Consolidation of complex-shape zircon compacts through agar gelation

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ABSTRACT
Zirconium silicate (zircon, ZrSiO4) is a ceramic material with excellent thermal properties, such as low thermal conductivity and high thermal shock resistance. In this work, dense zircon complex shaped parts were obtained by aqueous gelcasting through agar gelation. The colloidal stability study was performed through zeta potential measurements as a function of pH and polyacrylic-based deflocculant concentration (PAA). The rheological study was carried out varying the solids content, the dispersant concentration, and the sonication mixing time, the best results being obtained for 0.1 wt.% PAA and 1 min sonication. The viscosity versus temperature curves were recorded on cooling for the zircon-agar mixtures showing a gelling temperature of approximately 35°C. Better gelcasting performance was achieved with suspensions prepared at a solids loading of 40 vol.%. Dynamic sintering (25–1550°C) and isothermal sintering tests (1550°C and 1600°C) were carried out, studying the shrinkage and densification of the material. Finally, the evolution of phases and the microstructure of the sintered parts were studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Relative densities of 94.5% TD were reached at 1600°C/2 h, but increased to 96% with 8 h holding, with a small grain size increase from 1.8 to 2.4 µm.

1. Introduction
Zircon is an abundant and inexpensive ceramic material widely used for the production of refractories applied in the steel and glass industry (Kaiser, Lobert, & Telle, 2008; Mel’nikova, Nesterova, & Razdol’skaya,
The excellent thermal properties of zircon, such as low heat conductivity coefficient (5.1 W/m°C at room temperature and 3.5 W/m°C at 1000°C) (Rendtorff, Garrido, & Aglietti, 2008), low thermal linear expansion (4.10⁻⁶ °C⁻¹ from room temperature to 1400°C) (Rendtorff et al., 2012a), high resistance to chemical attack and to thermal shock (Rendtorff et al., 2008, 2011), and high dissociation temperature (1675°C) (Kaiser et al., 2008) make it an ideal material for high temperature applications.

Besides having excellent thermal properties, zircon can reach good mechanical properties, such as high hardness and fracture toughness, if high relative densities are achieved in the final parts. This is a difficult task due to the low sinterability of zircon, which requires the use of temperatures close to the melting point. Therefore, to achieve high densities in this type of material, an accurate control of shaping and sintering steps becomes essential.

Looking at the literature, one can find numerous works reporting the density obtained for zircon parts shaped and sintered by different methods. Table 1 summarizes the final densities obtained for zircon materials according to the literature. One of the most widely accepted strategies

| Date   | Shaping method                      | Sintering method            | Relative density (%) | Ref.          |
|--------|-------------------------------------|-----------------------------|----------------------|---------------|
| 1986   | Slip casting                         | Pressureless sintering (1600°C/4 h) | ≈ 95 | Moreno et al. (1986) |
| 1997   | Isostatic pressing (200 MPa)         | Pressureless sintering (1615°C/8 h) | ≈ 95 | Carbonneau et al. (1997) |
| 2008   | Attrition milling, isostatic pressing (30 MPa) | Pressureless sintering (+SiO₂, 1500°C/1 h) | ≈ 95 | Lee and Kang (2008) |
| 2015   | Slip casting                         | Pressureless sintering (1600°C/2 h) | ≈ 92 | Suárez et al. (2015) |
| 2012   | Attrition milling, axial pressing (250 MPa) | Pressureless sintering (+Al₂O₃, 1600°C/1 h) | < 85 | Anjali et al. (2012) |
| 2018   | Hydrothermal-assisted sol-gel, isostatic pressing (15 MPa) | Pressureless sintering (+ZrO₂, 1400°C/6 h) | < 95 | Ding et al. (2018) |
| 2021   | Ball milling, axial pressing (25 MPa) + isostatic pressing (100 MPa) | Pressureless sintering (+TiO₂, 1400°C/2 h) | ≈ 97.5 | Gauna et al. (2021) |
| 2021   | Ball milling, axial pressing (25 MPa) + isostatic pressing (100 MPa) | Pressureless sintering (1500°C/2 h) | ≈ 93.5 | Gauna et al. (2021) |
| 2018   | Ball milling, isostatic pressing (1000 MPa) | Pressureless sintering (1500–1600°C/2 h) | > 99 | Gauna et al. (2018) |
| 1997   | Sol-gel                             | Hot-pressed (1600°C/1 h, 25 MPa) | ≈ 98.5 | Shi et al. (1997) |
| 2012   | Ball milling                         | SPS (1400°C/10 min, 100 MPa) | ≈ 99.5 | Rendtorff et al. (2012a) |
is based on the use of certain sintering additives, such as SiO$_2$ (Lee & Kang, 2008), Al$_2$O$_3$ (Anjali et al., 2012), TiO$_2$ (Gauna, Martinez, Conconi, Suárez, & Rendtorff, 2021), ZrO$_2$ (Moreno, Moya, & Requena, 1986), to promote a transient liquid phase sintering that enhances densification. There are also well-established colloidal shaping methods, such as the slip casting technique (Moreno, Moya, & Requena, 1991; Moreno et al., 1986; Suárez, Acevedo, Rendtorff, Garrido, & Aglietti, 2015), in which stable and well-dispersed slurries can be obtained by using different dispersants, resulting in final materials without agglomerates and with high homogeneity, which lead to high densities without the need for costly pre-treatments. As colloidal shaping methods, it is also worth mentioning those in which pure zircon powders are obtained by sol-gel synthesis routes starting from organic and inorganic precursors (Ding et al., 2018), by hydrolysis of liquid aerosols (Tartaj, Sanz, Serna, & Ocaña, 1994), reverse micelle process (Tartaj, 2004), and micro-emulsion process (Tartaj & De Jonghe, 2000), usually resulting in microstructured and nanostructured materials with enhanced mechanical properties.

