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Colloidal processing, sintering and mechanical properties of zircon ($ZrSiO_4$)

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Abstract

Dense Zircon ceramics were prepared from a commercial Zircon powder via the colloidal route, and critical processing variables were explored. To achieve highly dispersed suspensions, the zeta potential of Zircon was evaluated by adding different concentrations of a dispersant (ammonium polyacrylate). Zircon suspensions with high solid loading were slip cast in plaster molds and sintered at different temperatures. Final density was evaluated considering the amount of dispersant used in the original suspension. Crystalline phases were analyzed. Partial dissociation was observed in materials fired at 1600 and 1680 °C. Microstructure and mechanical properties, Vickers Hardness (Hv) and Fracture toughness (K_1c), were evaluated and explained in terms of dispersant content, sinterization and partial dissociation. The achieved mechanical properties (Hv:8.5 GPa and K_1c:1.7 and 2.7 MPa/$m^{1/2}$) were also compared with the values obtained by other authors who used different processing routes.

Keywords: C. Mechanical properties; Colloidal processing; Zircon

1. Introduction

Zircon is an easily accessible raw material, and Zircon ceramics has interesting physical and chemical properties for technological use. Its main properties are: a moderately low linear thermal expansion (4.10^{-6} °C^{-1}) [1] and a high dissociation temperature (1675 °C) [2]. It is also highly inert, even in contact with molten glass or slag. That is why it is used in applications at elevated temperatures (1300–1500 °C) with low chemical attack, as in the steel or glass industry.

Due to their high melting point, high density sintered ceramics from pressed powders are difficult to achieve. Additives or their combination with other phases such as SiO_2 TiO_2, Al_2O_3, clays, etc. are commonly used to increase the final density and reduce porosity. However, these additions may be detrimental to mechanical properties such as hardness or fracture toughness.

To achieve high densification of Zircon materials, it is also possible to use advanced sintering techniques such as Spark Plasma Sintering [1] (SPS). In fact, because of SPS high cost and the geometry restriction associated to the uniaxial pressing inherent to this technique, its access is limited. To improve the processing of the starting powder using high energy milling is also possible, although it can be extremely expensive and difficult to scale up to industrial production.

The slip casting technique is an adequate route to obtain materials from powders. Well dispersed suspensions can be packed at high relative green densities without causing large pores or agglomerates. A poor dispersion of powders in suspension makes densification difficult and the presence of agglomerates is responsible for poor mechanical properties.

Studies of colloidal processing using different materials such as TiO_2 [3], Al_2O_3 [4], MgO [5] and ZrO_2 [6] among others were done in the past. It has been widely demonstrated that this processing route is suitable for obtaining materials of a high density, with no agglomerations, and without using additives. Two advantages of this route are: its capacity for obtaining a wide range of geometries, and its relatively low cost. Earlier studies were performed on the processing of Zircon and

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Zircon–Alumina mixtures adopting different approaches. Garrido et al. [7,8] studied the effect of pressure filtration of mixed Zircon–alumina suspensions but they did not have an approach to the effect of the dispersant on the final mechanical properties. Moreno et al. [9,10] also studied the colloidal processing of Zircon but without relating the effect of the processing to the mechanical properties.

Zircon based materials are industrially prepared by slip casting in plaster molds, vibro cast or they are pressed in metallic matrix. The optimization of the colloidal processing has proved to be a suitable route for studying its dispersability in order to improve the final properties. This method is still being used and is under research for different materials.

In this work, a commercially Zircon powder without previous treatment (milling)- is formed and sintered using the slip cast route. The optimum experimental conditions for colloidal processing of the suspension were determined by measuring the zeta potential, the effect of pH, and the particle size in relation to the dispersant content. The final sintered material is also analyzed by testing the densification degree, the phase evolution, and the effect of dispersant addition on density. Mechanical properties as Vickers hardness (Hv) and Fracture toughness (K_{IC}) are related to the processing parameters.

