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Alumina bodies with near-to-theoretical density by aqueous gelcasting using concentrated agarose solutions

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Abstract

Aqueous gelcasting with agarose has demonstrated to be a suitable method for near-net shaping of ceramics. Improved reliability is reached when agarose is added as an aqueous solution, but this introduces an additional contribution of water that reduces solids loading (i.e. green density) and increases the drying shrinkage and weight loss (i.e. the dimensional tolerance and reliability). To avoid such problems the feature is to increase the concentration of the agarose solution and the solids loading. This work reports the preparation of agarose solutions to concentrations of 3.0 and 5.6 wt.% by simply heating at 90 °C and by overpressure heating (>110 °C). The dissolution and gelling behaviour have been studied from the flow curves and measurements of viscosity as a function of temperature on cooling. The rheological properties of alumina suspensions with solids loadings of 80, 83 and 84 wt.% (50, 55 and 57 vol.%) are studied, focusing on the gelling behaviour after the addition of agarose. Gelcasting into metallic moulds leads to green bodies with relative densities higher than 60%, and the shrinkage reduces below 5%, which is one half of that reported in previous works. Sintering at 1500 °C/2 h leads to relative sintered densities >99% of theoretical, similar to those obtained by slip casting.

Keywords: A. Shaping; A. Suspensions; D. Al_2O_3; Aqueous gelcasting

1. Introduction

Colloidal processing allows obtaining complex-shaped parts with reduced number and size of pores and higher reliability [1]. The great importance of alumina in the production of technical ceramics, and the needings for manufacturing complex-shaped pieces, have promoted current interest in the development of novel near-net shaping techniques. Great effort has been recently devoted to the gelcasting process [2–4], and more recently, to study the consolidation of aqueous ceramic suspensions through thermogelation of water soluble polysaccharides as additives, using conventional shaping techniques such as low-pressure injection moulding (LPIM) [5–7] or direct pouring into the cavity of a non-porous mould [8]. This processing route implies the heating of the suspension above the T_g of the polysaccharide to avoid premature gelation before shaping. Several studies [9,10] demonstrated that the stability of suspensions dispersed with polymers is strongly affected by temperature changes, this being a fundamental phenomenon to be studied.

The use of agarose as gelling agent for aqueous ceramic processing has been widely studied because it forms very strong gels on cooling that allow fast consolidation and enhanced green strength. The seminal works dealing with polysaccharides gelation mixed agarose powder with the suspensions at room temperature [5–7,11], but the resulting green samples had large defects and low relative densities, because viscosity strongly increased on heating and agarose agglomerates could not be removed. In order to improve the properties of the green samples, agarose was added to the ceramic suspensions as a solution at temperatures about 60 °C [8,12]. These solutions were prepared by direct heating in a beaker, but the high viscosity reached during the melting of agarose powder limited its

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maximum concentration in solution to 3–4 wt.%. However, below 100 °C it was impossible to complete the dissolution, and viscous solutions were obtained. Furthermore, the high viscosity provided by the agarose solution restricted the maximum solids loading of the suspensions to 80 wt.% (50 vol.%). The relatively low starting solids loading and the additional water added with the solution led to relatively low green densities (typically by 55% of theoretical) and large drying shrinkage (usually larger than 10%), which reduced reliability and dimensional tolerance, respectively. As a consequence, maximum sintered densities were at least 2–3 units below theoretical density. Although aqueous gelcasting with polysaccharides is an easy, fast and versatile shaping route, it is necessary to overcome the above mentioned drawbacks before the industry can benefit from this technology.

The aim of this work is to improve the agarose gelcasting performance to allow manufacturing of near-to-theoretical density complex-shaped parts. For this purpose, agarose solutions have been prepared under overpressure conditions, to a concentration of 5.6 wt.%. Overpressure conditions in a closed vessel leads to higher temperatures (110–115 °C), so that complete dissolution is achieved and hence, the solution viscosity decreases. This makes it possible to increase the solids loading of the gelcasting suspension to 83 wt.% (55 vol.%), which results in lower shrinkage and higher green densities.