Other authors have reported the in situ formation of pure zircon powders from amorphous SiO$_2$ and ZrO$_2$, both by conventional thermal treatments (Tartaj et al., 1996) or using laser post-treatments (Schelz et al., 2008). Probably the most extensively studied processing route consists on the shaping of zircon materials by either uniaxial or isostatic pressing of commercial powders (Carbonneau, Hamidouche, Olagnon, Fantozzi, & Torrecillas, 1997; Gauna, Conconi, Suarez, Aglietti, & Rendtorff, 2018; Gauna et al., 2021), which in some cases need to be previously activated by high energy milling treatments. It should be noted that in those methods in which the materials have been pressureless sintered (without additives), the maximum relative densities achieved for the final parts are $\leq 95\%$. As an exception, it is noteworthy the density above 99% obtained in the work carried out by Gauna et al., employing as shaping method the isostatic pressing of powders but applying a very high pressure (1000 MPa) (Gauna et al., 2018), which largely exceeds the common pressures used in this shaping method, usually around 200 MPa.

Conversely, advanced non-conventional sintering methods, such as hot-pressing (Huang, Li, Wang, Cheng, & Wen, 2017; Shi, Huang, & Yan, 1997) or SPS (Rendtorff 2012a, 2012b), have been developed in recent years, allowing the production of materials with higher densities at lower sintering temperatures and shorter sintering times. However, there are certain limitations to these techniques due to their high cost and the impossibility of obtaining parts with tailored 3D complex shapes.

Another well-known colloidal shaping technique for ceramic materials is gelcasting. This technique is characterized by the possibility of
obtaining complex shaped parts by thermal gelation of ceramic suspen-
sions through the addition of a gelling agent, normally a polysaccharide
such as agar (Huang & Yang, 2010; Nieto, Santacruz, & Moreno, 2014).
These suspensions must be previously optimized by studying the colloidal
stability by means of rheological measurements, taking care also of the
deleterious effect of temperature on the stability of the suspensions. It
is worth mentioning that to the best of our knowledge no previous works
have been reported regarding the manufacture of dense zircon materials
by thermal gelation. The purpose of the present work is to study the
manufacture of zircon compacts using the gelcasting technique with agar,
with the consequent optimization of the different suspensions, as well
as the study of the sintering behaviour and the microstructure of the
sintered specimens.

2. Experimental

The starting raw material was a commercial zircon powder (Zircobit,
Colorobbia, Spain) with an average particle diameter of 1.6 µm and all the
population lower than 5 µm, a specific surface area of 7.9 m²/g and an
average density of 4.462 g/cm³. Particle size distribution was measured by
laser diffraction (Mastersizer S, Malvern, UK), the surface area by one-
point BET method (Monosorb Surface Area Analyser MS-13, Quantachrome,
USA) and the density was measured by He-pycnometry (Multipycnometer,
Quantachrome, USA). The crystalline phases were identified by X-ray
diffraction (XRD; Advance diffractometer, Bruker Theta-Theta, Germany)
demonstrating the unique presence of the peaks associated to ZrSiO₄ (PDF
00-006-0266). More details on the powder characteristics and morphology
are shown in previous paper (Cañas et al., 2022).