2. Materials and methods

2.1. Suspension, preparation and characterization

Commercial Zircon powder (Mahlwerke Kreutz Mikron, Germany) was used. The chemical composition is (wt%): ZrO_2:64–65.5, SiO_2:33–34, $Fe_2O_3 \leq 0.1$, $Al_2O_3 \leq 0.1$, $TiO_2 \leq 0{,}15$. The average particle size is D_{50}=2.0 μm, and it has a surface area of 4.1 m^2/g. The theoretical density of 4.56 g/cm^3 was used for calculations.

Suspensions with a solid content of 75 wt% (39.5 vol%) were prepared using different ammonium polyacrylate (Dolapix CE64, Zchimmers and Schwartz) content: 0.0, 0.1, 0.3, 0.5 and 1 wt% related to the total solid loading.

The suspensions were prepared by adding the dispersant to the distilled water and the pH was controlled with NH_4OH. The powder was added to the stirred water solution using a Qsónica Q500 sonicator with 40% of intensity, 10 s pulse and pauses of equal length. This treatment enhances dispersion and breaks the particle agglomerates.

2.2. Sample preparation and forming

The suspensions were prepared as it was mentioned above. The mean particle size was measured as a function of the pH with a Sedigraph 5000D Micromeritics. The zeta potential was determined by electroacustic technique on a 1 vol% suspension -with (0.1 wt%) and without dispersant 7,8- using a ESA 8000 Matec Instrument equipment.

The consolidation of the suspension by slip casting was carried out in plaster moulds obtaining discs of 5 cm of diameter and 5 mm of thickness. The compacts were cut in pieces and dried for 24 h at room temperature and then at 110 °C up to a constant weight. Green density and relative density (% of the theoretical) were measured by Archimedes method in kerosene (density 0.788 g/cm^3).

2.3. Sintering and characterization

Samples were sintered at different temperatures (1000, 1100, 1200, 1300, 1400, 1500, 1600 and 1680 °C) at a heating rate of 5 °C/min and a soaking time of 2 h at the maximum temperature. Sintered density was measured with the Archimedes method in water. Phase evolution was followed by XRD with a Phillips 3020 goniometer Cu-*K*α radiation and Ni filter at 40 kV–20 mA. Mechanical properties were measured on polished samples and flat surface. Vickers hardness (Hv) was evaluated by indentation method with a Buehler Indentamet 1100 equipment at 0.5 and 1 kg loading for 15 s. Fracture toughness (K_1c) was determined by using the indentation method by which the crack length was measured with a 3.0 kg of loading and it was calculated using the following equation [11]:

$$K_{IC} = \delta\left(\frac{E}{H}\right)^{1/2}\frac{P}{C^{3/2}} \quad (1)$$

where E is the elastic modulus (240 GPa for Zircon); δ is a material constant $=0.018$; H=Vickers hardness; P is the loading (3 kg) and C is the crack length in mm[8].

3. Results and discussion

3.1. Suspension characterization

A ceramic material prepared by colloidal processing requires optimization and study of many variables which depend on different factors. To achieve dense ceramic materials, it is necessary to work with an optimum amount of dispersant content and a pH at which the dispersant used operates with maximum dispersion.

The zeta potential of Zircon suspension was measured with and without dispersant addition. Fig. 1 shows the variation of the zeta potential of Zircon particles as a function of pH.

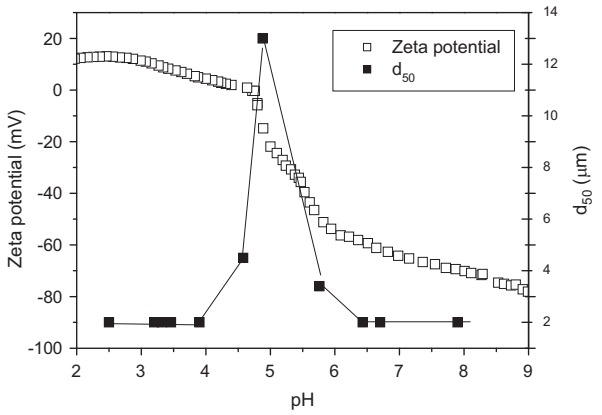

Fig. 1. Zeta potential and mean particle size as a function of pH suspension.