2. Experimental procedure

As ceramic powder a commercial α-Al_2O_3 was used (Condea HPA05, USA) with a mean particle size of 0.35 μm and a specific surface area of 9.5 m^2/g. Aqueous suspensions were prepared to solids loadings of 80, 83 and 84 wt.% (50, 55 and 57 vol.%) by ball milling for 6 h with alumina jar and balls. As deflocculant an ammonium salt of polyacrylic acid (Duramax D3005, Rohm & Haas, USA) was used at a fixed concentration of 0.8 wt.%, on a dry solids basis. The resulting pH value was 9.0 ± 0.1. The suspensions were shacked in closed flasks for 24 h prior to binder addition in order to reach an adequate surface equilibrium.

As gelling additive, agarose powder (D1 LE, with an average size of 150 μm) supplied by Hispanagar (Burgos, Spain) has been used. It was dissolved following two routes: (1) 3 wt.% solution was prepared by mixing with water and heating up to 90 °C in open flask and (2) 5.6 wt.% solution was prepared under overpressure conditions using a pressure cooker, where a temperature >110 °C is reached. In both cases, agarose solutions were maintained at 60–65 °C and added to the ceramic slurries at this temperature.

For preparing the gelcasting suspensions, the well-dispersed alumina suspensions were heated at 60 °C, where the rheological properties are not yet affected by a significant evaporation, except in the largest solids loading (84 wt.%). The binder solution (either 3 or 5.6 wt.%) was added at this temperature until the total amounts of polysaccharide introduced into the ceramic slurry were 0.25, 0.5 and 1.0 wt.% with regard to dry solids. Table 1 shows the initial and the final solids loading of the suspensions, as well as the agarose content for the different compositions.

Rheological measurements were performed using a rheometer (Haake RS50, Germany) with a double cone and plate system (60 mm in diameter, cone angle 2°). A solvent trap was coupled to the measuring unit to reduce evaporation. The evolution of viscosity with temperature was measured using a probe of temperature, which enables the continuous recording of viscosity data on cooling. All these tests were made at constant shear rate of 5 s^{-1}.

Alumina green bodies were obtained by pouring the suspensions heated to 60 °C in stainless steel moulds with dimensions of 60 mm × 10 mm × 10 mm, and subsequent cooling with tap water. Consolidation of the bodies occurred in few seconds, after which the tests bars were demoulded and left in air to dry for 48 h. The green densities were measured by Archimedes' method in Hg. Drying shrinkage and weight loss were also measured. Sintering was

Table 1
Contents of agarose and solids of the studied suspensions

Nomenclature (wt.%)	Initial solid loading (wt.%)	Agarose (referred to solid) (wt.%)	Agarose solution (wt.%)	Agarose (referred to water) (wt.%)	Final solid loading
1	80	0.50	3.0	1.21	70.8
2		0.25	5.6	0.86	77.4
3	80	0.50		1.50	74.9
4		1.00		2.40	70.5
5		0.25		1.01	80.2
6	83	0.50		1.73	77.6
7		1.00		2.68	72.8
8		0.25		1.07	81.1
9	84	0.50		1.82	78.4
10		1.00		2.78	73.6

performed at 1500 °C/2 h in an electric furnace. Sintered bodies were polished and thermally etched for microstructural observations by scanning electron microscopy observations (Zeiss DSM400, Germany). The sintered densities were measured by immersion in water.

3. Results and discussion

Fig. 1 compares the flow curves measured at 60 °C (Fig. 1a), and the variation of viscosity on cooling measured at 5 s^{-1} (Fig. 1b) of 3 and 5.6 wt.% agarose solutions. Both solutions have a Newtonian flow behaviour, but the solution of 5.6 wt.%, prepared under overpressure conditions, has a very low viscosity, near one order of magnitude lower than the solution obtained by simply heating, although concentration roughly duplicates. This means that total dissolution is only reached under overpressure conditions. During cooling the viscosity of both solutions is nearly constant up to reach the gelling temperature, where the slope sharply increases. This effect is more pronounced in the concentrated solution, where the gap of viscosity on gelation is greater than three orders of magnitude. The gelling properties of both solutions, such as T_g, viscosity before and after gelation (η_i and η_f, respectively) and the corresponding viscosity ratios ($\eta_f - \eta_i$ and η_f/η_i) are presented in Table 2. The T_g of agarose solutions is not depending on the solution concentration, but the initial and final viscosities relay on the dissolution conditions, and hence the increment of viscosities.