As a deflocculant, a commercial ammonium salt of polyacrylic acid
(PAA; Duramax™ D-3005, Rohm & Haas, USA, with 35 wt.% active
matter) was employed. As gelling additive, a commercial agar powder
(Grand Agar, Hispanagar, Burgos, Spain) with an average size of approx-
imately 150 µm was used. Concentrated aqueous solutions of agar were
prepared under overpressure conditions using a pressure cooker at con-
centrations of 6, 8, and 10 wt.%. The agar was introduced into the ceramic
slurries using these differently concentrated solutions but maintaining a
final concentration of agar of 0.5 wt% with regard to the zircon powder
dry weight.

The colloidal properties of zircon diluted suspensions were character-
ized in terms of zeta potential using the laser Doppler velocimetry tech-
nique with a Zetasizer NanoZS instrument (Malvern, UK). Suspensions
were prepared to a total solids concentration of 0.1 g/L using KCl 10⁻²
M as inert electrolyte by pH adjustments with HCl and KOH. The effect of the polyelectrolyte on the colloidal stability was evaluated at the same conditions, measuring the complete curve of zeta potential as a function of pH for diluted suspensions containing PAA at concentrations ranging from 0 to 1 wt% to determine the shift of the isoelectric point (IEP) occurring as a consequence of the addition of anionic polyelectrolyte.

Concentrated suspensions were prepared to solids loadings ranging from 10 to 50 vol.% with different contents of deflocculant (0.05 to 1.5 wt.%) using a sonication probe (dr. Hielscher, UP400S, Germany). Different sonication times (0, 1, and 2 min) were tested to determine the optimum time for an effective dispersion. All prepared suspensions were characterized measuring the flow behaviour using a rotational rheometer (MARS, Thermo Haake, Germany) with a double-cone and plate measuring system with a cone angle of 2° and a diameter of 60 mm. Flow curves were determined at room temperature and in the case of slurries containing agar, measurements were also performed at 60 °C. The rheological characterization was completed measuring the viscosity at constant shear rate (100 s⁻¹) on cooling from 85 °C to room temperature to determine the gelling temperature. The same curves were determined for the agar solutions as a reference of the gelling behaviour. Concentrated suspensions with solids loadings of 40 vol.% were shaped by gelcasting with 0.5 wt.% total agar content using the different solutions described above. Several complex shaped parts were cast to assess the quality of the gelcasting method as a complex-shape manufacturing technique for zircon. Gelcast bodies were left to dry in air for 48 h. Green densities were measured by Archimedes' method in mercury.

Sintering studies were performed by both dynamic sintering and isothermal sintering. Dynamic sintering was studied with a dilatometer (SETARAM TMA Setsys 16/18, Germany) up to a maximum temperature of 1550 °C. Isothermal tests were performed in a conventional air furnace (Nabertherm HTCT01/16, Germany) with thermal treatments of 1550 and 1600 °C and dwell times of 2, 4, and 8 h. The relative densities were measured by water immersion using a value of 4.56 g/cm³ as theoretical density of zircon.

Microstructures were observed by field emission gun scanning electron microscopy (FEG-SEM, Hitachi S4700 Type I, Japan) on polished and thermally etched surfaces. Sintered specimens were polished down to 1 µm using diamond paste and subsequently thermally etched at temperatures 10% lower than the sintering temperature. Grain sizes were evaluated by the linear intercepting method. XRD measurements were also done on the sintered specimens to confirm whether there was zircon decomposition into zirconia and silica or not.
3. Results and discussion

Figure 1 shows the evolution of zeta potential with pH of the zircon aqueous suspensions with and without anionic polyelectrolyte. The measured isoelectric point occurs at pH 3.6, which is slightly lower than the value of about 4.5 previously reported by other authors (Moreno et al., 1991; Suárez et al., 2015). The addition of PAA provokes the isoelectric point (IEP) to shift down towards more acidic pH values, reaching values of 3.2, 2.3, and 2.0 for PAA contents of 0.1, 0.5, and 1.0 wt%, respectively. This is the shift expected for the addition of an anionic polyelectrolyte demonstrating that it readily adsorbs onto the particles surface. In previous work (Huang & Yang, 2010) the same powder was used for suspension plasma spraying using suspensions dispersed with 0.5 wt% PAA. However, more important than the shift of the IEP, the incorporation of only 0.1 wt.% gives very high values of zeta potential at the working pH (~70 mV), which are similar for any deflocculant concentration.