In agreement with previous works [12,13], it was observed that the isoelectric point of Zircon without the addition of dispersant is near pH 5. Then, the particles increased their surface charge up to −80 mV at pH 9. In suspension, particles with low surface charge tend to agglomerate. The pH control and the addition of polyelectrolyte as dispersant not only produced an esteric stabilization but also increased the surface charge in order to produce high electrostatic repulsion among particles. This fact increased the dispersion degree of particles which was made evident when particle size distribution was analyzed. Fig. 1 also shows the average particle size as a function of pH suspension. It was observed that the larger particle size resulted at pH between 4 and 6, where the zeta potential was close to zero thus producing low dispersion, agglomeration and, consequently, a high average particle size. At a pH higher than 7, the high zeta potential allowed to obtain a dispersed suspension presenting a low particle size.

For the Zircon slip with adsorbed dispersant (Fig. 2), the zeta potential showed the zero charge at pH = 3.5. From pH 4, the surface charge increased the negative value up to −140 mV at pH between 7 and 9. The ceramic suspension remained dispersed in water due to the high zeta potential of the particles generating important electrosteric repulsion among them. Consequently, a good dispersion of Zircon powders was expected at a pH higher than 7. Fig. 2 also showed the variation of Zircon particle size with pH; this figure indicates that agglomeration existed at pH between 3 and 5, having a maximum particle size in accordance with zeta potential measurements. From pH 5, the particle size attained the minimum value evidencing good dispersability.

The suspensions were also prepared at a pH near 9 using dispersant. The amount of dispersant was an important factor to be taken into account. An excess of a polyelectrolyte [7] could generate an increase in the ionic strength, followed by a compression of the electric double layer. Consequently, agglomerates were formed by this coagulation effect. An insufficient amount of dispersant could also generates agglomeration. Only a well-dispersed suspension with no agglomeration can generate a better packing of particles during slip casting. This effect was evaluated after forming the material by measuring the green density.

Fig. 3 shows the green density as a function of the amount of dispersant. It was observed that a relative low green density was obtained without dispersant addition, even if the zeta potential is −80 mV at pH 9 as it is shown in Fig. 1. The dispersant addition generated an increment in the zeta potential charge and the degree of agglomeration was reduced. Dispersant content higher than 0.3 wt%, must be considered an excess of dispersant addition which also produces agglomeration. This agglomeration effect can be attributed to the increase in the ionic strength and it was evaluated observing a reduction of the relative green density.

The suspensions prepared at pH 9 and 0.3 wt% of dispersant (Fig. 2) generated better particle packing and maximum green density that is why this was considered the optimum processing condition to prepare a well dispersed Zircon suspension for slip casting.

3.2. Sinterability

The effect of the dispersant was not only evident on the green density or viscosity, as it is reported in previous works [7,8], the effect of the agglomerates on a suspension was also evident after the sintering process. Agglomeration affected the final microstructure and properties of the sintered material. They are a cohesive group of particles present in a suspension which cause high microestructural heterogeneity in green and sintered bodies. During sintering, shrinkage was produced in the agglomerates before it was produced in the bulk material. Consequently, each agglomerate generated inter-agglomerated pores which are very difficult to remove when temperature increases.

Fig. 4 shows the sintering curves of the different Zircon compacts as a function of the dispersant content of the original suspension. It was observed that compacts with high green density reached the highest densification at each temperature.

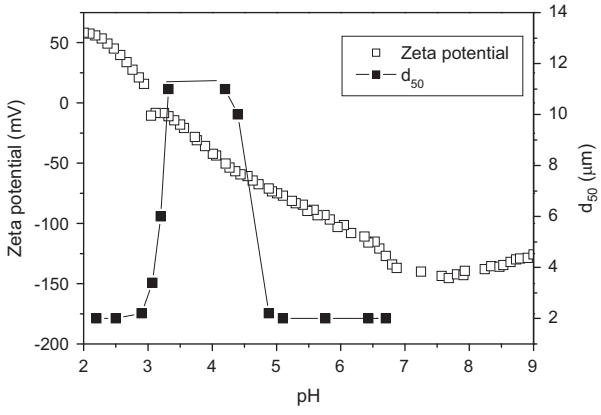

Fig. 2. Zeta potential and mean particle size (d50) as a function of pH for Zircon slip with adsorbed dispersant. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