Table 2
Rheological properties of agarose solutions (3 and 5.6 wt.%)

Concentration (wt.%)	T_g (°C)	η_f (mPa s)	η_i (mPa s)	η_f/η_i	$\eta_f - \eta_i$ (mPa s)
3	38.5	>17,000	74	>200	>17,000
5.6	38.9	>28,000	8	>3500	>28,000

The rheological behaviour of alumina suspensions prepared to 80, 83 and 84 wt.% solids (i.e. 50, 55 and 57 vol.%) was studied at 25° and 60 °C, since these are the temperatures at which the suspensions were prepared and mixed with the polysaccharide solution, respectively. Fig. 2 plots the flow curves of agarose-free suspensions at 25 °C (Fig. 2a) and 60 °C (Fig. 2b). In both cases, the viscosity increases with the solids loading. 84 wt.% suspensions present high viscosity and thixotropy values at 25 °C and no reliable measurements could be taken at 60 °C, due to water evaporation at this high solids content.

Fig. 3 plots the flow curves of suspensions with different agarose contents (0.25, 0.5 and 1.0 wt.%, Fig. 3a–c, respectively) and different solids loadings measured at

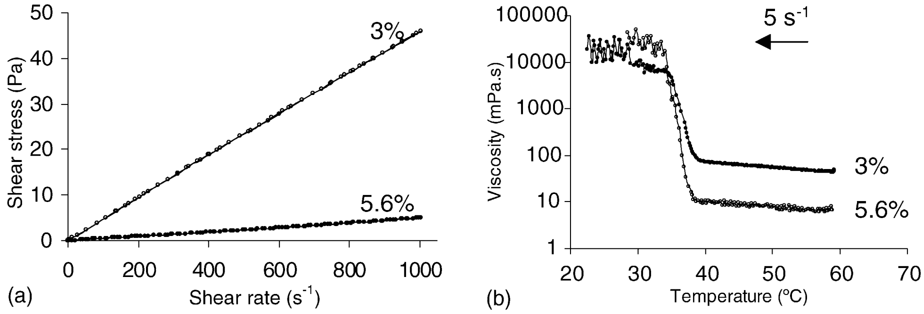

Fig. 1. Rheological behaviour of 3 and 5.6 wt.% agarose solutions: (a) flow curves at 60 °C and (b) variation of viscosity on cooling at a shear rate of 5 s^{-1}.

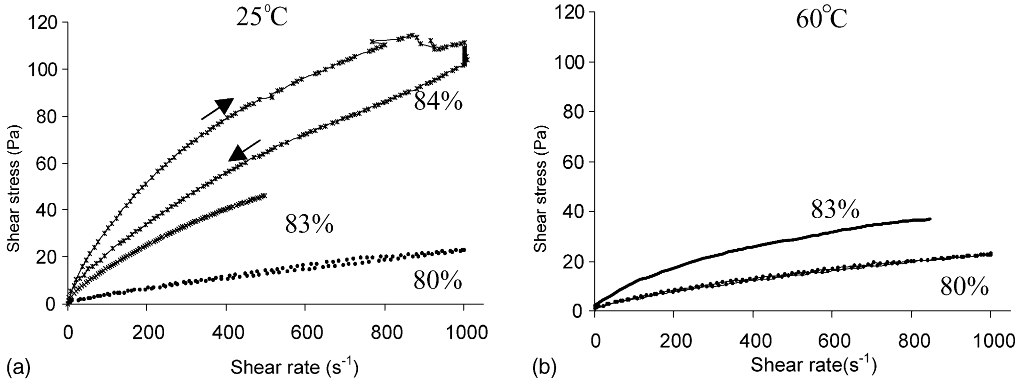

Fig. 2. Flow curves of alumina suspensions (80, 83 and 84 wt.%) at 25 °C (a) and 60 °C (b).

