintered at 1350 and 1550 °C for 1 h and the apparent density was measured. In the present work it is shown that the most deleterious effect of sulphur was observed in 3 mol% yttria stabilized zirconia, especially when the pellets were obtained at high pressures and sintered at 1500 °C. The elimination of sulphur at higher calcination temperatures minimizes the effects caused by this contamination, despite the reduction of powder surface area. The best processing condition to obtain high density zirconia ceramics from powders contaminated with sulphur was established. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: ZrO_2; Impurities; Sintering; Microstructure-final; Porosity

1. Introduction

In the field of ceramic materials, zirconia attracts great attention due to its wide range of applications. Traditionally used as refractories, pigments and abrasives, zirconia can also be applied as solid electrolyte and structural materials. This remarkable potential is possible by the addition of oxides, such as MgO, CaO, CeO_2 and Y_2O_3, that allows the stabilization of the tetragonal and/or the cubic phases of zirconia.[1,2] Nevertheless, to obtain the maximum benefit from this material, the microstructure design of the ceramic product, suitable for each application, is considered a critical step.[3–5] Therefore it is necessary not only to optimize the ceramic processing but also to control the chemical and physical characteristics of the raw material.

The role of physical characteristics of starting powders in the sintering behaviour has been extensively discussed in the literature. It is generally accepted that the fabrication of dense stabilized zirconia is achieved by using nanosize powders, free from hard agglomerates.[6] Wet chemical methods, such as hydrolysis of metal alkoxides and synthesis of a polymeric precursor, have

been employed for this purpose.[7–9] The control of composition and dopant distribution is also attained by these procedures. However, for industrial scale, coprecipitation of hydroxides is still an important method due its low cost and simplicity.[10,11] The use of organic liquids to dehydrate the precipitate[12–17] and wet milling[18–20] has also been employed to control particle size and the state of agglomeration of calcined powders. Chemical purity level of stabilized zirconia raw materials is another aspect that has to be focused. The first step for zirconium solution purification is the decomposition of its ores, represented mainly by zircon (ZrO_2 SiO_2), the most common and widely distributed source of zirconium, and by baddeleyite, a direct source of zirconium oxide. An industrial process to decompose these ores is the alkaline fusion with sodium hydroxide. This reaction is carried out at temperatures above 600 °C, producing a mixture of sodium zirconate, sodium zirconium silicate and sodium silicate, which is leached with water and hydrochloric acid to eliminate sodium and silicon, respectively. The zirconium fraction is a zirconium oxychloride solution, containing impurities such as iron, aluminum, titanium, copper and lead, that are generally separated by the precipitation of zirconium basic sulphate. An addition of ammonium hydroxide to this precipitate replaces the sulphate ions

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by the hydroxyl groups, yielding zirconium hydroxide that is further dissolved with hydrochloric acid to obtain a purified zirconium oxychloride solution that can be used for zirconia synthesis.[21–24]

The effects of silica and alumina on the densification and microstructure characteristics of yttria stabilized zirconia have been previously reported. These oxides can form a continuous glassy phase rich in Al, Si and Y, located along the grain boundaries and at the triple points.[25–28] Alumina can also be found as inclusions.[28] It is important to notice that, in spite of the improvement on the densification by the presence of a glassy phase, detrimental effects on mechanical[25] and electrical properties can be observed.[28] The degradation of these properties can be attributed to the destabilization of the cubic/tetragonal matrix due to selective leaching of yttria by the silicate grain boundary phase, as well as to the presence of a brittle phase in the sintered microstructure.[26] Sulphur represents a class of impurity introduced during the chemical processing of zirconia. Originated from the precipitation of zirconium basic sulphate, sulphur can reduce the density of zirconia ceramics due to the evolution and entrapping of SO_3 gas during sintering.[29] Chlorine and carbon can cause a similar effect.[30–32]

In the present study, calcination and ceramic processing conditions of 3 and 9 mol% yttria stabilized zirconia powders were optimized to prevent the deleterious effect produced by the presence of sulphur impurity in ceramic bodies. These two compositions were selected due to their importance in the production of Y-TZP (yttria tetragonal zirconia polycrystals) and Y-CSZ (yttria cubic stabilized zirconia), used as structural ceramics and solid electrolyte in solid oxide fuel cells, respectively.