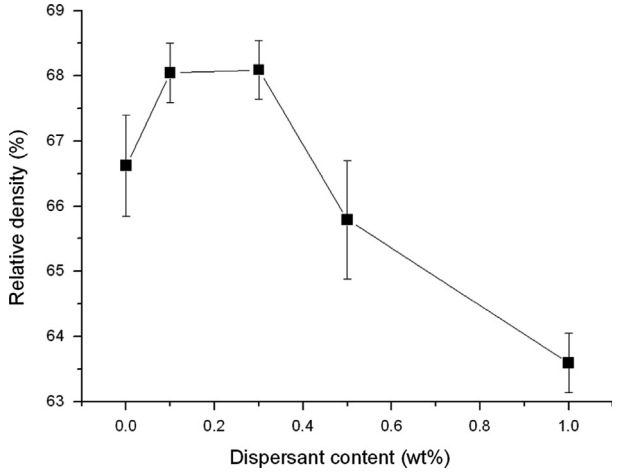

Fig. 3. Relative green density as a function of the amount of dispersant (wt%). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Bodies with some kind of agglomeration content showed a low final density remaining likewise at all the studied temperatures. The optimum amount of dispersant required to obtain high stabilization and higher density is 0.3 wt%. Compacts prepared with 0.1 wt% of dispersant had similar characteristics. These suspensions consolidated by slip casting and sintered in a material with maximum density and minimum porosity, as shown in Fig. 4, confirm that using 0.3 wt% was the optimum amount of dispersant.

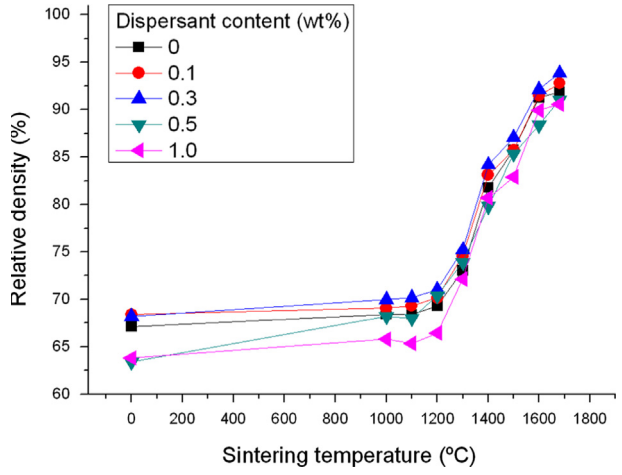

Fig. 4. Zircon relative density as a function of sintering temperature for different dispersant content. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

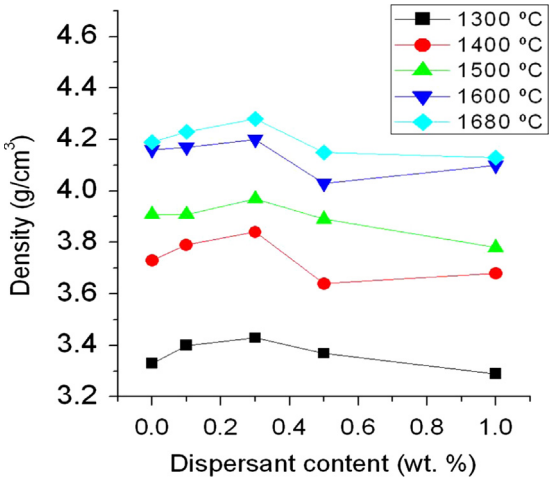

Fig. 5. Effect of the dispersant content on the sintered density as a function of the dispersant content at different temperatures.

Fig. 5 shows the densification curves by plotting density as a function of the dispersant content at different temperatures. This graphic shows that for each isothermal the curve shows a high density for those suspensions prepared with 0.3 wt% of dispersant thus, supporting the observation that a well-dispersed suspension produces less porosity which results in higher density.