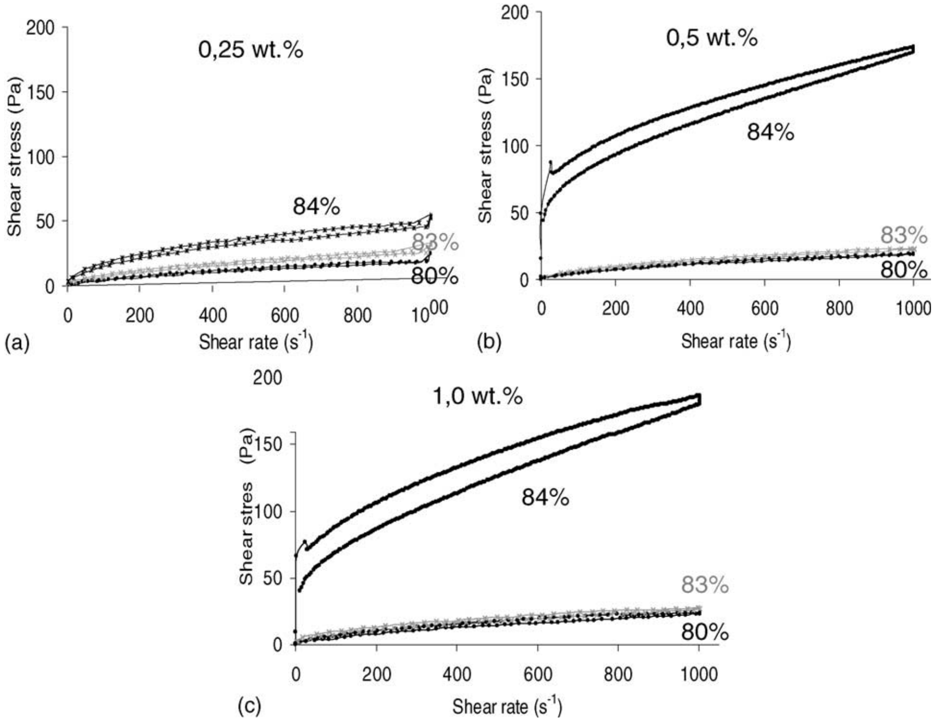

Fig. 3. Flow curves at 60 °C of alumina suspensions (80, 83 and 84 wt.%) prepared using 5.6 wt.% solutions up to total agarose contents of: (a) 0.25, (b) 0.5 and (c) 1.0 wt.%.

60 °C. Viscosity increases with solids loading for constant agarose content. However, 84 wt.% suspensions with 0.5 and 1.0 wt.% of agarose (samples 9 and 10 in Table 1) show a large increase of viscosity and thixotropy, although their final solids loading is lower than that of other suspensions with lower viscosity. This means that this solids loading acts as a maximum effective volume fraction of solids to avoid agglomeration on heating.

The gelling behaviour of the agarose-containing suspensions is shown in Fig. 4, which plots the evolution of viscosity on cooling at a shear rate of 5 s^{-1}. The gelling temperature slightly increases with the agarose content. The curves of suspensions prepared with solids loadings of 80 and 83 wt.% (Fig. 4a and b) are very similar, but when solids loading increases up to 84 wt.%, the initial viscosities are one order of magnitude higher. The high viscosity and the presence of entrapped bubbles are important restrictions for further shaping, which leads to samples with defects. The homogeneity of the mixtures of ceramic slurries and gelling solutions is essential for obtaining dense and defect-free green bodies.

The viscosity gap occurring on gelation is directly dependent on the properties of the gel-former, the initial solid content, the final solid loading, and their relative concentrations. The results obtained from the curves are shown in Table 3. For a similar agarose content, the viscosity increases with solids loading, but the gap of viscosity on gelation decreases. For a given solids loading the viscosity tends to decrease with increasing agarose addition, as more water is being added, but the gap (i.e. the gel strength) tends to increase. Exceptions are again suspensions with 84 wt.% solids and 0.5–1.0 wt.% agarose.

These suspensions were gelcast on stainless steel moulds and left to dry for 48 h at room conditions. Homogeneous green bodies were obtained with very good appearance in terms of surface homogeneity and density. Table 4 summarises the green properties of the samples obtained from the suspensions with different solids loadings and agarose contents using 5.6 wt.% solutions, and compared with those obtained using 3 wt.% agarose solution (composition 1). After casting these suspensions, the demoulded bars containing concentrated agarose were rigid and did not deform during drying.