2. Experimental procedure

2.1. Powder synthesis

Zirconium oxychloride (purified by the basic zirconium sulphate precipitation process—IPEN, Brazil) and yttrium chloride (hydrochloric acid dissolution of 99.99% Y_2O_3—Aldrich Chemical Co., USA) were the starting raw materials used in this investigation. Appropriate amounts of these reagents were mixed and diluted in water to obtain a solution containing 35 g L^{-1} of 3 and 9 mol% of yttria stabilized zirconia. Coprecipitation was carried out by spraying the mixed chlorides into a 3 molar ammonium hydroxide solution at an approximate rate of 50 mL min^{-1}. The reaction was conducted under a vigorous stirring maintaining the pH of the solution at 10. The gel suspension was filtered and washed with water until no indication of residual Cl^- (determined by the precipitation of AgCl in the filtrate

when tested with $AgNO_3$). To avoid the formation of hard agglomerates the precipitate was washed with ethanol and treated by azeotropic distillation with butanol. In this later process the azeotrope, containing 44.5 wt.% water and 55.5 wt.% *n*-butanol, is first evaporated at 93 °C. By the time the temperature reaches 117 °C, the boiling point of n-butanol, all the water has been removed from the gel.

The distilled gel was oven-dried at 80 °C for 24 h. Calcination experiments were carried out at a temperature range between 600 and 1100 °C for 1 and 2 h. Attrition milling (A) in ethanol for 4 h, using zirconia balls as milling media, was employed to destroy large agglomerates. Powders were also submitted to ball milling (B) in ethanol for 16 h for ceramic processing studies. Samples were designated 3P and 9P for 3 and 9 mol% yttria stabilized zirconia, respectively.

2.2. Powder pressing and sintering

Uniaxial pressing (U) at 100 MPa and association of uniaxial and isostatic pressing (U/I) at 100 and 200 MPa, respectively, were used to prepare green pellets. For the optimization of the calcination temperature, sintering experiments were performed in air, in an electrical box furnace at 1350 and 1550 °C for 1 h. The heating rate was set to 5 °C min^{-1} up to 800 ° C and 10 °C min^{-1} until the sintering temperature. To select the best ceramic processing conditions, sintering kinetics of the compacts were first studied by dilatometry (402 E/7, Netzsch). These studies were conducted in air, fixing the heating rate at 10 °C min $^{-1}$ up to 1650 °C. In the later set of experiments samples were also sintered in an electrical box furnace in the temperature range of 1150 and 1650 °C for 1 h.

2.3. Characterization techniques

Powders were characterized by thermogravimetric analysis (STA 409, Netzsch) to verify the degree of weight loss of the dried hydroxides, infrared analysis for sulphur detection (CS-400, Leco), gas adsorption (Quantachrome, Nova 1200) for BET specific surface area measurements, laser diffraction (Cilas granulometer) for determination of agglomerate size distribution and scanning electron microscopy—SEM (XL30, Philips) to observe particle and agglomerates morphology.

Green pellets were characterized by geometric density measurements and mercury porosimetry (Autopore III, Micromeritics). The characterization of as-sintered samples was performed by the examination of fracture surface (SEM) and by density determinations (Archimedes method). The determination of theoretical density values and quantitative phase analysis were performed by the Rietveld refinement of the X-ray diffraction patterns (DMAX 2000, Rigaku).

3. Results and discussion

3.1. Influence of calcination conditions on the sintering behaviour

Fig. 1 shows the TG-DTA curves, carried out up to 1000 °C, in air, for the as-dried coprecipitated powders. In the temperature range of 18–450 °C, a sharp weight loss of 13 and 21% is observed for the samples 3P and 9P, respectively, which may correspond to the loss of residual water and/ or organic solvent. The exothermic peak at 334–345 °C indicates the crystallization of zirconia. Above 800 °C, a weight loss of 1–2% occurs due to decomposition of sulphate ions, as confirmed by the results of sulphur content in calcined zirconia, presented in Table 1. It is also shown in Table 1 that sulphur elimination occurs above 1000 °C, where a great reduction of specific surface area is observed, in spite of the attrition milling of the powders. Fig. 2 shows that agglomerate mean size of these powders is in the range of 0.1 and 1 μm. For powders calcined at temperatures lower than 1000 °C, similar agglomerate sizes were observed by SEM (Fig. 3). It was also observed that particle sizes are in the nanoscale. At 1100 °C the particle size increased because the onset of the sintering process.