Also, in Fig. 6, the effect of dispersant content on the microstructure of samples sintered at 1600 °C and prepared with different dispersant concentration is observed. The images present homogenous distribution of porosity with similar morphology and size. Qualitative observation allowed to determine that extreme dispersant content, 0 and 1 wt% produced large porosity with some pores larger than the average ones, possibly produced by the initial inter agglomeration sintering.

The optimum dispersant content (0.3 wt%) as well as the samples presented some porosity. This was due to the characteristics of Zircon which is difficult to sinter, especially with coarse initial powder as it was studied in the present work. However, the microstructure obtained with the optimum dispersant content (0.3 wt%) presented homogeneous and small size pores.

An optimum colloidal processing minimized agglomerations and the porosity of sintered material and green compacts as well. The excessive or insufficient dispersant content also produced agglomeration and porosity which was made evident in the density level of green sintered compacts and when observing the microstructure.

3.3. Mechanical properties

The process of obtaining an optimum slip dispersion of particles was necessary to achieve the maximum mechanical properties of ceramics. The porosity produced a diminution in the mechanical properties.

Vickers hardness (Hv) as a function of dispersant content was measured for the Zircon material sintered at 1600 °C. Fig. 7 shows these results. It was observed that a well dispersed suspension allowed to obtain a better packing of particles in a green compact which remained as a well compact material after the sintering process. The Vickers hardness presented its maximum at 0.3 wt% of dispersant, supporting the idea that a well stabilized suspension generates a better hard ceramic (H_V: 8.5 GPa). Fig. 8 shows the fracture toughness (K_1c) behavior as a function of the dispersant content at 1600 °C. At this temperature, no dissociation took

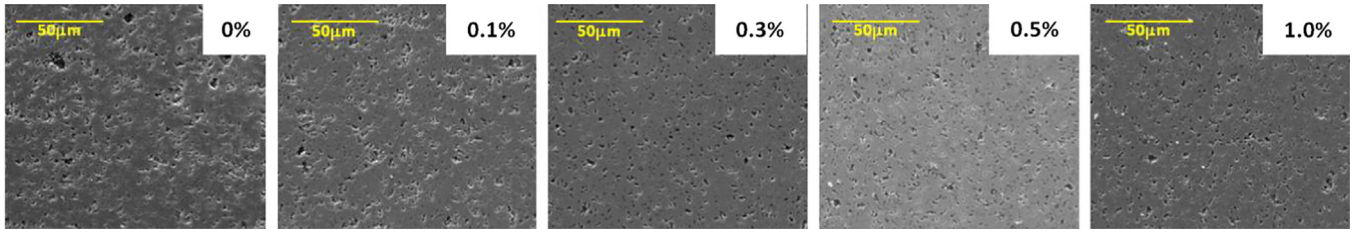

Fig. 6. SEM micrographs of Zircon samples at sintered 1600 °C prepared with different dispersant content.

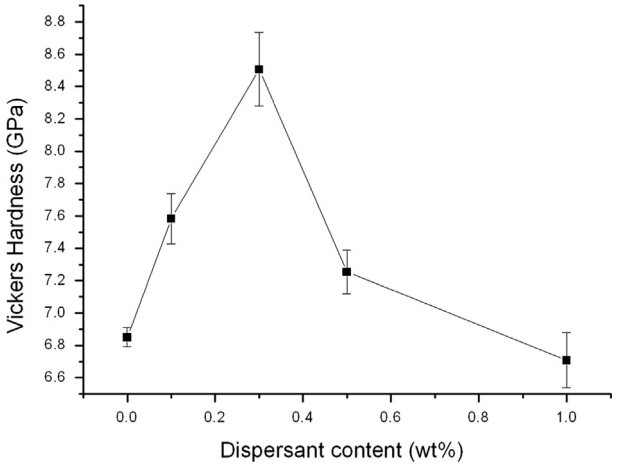

Fig. 7. Vickers hardness (Hv) of Zircon samples sintered at 1600 ºC as a function of dispersant content. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