The rheological behaviour of zircon suspensions prepared at a solids loading of 40 vol.% and different concentrations of polyelectrolyte can be seen in Figure 2a, where the corresponding flow curves are plotted. It can be clearly seen that the increase of PAA content leads to higher viscosity and higher thixotropic cycle, with the lowest values occurring for a concentration of 0.1 wt%, in good agreement with the zeta potential measurements at the pH values provided by the deflocculant (around pH 6.5). All suspensions were prepared after 1 min sonication, since it was proven that sonication improved the rheological behaviour. This can be observed in Figure 2b, which shows the flow curves of a

![Figure 1. Evolution of zeta potential with pH for zircon suspensions with and without PAA additions.](image-url)
Figure 2. Flow curves of zircon suspensions prepared at a solids loading of 40 vol.% and different concentrations of polyelectrolyte (a) and effect of sonication on the flow behaviour of the suspension prepared with 0.1 wt% PAA (b).

suspension prepared with 0.1 wt% deflocculant with and without sonication.

Figure 3 shows the viscosity measured at 1000 s⁻¹ in the up-curve and the thixotropy values of the suspensions plotted in Figure 2. This plot confirms the selection of 0.1 wt% deflocculant for further studies.

After the optimization of the dispersing conditions, a next step was to evaluate the effect of the solids content on the flow behaviour, trying to maximize the amount of solids maintaining a good flowability. Figure 4 shows the flow curves of suspensions prepared at optimum dispersing conditions (0.1 wt% PAA and 1 min sonication). Suspensions are Newtonian for solids loadings up to 40 vol.%, with a low thixotropy (always below 200 Pa/s), whereas the 45 vol.% slurry has a significant thixotropy (by 900 Pa/s) and the most concentrated one (50 vol.%) has very high viscosity and a broad hysteresis cycle, with a thixotropic area of 7660 Pa/s. The inlet in the figure shows the evolution of viscosity with volume fraction of solids, demonstrating that above 45 vol.% the viscosity sharply increases towards infinity. The resulting suspensions become too viscous to be suitable for further processing. Moreover, agar solutions have to be added to the hot slurries and this will produce a significant increase of the interactions between particles, and therefore, a viscosity raise.

As a first approach to the addition of agar, three solutions were prepared with a pressure cooker, to obtain 6, 8, and 10 wt% solutions. The variation of viscosity during cooling is plotted in Figure 5, where a clear, sharp viscosity gap at about 37 °C, corresponding to the gel formation is observed, as described elsewhere (Millán, Moreno, & Nieto, 2002). It is evident that the 6 wt% solution has much lower viscosity than the others and it does not increase during cooling until the formation of the gel network, which makes an important difference with
with the other two agar solutions. This makes this solution much easier to handle than the others. Following the same procedure, these three agar solutions were used to prepare agar-containing ceramic slurries, always adding the solution concentration required to obtain an active matter of agar of 0.5 wt% on a dry ceramics solids basis. Figure 5b shows the cooling viscosity of suspensions containing 6 and 8 wt% agar solutions. That with 10 wt% could not be measured due to the excessively high viscosity and lack of homogeneity. Again, the suspension with 8 wt% agar solution shows higher viscosity and a higher gap during gelation, but the \( T_g \) is not clearly observed due to the rupture as a consequence of the high shear conditions of the measurement.

**Figure 3.** Variation of viscosity (at a shear rate of 1000 s\(^{-1}\)) and thixotropy of suspensions prepared with different polyelectrolyte concentrations according to the flow curves plotted in Figure 2.

**Figure 4.** Flow curves of suspensions prepared with 0.1 wt% PAA and 1 min sonication at different solids loadings from 10 to 50 vol.%. The inlet shows the variation of viscosity with volume fraction.
According to these results, it can be stated that the use of the 6 wt% solution is preferred because it has lower viscosity, thus facilitating handling, more defined gelling point and better reproducibility. The performance of this suspension can be confirmed in the picture of Figure 6, which shows some green bodies obtained by gelcasting from the suspension prepared with the 6 wt% agar solution (Figure 6a). In the same picture, the same pieces sintered at 1600 °C/2 h are also shown (Figure 6b) to visualize the dimensional changes occurring on sintering. Sintered specimens of zircon tend to show a slight yellowish tone, not evident at the pictures.