Table 2 shows the relative density values of the as-prepared green compacts, considering the theoretical density (TD) calculated by Rietveld refinement of XRD

data of sintered pellets: 6.1 g cm^{-3} for 3P samples (composed by 98% of tetragonal phase + 2% of monoclinic phase) and 6.0 g cm^{-3} for 9P samples (composed by 100% of cubic phase). As can be observed, higher calcination temperatures and isostatic pressing increase the green density values. In spite of this increment, a

Table 1
Sulphur content and specific surface area of attrition milled 3 and 9 mol% yttria stabilized zirconia powders, as a function of calcination conditions

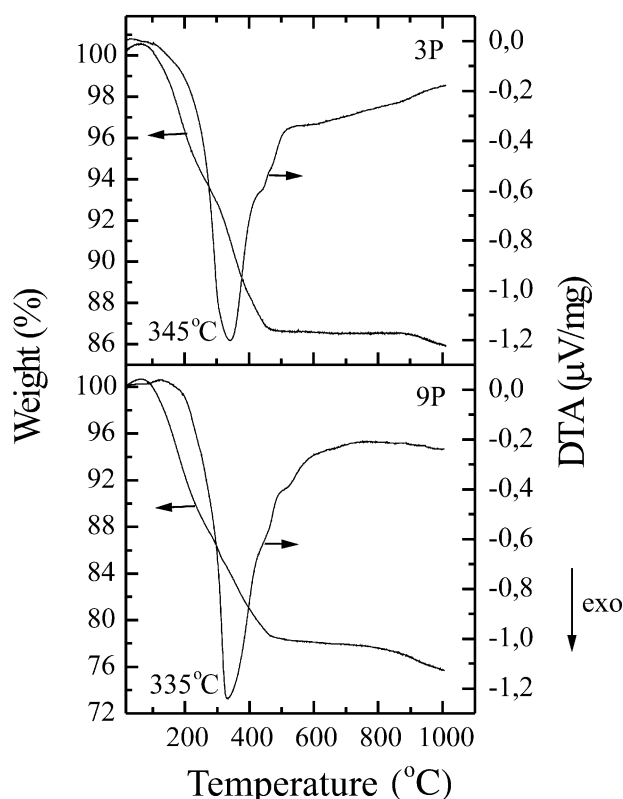| Sample	Calcination conditions	Sulphur content (mass%)	S_{BET} (m^2 g^{-1})
3P	600 °C/1 h	0.52	104.5
	800 °C/1 h	0.52	59.5
	900 °C/1 h	0.22	–
	900 °C/2 h	0.15	–
	1000 °C/1 h	0.01	27.1
	1000 °C/2 h	<0.01	–
	1100 °C/1 h	<0.01	10.9
9P	600 °C/1 h	0.34	129.2
	800 °C/1 h	0.34	66.0
	900 °C/1 h	0.31	–
	900 °C/2 h	0.21	–
	1000 °C/1 h	0.03	23.6
	1000 °C/2 h	0.01	–
	1100 °C/1 h	<0.01	13.7

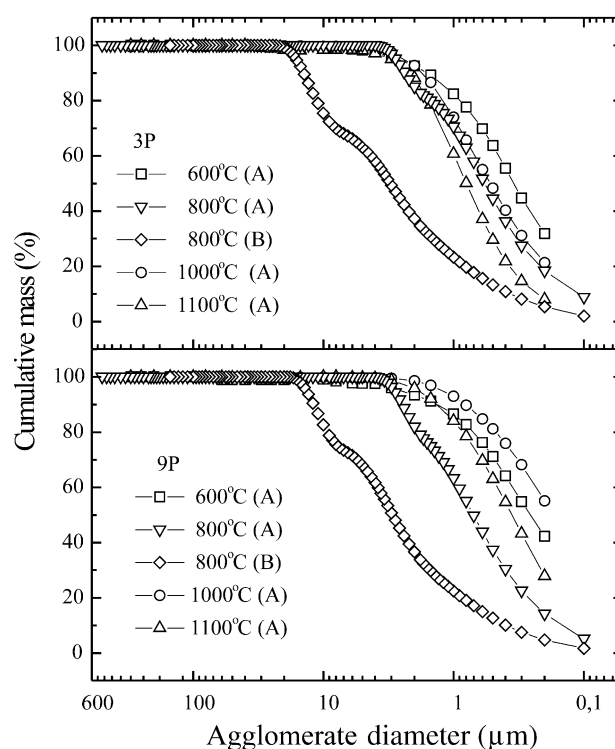Fig. 1. TG-DTA curves for the as-dried coprecipitated powders.