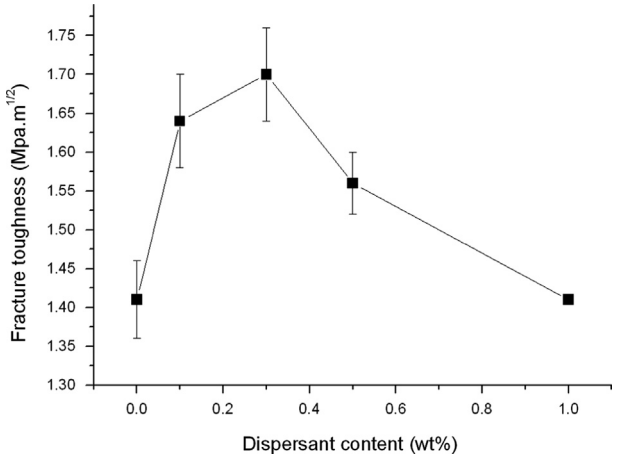

Fig. 8. Fracture toughness for Zircon materials sintered at 1600 ºC as a function of dispersant content.

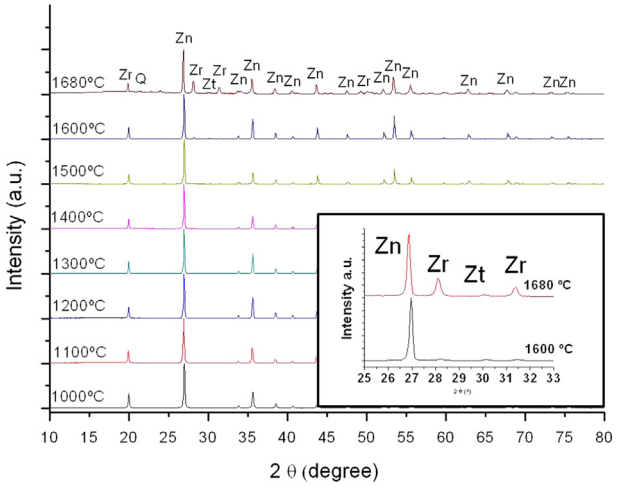

Fig. 9. XRD patterns of Zircon at different sintering temperatures. Zn=Zircon ($ZrSiO_4$), Zr=Monoclinic Zirconia (m-ZrO_2), Zt=Tetragonal Zirconia (t-ZrO_2) and Q=Quartz (SiO_2).

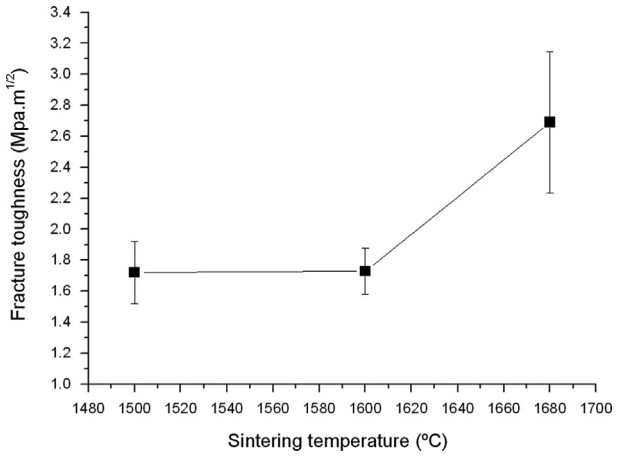

Fig. 10. Fracture toughness as a function of temperature (°C) for samples prepared with 0.3 wt% of dispersant.

place and porosity was the main factor affecting this measure therefore, the higher the porosity, the lower the fracture toughness. Samples prepared with 0.3% of dispersant presented the higher fracture toughness: K_1c: 1.7 (MPa/$m^{1/2}$).

Zircon can dissociate in SiO_2 and ZrO_2 at temperatures higher that 1500 °C depending on the system conditions [2,11,14,15]. The Silica can produce a glassy phase, which is not possible to observe by XRD, this glass phase can crystallize into quartz or cristobalite which can be detected by XRD. Zirconia, the second product of Zircon dissociation, can also be observed by XRD. At room temperature, monoclinic Zirconia (m-ZrO_2) is the stable form. However, if the particle size is small enough the high energy tetragonal phase (t-ZrO_2) can be stabilized and detected at room temperature. The Zirconia present in the material suffers a martensitic transformation which can enhance the fracture toughness [15,16].