Table 3
Rheological properties of the suspensions with different contents of agarose added from 5.6 wt.% solution

Suspension	T_g (°C)	η_i (mPa s)	η_f (Pa s)	η_f/η_i
1	–	–	–	–
2	33.0	400	>16	>40
3	34.0	280	>17	>60
4	35.5	290	>22	>80
5	33.6	1000	>22	>20
6	36.4	650	>21	>30
7	34.8	750	>22	>30
8	32.9	2	>27	>10
8	38.1	12	>43	>3
10	38.3	9	>42	>5

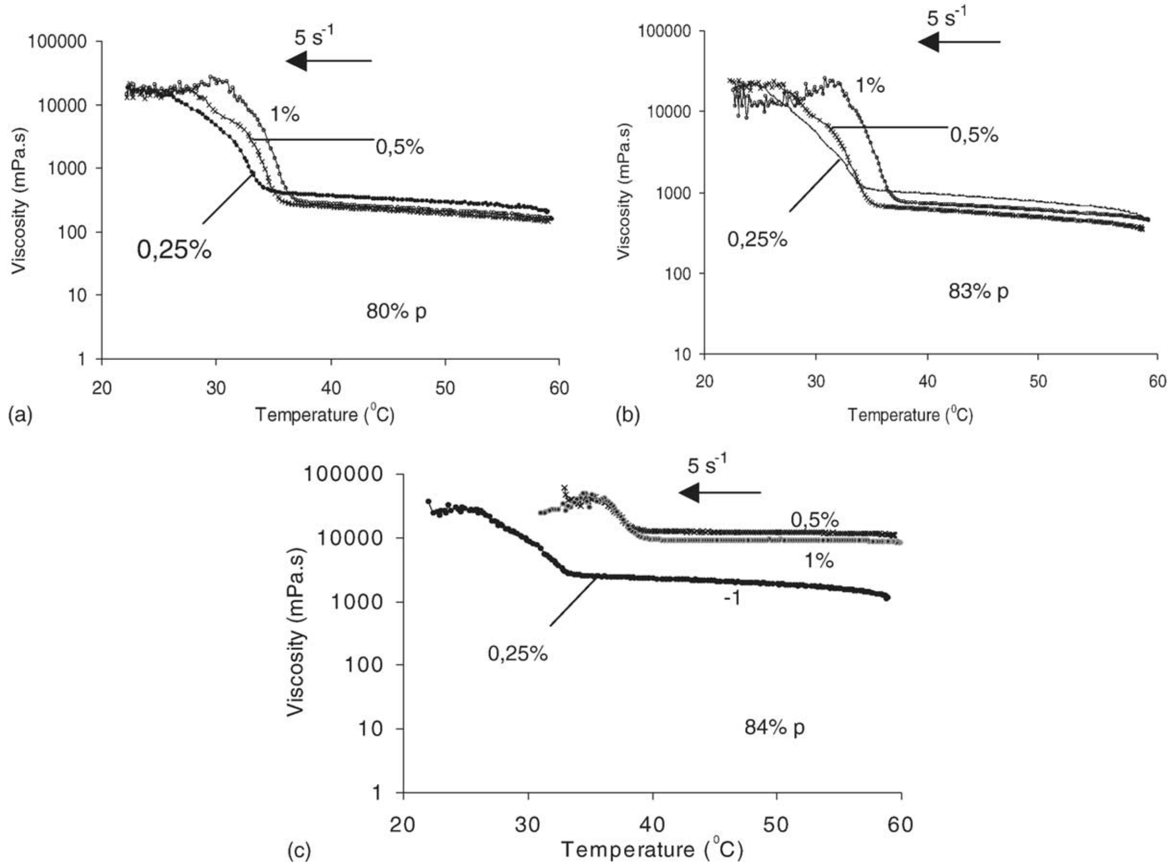

Fig. 4. Evolution of viscosity with temperature (on cooling) for alumina suspensions prepared with 0.25 wt.% agarose added from 5.6 wt.% solutions and starting solids loading of: (a) 80, (b) 83 and (c) 84 wt.% (shear rate 5 s^{-1}).