Dynamic sintering studies were performed on gelcast green parts up to a temperature of 1550 °C, due to the limitations of the equipment. The resulting linear shrinkage and its derivative are plotted in Figure 7. It can be observed in the derivative curve that the maximum sintering rate takes place at around 1350 °C but the linear shrinkage does not reach a plateau, so that sintering temperatures above 1550 °C are necessary, in good agreement with previous studies on zircon (Moreno et al., 1991). For this reason, in the present study two isothermal treatments were considered, 1550 °C and 1600 °C, but the relative density of the former was relatively low (90.4 ± 0.2%TD), so that the last was selected for further studies.

The relative densities achieved after 2 h holding time is in the range of other values reported in the literature (Carbonneau et al., 1997; Gauna et al., 2021; Moreno et al., 1986, 1991; Suárez et al., 2015), i.e., around 95%TD. However, it could be enhanced with longer holding time, as it is reflected in Figure 8, which shows the variation of relative density of gelcast bodies prepared from both agar solutions as a function of holding time. It can be seen that the densification of samples prepared with the 8 wt% agar solution is always significantly lower than the achieved with the 6 wt% solution. This confirms the rheological behaviour measurements...
Figure 6. Shaped parts obtained by gelcasting from the 40 vol.% suspension with 0.5 wt% agar added from the 6 wt% solution: green bodies (a) and pieces sintered at 1600 °C/2 h (b).

Figure 7. Dynamic sintering behaviour of gelcast zircon specimens.

and the observations on handleability. A first observation is that increasing the holding time has a direct effect on densification, with an increase of around 2%. It is worth noting that when agar is added using the
6 wt% solution the densities reached after 4 h holding time are above 95% TD, and for 8 h the density is higher than 96%. These values are in the top of the values reported in the literature even for other processes such as slip casting, where the consolidation occurs by capillary filtration, which is a much slower process than the thermal gelation occurring in agar gelcasting and, consequently, leads always to better packing of the particles, i.e., higher green densities.

Figure 9 shows the SEM microstructure of zircon specimens treated at 1600 °C for 2, 4, and 8 h at two different magnifications. Although some closed porosity still remains the density is high and the microstructures are similar to the denser ones reported for zircon obtained by slip casting. However, it is worth noting that there is a slight increment

![Figure 8](image-url)  
*Figure 8. Variation of relative density of sintered gelcast zircon bodies prepared using both 6 and 8 wt% agar solutions as a function of holding time. Sintering temperature was 1600 °C.*

![Figure 9](image-url)  
*Figure 9. SEM microstructures of zircon specimens obtained by gelcasting and pressure-less sintering at 1600 °C for 2 (a,d), 4 (b,e), and 8 h (c,f) holding time.*
of the grain size with holding time, from 1.8 µm to 2.4 µm for specimens treated for 2 h and 8 h, respectively.

Finally, Figure 10 shows the diffractograms of both the zircon powder starting material and the zircon specimen sintered at the highest temperature (1600 °C) and the longest dwell time (8 hours). It can be seen that both diffractograms show the same signals, which proves that zircon materials do not undergo decomposition during the sintering process, since no traces of zirconia and silica are observed.

4. Conclusions

In view of the results obtained, the following conclusions can be drawn for this research:
• Stable low viscosity zircon suspensions with up to 45 vol.% solids contents have been obtained with the addition of 0.1 wt% of an anionic polyelectrolyte (PAA) and 1 min of sonication.
• Zircon compacts have been obtained by aqueous gelcasting for the first time using 40 vol.% suspensions and concentrated solutions of agar (6 and 8 wt%) added to a total content of biopolymer of only 0.5 wt%.
• Relative densities as high as 94.5% TD have been reached for materials shaped by gelcasting and pressureless sintered at 1600 °C (2 h), which is in good agreement with those reported in the literature (≤95% TD). Moreover, relative densities above 96% can be reached using holding times of 8 h at 1600 °C, although this leads to some grain growth, from 1.8 to 2.4 µm.

Disclosure statement
No potential conflict of interest was reported by the authors.

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