Fig. 9 shows the XRD of the sintered samples where ZrO_2 peaks appeared at 1600 °C, and became more important at 1680 °C. It can be observed that at 1680 °C near $2\theta=21°$ a low peak of quartz was detected (quartz highest peak is at 26.7° overlapped with the Zirconia one). Most of the silica formed was not crystalline and apparently formed a glassy phase. The peaks of monoclinic Zirconia (around $2\theta=28°$ and $2\theta=31°$) were evident at temperatures over 1600 °C coming from the Zircon dissociation. Even smaller t-ZrO_2 peaks were seen in the sintered samples. It is important to point out that the dissociation observed by XRD was corroborated with both SEM and EDX local chemical analysis.

This dissociation is known to be responsible for fracture toughness reinforcement by transformation toughening mechanism and micro cracks formation among other mechanisms [16,17].

Fig. 10 shows this effect and at temperatures higher than 1600 °C, with the dissociation of Zircon, the fracture toughness increased up to values similar to those presented by other authors for materials with pressureless sintering (K_1c: 2.7 MPa/$m^{1/2}$) [9,18,19].

Table 1 shows a comparison of some data obtained by other authors with the results of this work. The results presented here are comparable to others done under similar conditions.

Table 1
Comparison of properties of dense zircon ceramics with the data reported in literature.

Method	Maximum temperature, holding time and pressure	Relative density (%)	Hv (GPa)	K_{IC} (MPa/m $^{1/2}$)	Dissociation
Pressureless sintering without sintering additives [9,18]	1600 °C; 2–48 h; pressureless	95	–	2.2–2.8	Yes
Pressureless sintering with sintering additives [20,21]	1500 °C 1 h; pressureless	90–95	11–12	–	Yes
Sintered from pure amorphous SiO_2–ZrO_2 [22]	1500 °C; 4 h; pressureless	99.7	–	–	Complete formation
Hot pressing of pure Zircon powders obtained by sol–gelwithout sintering additives [19]	1600 °C; 1 h; 25 MPa	99.1	10	3.0	No
SPS of high energy milled commercial Zircon powder without sintering additives [1]	1400 °C; 10 min; 100 MPa	≈99.5	11.4–13.7	3.6	No
Colloidal processing, sintering and mechanical properties of Zircon ($ZrSiO_4$) [Present study]	1600 °C; 2 h min; pressureless	≈92	8.5	1.7	No
Colloidal processing, sintering and mechanical properties of Zircon ($ZrSiO_4$) [Present study]	1680 °C; 2 h min; pressureless	≈94	8.6	2.7	Yes