Fig. 2. Cumulative size distributions of 3 and 9 mol% yttria stabilized zirconia powders, as a function of calcination and milling conditions (A = attrition milling, B = ball milling).
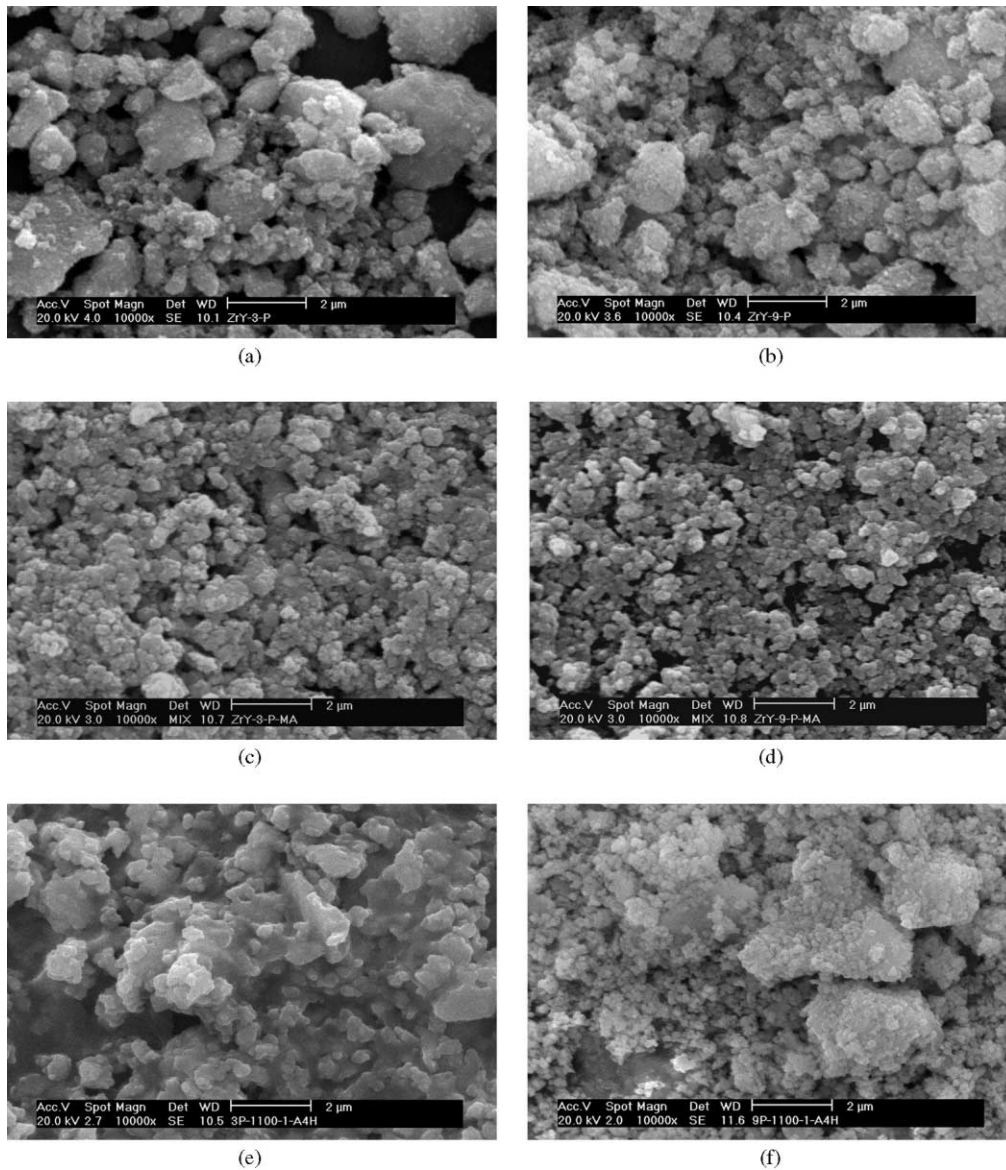
Fig. 3. SEM micrographs of 3 and 9 mol% yttria stabilized zirconia powders, as a function of calcination and milling conditions: (a) 3P-800-B, (b) 9P-800-B, (c) 3P-800-A, (d) 9P-800-A, (e) 3P- 1100-A and (f) 9P-1100-A (A = attrition milling, B = ball milling).

rising of as-sintered pellets density is not always observed in the densification curves shown in Fig. 4. At 1350 °C, the relative density of ceramics, prepared from powders calcined at 600 and 800 °C, is upper to 95% TD. These results indicate that in this sintering condition sulphur elimination, increasing calcination temperature decreases the powder reactivity and therefore the ceramic density. When sintering was conducted at 1550 °C another behaviour was observed, especially for the pellet 3P, prepared by uniaxial and isostatic pressing of powders calcined at 800 °C. The final porosity of this sample is probably a consequence of SO_3 evolution during the densification process.[29] It seems that gas entrapping is promoted by higher green density values and by the enhancement of densification kinetics. This

later behaviour is a consequence of good reactivity of powders and higher sintering temperature. This effect is not so remarkable for the 9P samples, possibly because of the differences observed in the sintering kinetics of cubic phase. It was also noticed in this set of experiments that isopressed pellets, produced from powders calcined at 600 °C, collapse during sintering. Probably, the higher densification rate of reactive powders increases the pressure inside the pores, after SO_3 evolution. From the above considerations, it was observed that stabilized zirconia powders containing sulphur as an impurity can be used to produce high density ceramics. Among the conditions investigated in this study, it was concluded that 800 °C is the best calcination temperature for this purpose.