Relative green densities higher than 60% TD have been obtained, this being a remarkable increase over the values reported in the open literature. In addition, linear shrinkage is reduced below 5% that represents a substantial reduction in the reported shrinkage values. These results mean that a significant step is given toward a higher dimensional control that opens an opportunity to the industrial viability of aqueous gelcasting for manufacturing complex-shaped parts. The better processability of the suspensions, the higher homogeneity (density), and the better precision in the dimensional control are key aspects in the reliability of the process. In general, density tends to increase with increasing final solids loading when starting from a similar suspension, but some divergences are found when comparing suspensions with similar final solids content and different starting solids content, due to the differences on viscosity values observed.

Homogeneity of green samples can be observed in Fig. 5, which compares the SEM microstructure of samples with compositions 5 and 7, whose relative densities are 63.0 and

Table 4
Characteristics of gelcast Al_2O_3 bodies in the green state and after sintering

Suspension	Final solids content (wt.%)	Relative density (% TD)		Linear shrinkage (%)	
		Green	Sintered	Drying	Sintering
1	70.8	53.3 ± 0.3	97.6 ± 0.2	10.7 ± 0.7	18.3 ± 0.1
2	77.4	61.3 ± 0.8	98.8 ± 0.2	4.5	15 ± 3
3	74.9	57.8 ± 0.2	99.0 ± 0.1	7.7 ± 0.4	16.5 ± 0.9
4	70.5	56.2 ± 0.2	99.1 ± 0.2	10.6 ± 0.4	17 ± 1
5	80.2	63.0 ± 0.9	99.2 ± 0.1	5.0 ± 0.9	13 ± 3
6	77.6	59.2 ± 0.2	99.1 ± 0.1	6 ± 1	15 ± 1
7	72.8	56.4 ± 0.8	98.9 ± 0.1	8.8 ± 0.8	18 ± 1
8	81.1	63.2 ± 0.5	98.9 ± 0.2	4.9	11 ± 2
9	78.4	57.2 ± 0.8	98.5 ± 0.1	4.3 ± 0.9	18.2 ± 0.8
10	73.6	54.1 ± 0.8	97.4 ± 0.1	7.6 ± 0.5	18.4 ± 0.8

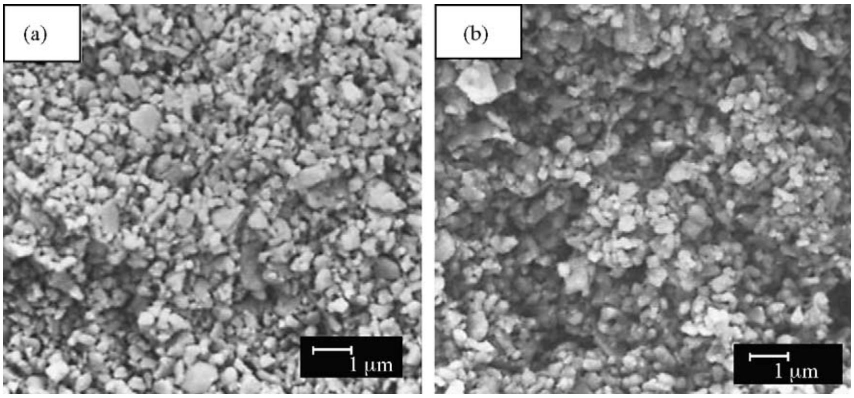

Fig. 5. SEM micrograph of alumina green bodies prepared with 83 wt.% suspensions and agarose contents of: (a) 0.25 and (b) 1 wt.%.