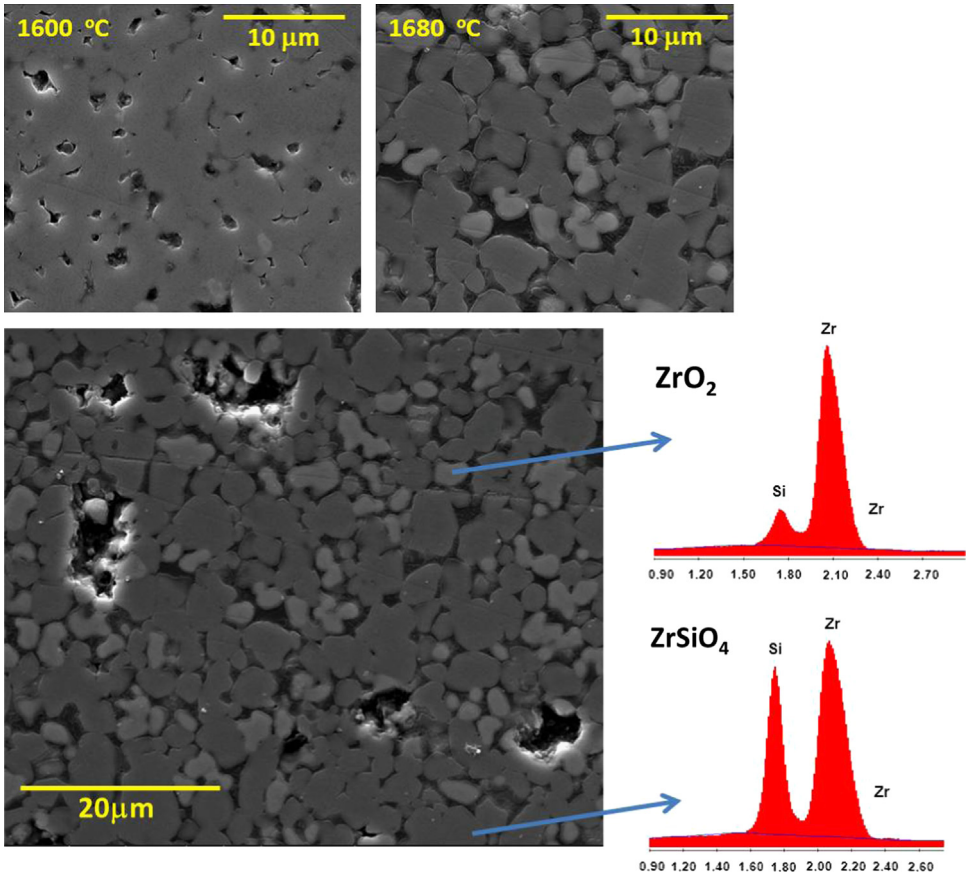

Fig. 11. SEM micrograph of Zircon samples showing dissociation at 1600 and 1680 °C with EDX analysis of different grains.

The increment in fracture toughness observed in Fig. 10 is well documented in literature. Zircon dissociated in silica and Zirconia producing the transformation toughening mechanism in Zirconia grains [16,17].

Fig. 11 shows the SEM images of the samples fired at 1600 and 1680 °C, dense microstructures can be clearly observed in both images. Round and sintered middle gray Zircon grains which show some porosity can be observed in the first one. The round Zircon grains are accompanied by smaller (also round) light gray Zirconia grains. The presence of a darker glassy phase can be observed round some Zirconia grains. The phases were identified by a EDX analysis, shown in Fig. 11 as well. The analysis corresponds with the XRD analysis, and the observed mechanical enhancement effectively revealed that Zirconia appeared in low quantity at 1600 °C, but it was more evident at 1680 °C. The SEM micrograph with EDX analysis showed that the white grains formed at high temperature were actually Zirconia.

4. Conclusions

Commercial Zircon powder-without previous treatment- was employed in water suspensions and casted in plaster molds. The optimum conditions of dispersant content and pH were studied. The dispersant content (ammonium polyacrylate) was optimized by measuring the zeta potential, the particle size and the initial green density of the material. A dispersion of Zircon powders was expected at a pH higher than 7. Agglomeration existed at pH between 3 and 5, observing a maximum particle size in accordance with zeta potential measurements. The samples sintered from 1000 to 1680 °C showed a progressive increment in density related to the dispersant content in the slip. The suspensions prepared with 0.3 wt% of dispersant support the observation that a well dispersed suspension produces a lower porosity resulting in a high density material. The Vickers hardness (H_V) and fracture toughness (K_1c), measured on the sintered materials, depend on the dispersion degree obtained from the starting suspension. Values of H_V: 8.5 (GPa) and K_1c: 2.7 ($MPa/m^{1/2}$) were obtained at 1680 °C, comparable with other Zircon materials obtained by means of different processing routes. XRD analysis showed peaks of monoclinic Zirconia formed at temperatures over 1600 °C coming from the Zircon dissociation. Even smaller t-ZrO_2 peaks were observed after these thermal treatments as well. Dissociation observed by XRD was corroborated in the SEM analysis and the EDX local chemical analysis. This dissociation is known to be responsible for fracture toughness reinforcement by transformation toughening mechanism and micro cracks formation among other mechanisms.

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