Table 2
Relative density values of 3 and 9 mol% yttria stabilized zirconia green pellets, prepared by uniaxial (U) and association of uniaxial and isostatic (U/I) pressing, as a function of calcination and milling conditions

Calcination conditions	Milling equipment	Relative density (%)	
		3P - U	3P - U / I
600 °C / 1 h	Attrition mill	39.1±0.3	46.2±0.5
800 °C / 1 h	Attrition mill	41.3±0.5	48.5±0.8
	Ball mill	37.0±0.3	43.8±0.2
1000 °C / 1 h	Attrition mill	45.4±0.3	51.2±0.2
1100 °C / 1 h	Attrition mill	53.1±0.7	57.9±0.2
		9P - U	9P - U / I
600 °C / 1 h	Attrition mill	35.7±0.5	45.8±0.2
800 °C / 1 h	Attrition mill	39.7±0.7	47.0±0.5
	Ball mill	35.0±0.2	43.3±0.2
1000 °C / 1 h	Attrition mill	44.2±0.3	48.8±0.5
1100 °C / 1 h	Attrition mill	48.7±0.3	53.2±0.2

Fig. 5. Pore size distribution of 3 and 9 mol% yttria stabilized zirconia green pellets, prepared from ball (B) and attrition (A) milled powders pressed by uniaxial (U) and association of uniaxial and isostatic (U/I) compaction.
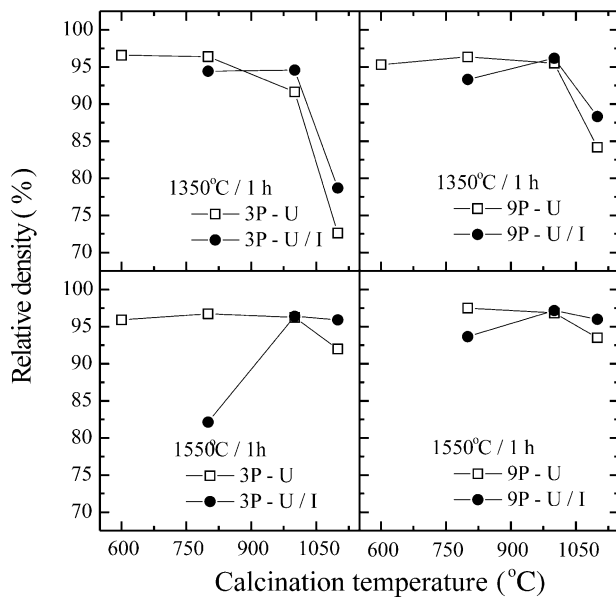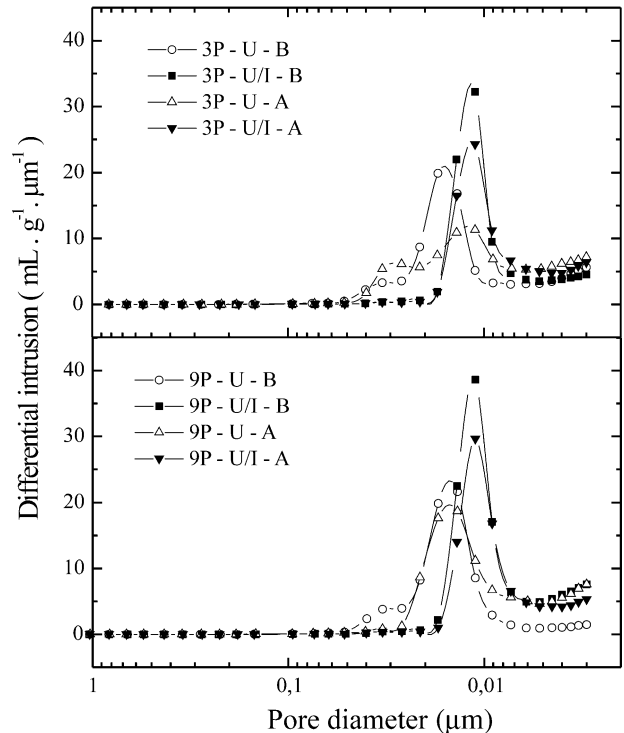

Fig. 4. Relative density values of 3 and 9 mol% yttria stabilized zirconia ceramics, prepared from attrition milled powders, pressed by uniaxial (U) and association of uniaxial and isostatic (U/I) compaction and sintered at 1350 and 1550 °C for 1 h, as a function of calcination temperature.