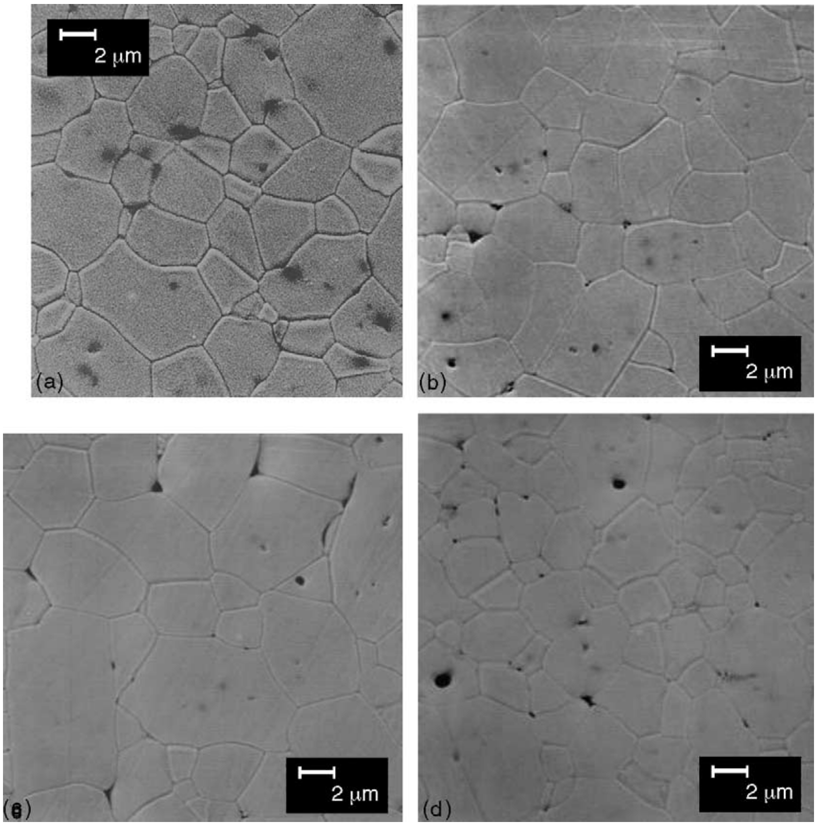

Fig. 6. SEM micrographs of sintered, polished and etched surfaces of Al_2O_3 prepared by gelcasting with diluted agarose solution (3 wt.%) (a), and by gelcasting with 5.6 wt.% agarose solution and initial solids loadings of 80 (b), 83 (c) and 84 wt.% (d).

56.4% of TD. The improved dissolution of agarose allows better packing of particles and no undissolved agarose agglomerates remain in the green body, as those reported in preliminary works [11].

Green casts were sintered at 1500 °C/2 h in air. Sintered relative densities were rather similar to those obtained by conventional slip casting (~99% TD), being the first time that so high sintered densities have been obtained by gelcasting with polysaccharides. The properties of sintered samples, such as density and shrinkage after thermal treatment are presented in Table 4, also. The worst values are obtained again with 84 wt.% suspensions with $\geq$0.5 wt.% agarose, because of the poorer homogenisation, as demonstrate by rheological measurements.

Fig. 6 shows the SEM microstructure of sintered Al_2O_3 bodies obtained from suspensions with different solid loading and 0.5 wt.% agarose content (compositions 3, 6 and 9), after polishing and thermally etching. For comparison purposes, SEM pictures of the same alumina processed by gelcasting with 0.5 wt.% agarose added from a 3 wt.% solution is also shown. Samples prepared with concentrated agarose solution show dense, homogeneous microstructures with small residual porosity located at triple points and inside the larger grains, similar to that obtained by slip casting, while 3 wt.% solutions lead to lower densification.

4. Conclusions

Conventional aqueous gelcasting with polysaccharides makes use of low concentration solutions of the gel-former, which cannot exceed a 4 wt.% by direct heating in open flask. This work describes a new procedure for preparing agarose solution with higher concentration (5.6 wt.%) by dissolving under overpressure conditions with a pressure cooker. The greater efficiency of the dissolution process makes the viscosity of the solution to be one order of magnitude lower than that of a solution with one half of agarose concentration prepared by direct heating. The lower viscosity of the gelling solution allows also to increase the initial solid loading of the suspensions (from 80 to 84 wt.%, that is from 50 to 55 vol.%), while maintaining low values of viscosity.

The use of more concentrated starting suspensions and the addition of less quantity of water with the agarose solution lead to better gelcasting performance. Green densities as high as 63% TD are obtained, similar to those obtained by conventional slip casting. Another key aspect is that drying shrinkage is reduced below 5%, while gelcasting with diluted agarose concentrations have a minimum shrinkage >10%, this meaning a substantial improvement toward a better dimensional tolerance for the processing complex-shaped parts. The improvement in the green characteristics allows obtaining near full density sintered bodies (>99% TD).

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