3.2. Influence of ceramic processing conditions on sintering behaviour

Yttria stabilized zirconia powders, calcined at 800 °C for 1 h and submitted to ball (B) or attrition (A) milling, were evaluated in this set of experiments. As indicated by the characterization results, presented in Figs. 2 and 3, ball milled powders have agglomerates with mean size in the range of 2–3 μm. As was observed with attrition milled samples, these powders are composed by nanometric particles. Specific surface area values are also similar (50–60 m^2 g^{-1}). The pore size distribution in the green pellets are given in Fig. 5. The compacts prepared by association of uniaxial and isostatic pressing have a narrow pore size distribution with a mean pore size diameter of about 10 nm, probably related to intra-agglomerate porosity. Larger pores (25–30 nm) in uniaxial pressed samples indicate the presence of inter-agglomerate porosity. This behaviour shows that agglomerates can easily be destroyed by increasing the compaction pressure.

Linear shrinkage rates of yttria stabilized zirconia pellets, as a function of sintering temperature, are illustrated in Figs. 6 and 7. Below 800 °C small or no shrinkage was detected. Above that temperature a continuous shrinkage was observed and the maximum densification rates were verified in the following ranges: 1060–1110 °C and 1100–1160 °C for 3P and 9P series, respectively. Despite the relative low green density values (Table 2), the presence of only one peak of maximum shrinkage rate, at low temperatures, also indicates the homogeneous porosity distribution in the green compacts.[14,33,34] This behaviour is enhanced by the elimination of inter-agglomerate porosity at higher compaction pressure (Fig. 5). Densification curves of samples 3P-U-B and 3P-U/I-B (Fig. 6) confirm this statement.

During the intermediate stage of sintering, densification curves are quite similar. On the other hand, at the final stage, an unusual expansion occurs for 3P-U/I-A sample, causing a great density reduction. As mentioned earlier, this phenomenon may be a consequence of SO_3 evolution during sintering.

Fig. 8 shows the densification results of yttria stabilized zirconia compacts, as a function of sintering temperature. It was observed that density reduction of the
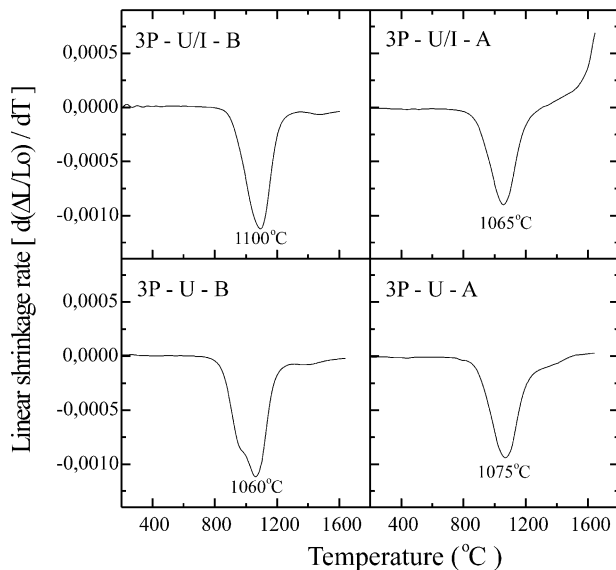

Fig. 6. Linear shrinkage rate as a function of sintering temperature of 3 mol% yttria stabilized zirconia ceramics, prepared from ball (B) and attrition (A) milled powders pressed by uniaxial (U) and association of uniaxial and isostatic (U/I) compaction.
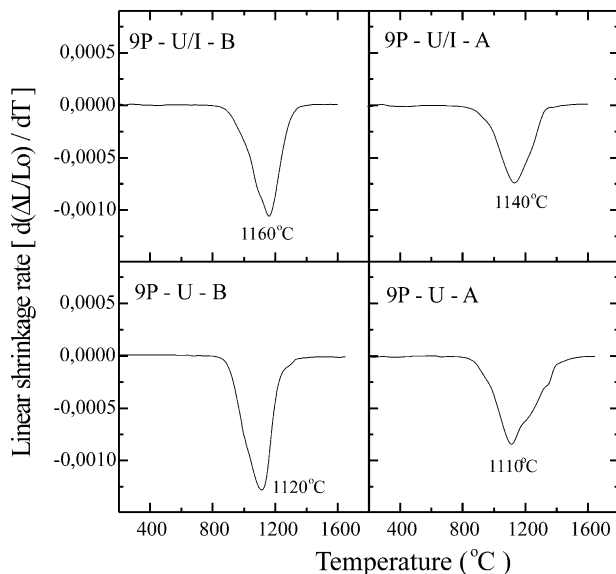
3P samples, pressed at high pressures (U/I), occurs above 1350 °C. It could be assumed that below 1350 °C there is enough time for SO_3 gas to escape from the ceramic body, due to the slower densification rate determined by this sintering condition. Considering this hypothesis, the promotion of sintering kinetics, by the increase of the sintering temperature, may contribute to the entrapping of this gas in zirconia ceramics. A similar effect was observed for yttria stabilized zirconia samples containing residual chlorines, sintered by fast heating rate (500 °C/min) until 1430 °C for 1 h.[31] The density reduction of Y-TZP ceramics can also be associated to the lower thermal conductivity of nanocrystalline microstructure. In this case it is supposed that the external surface of the sample densifies faster than inside.[35]

Density values of 9P samples increase as the sintering temperature is raised, despite the slight decrease observed above 1500 °C for isopressed ceramics. The influence of compaction pressure also depends on milling condition. Better densification is observed for pellets prepared by isopressing ball milled powders, while for attrition milled powders density is improved by uniaxial pressing. These results confirm that the presence of cubic phase in 9P sintered samples seems to decrease the deleterious effect of the entrapped SO_3.

Fracture surface of the as-sintered yttria stabilized zirconia pellets are shown in the SEM micrographs (Figs. 9 and 10). For samples stabilized with 3 mol% of Y_2O_3, the grain size is smaller than 1 μm. Intergranular porosity is observed when samples were isopressed and sintered at higher temperatures. Zirconia ceramics containing 9 mol% of yttria are formed by grains larger

Fig. 7. Linear shrinkage rate as a function of sintering temperature of 9 mol% yttria stabilized zirconia ceramics, prepared from ball (B) and attrition (A) milled powders pressed by uniaxial (U) and association of uniaxial and isostatic (U/I) compaction.
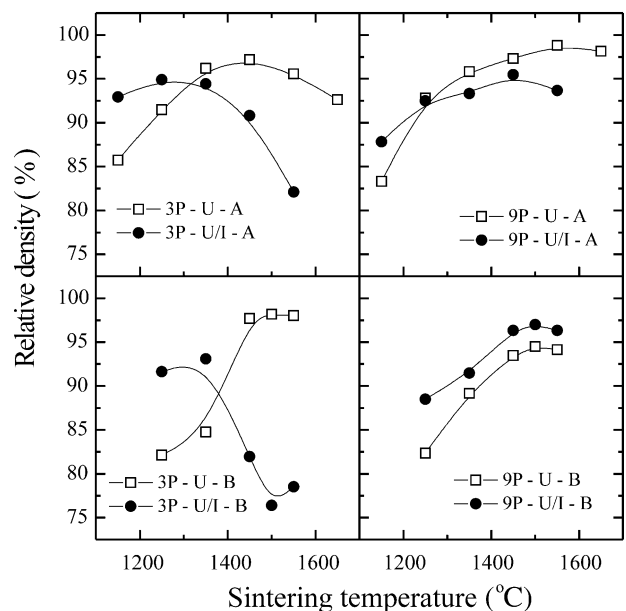

Fig. 8. Relative density values as a function of sintering temperature of 3 and 9 mol% yttria stabilized zirconia ceramics, prepared from ball (B) and attrition (A) milled powders pressed by uniaxial (U) and association of uniaxial and isostatic (U/I) compaction.
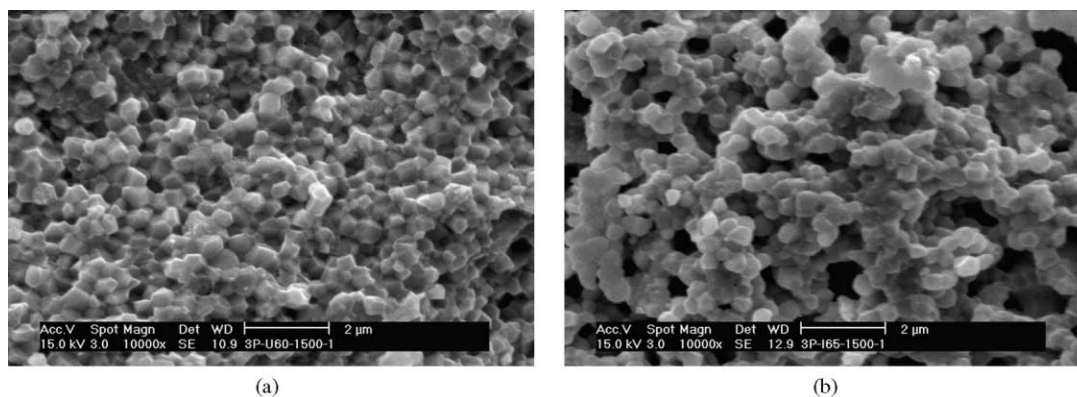
Fig. 9. SEM fracture surface micrographs of 3 mol% yttria stabilized zirconia ceramics sintered at 1500 °C for 1 h: (a) 3P-U-B and (b) 3P-U/I-B.
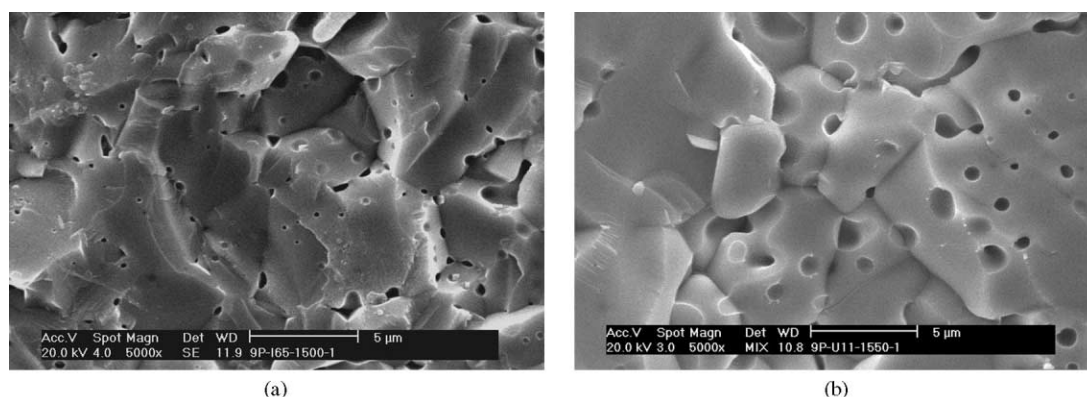

Fig. 10. SEM fracture surface micrographs of 9 mol% yttria stabilized zirconia ceramics sintered at 1500 and 1550 °C for 1 h, respectively: (a) 9P-U/I-B and (b) 9P-U-A.

than 5 μm in size, with intragranular fracture and porosity.

From the above discussion it is possible to suggest the following processing conditions for yttria stabilized zirconia powders containing sulphur impurity: ball milling with zirconia media, uniaxial pressing for 3P powders, association of uniaxial and isostatic pressing for 9P powders and sintering at 1500 °C for 1 h. These conditions allow the reaching of relative density values of 98% TD and 97% TD, respectively.

Attrition milling also allows the production of high density zirconia ceramics: 97% TD and 99% TD for 3P and 9P samples, prepared by uniaxial pressing and sintering at 1450 and 1550 °C for 1 h, respectively.

4. Conclusions

The present study shows that sulphur present as an impurity, originated from the precipitation of zirconium basic sulphate, can be removed from stabilized zirconia powders during calcination at elevated temperatures (> 1000 °C), decreasing the specific surface area of these powders and therefore the densification rate.

However, it was verified that the presence of sulphur is not always harmful for the production of zirconia ceramics, allowing the calcination of coprecipitated powders at 800 °C. The optimization of ceramic processing conditions of 3 mol% yttria stabilized zirconia powders has shown that SO_3 gas entrapping is minimized during sintering at high temperature, if the density of the green sample is relatively low. This result was associated with the slow densification rate of this compact, which leads to porosity reduction. Dense Y-TZP ceramics were prepared from ball milled powders, pressed by uniaxial compaction and sintered at 1500 °C for 1 h. Density as high as 98% of the theoretical value was achieved.

For 9 mol% yttria stabilized zirconia ceramics, no correlation was found between SO_3 evolution and green and final density results. In spite of the presence of intragranular porosity in sintered samples, high density values (99% TD) were obtained for attrition milled powders, pressed by uniaxial compaction and sintered at 1550 °C for 1 h. Ball milling was also considered a good process for isopressed compacts sintered at 1500 °C for 1 h, despite the slight decrease of ceramic density (97% TD).

Acknowledgements

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