Journal of the European Ceramic Society 22 (2002) 297–303

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Near-net shaping of aqueous alumina slurries using carrageenan

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Received 30 November 2000; received in revised form 8 March 2001; accepted 24 March 2001

Abstract

The production of alumina pieces by gelation of concentrated aqueous slurries using carrageenan is described. The potassium carrageenan forms a low viscosity solution when heated, that provides a strong gel on cooling. Aqueous suspensions of alumina are prepared at a solid loading of 50 vol.% at different polyelectrolyte concentrations. The optimum dispersing conditions are selected from zeta potential, particle size distribution and viscosity measurements. Afterwards, the effect of temperature on the rheological behaviour is studied. The rheological properties of carrageenan solutions are studied for different concentrations and the gelation hystheresis is determined. The evolution of viscosity of the alumina slurries containing 0.25 wt.% carrageenan is studied on cooling. Casting the hot blend in a refrigerated non-porous mould allows us to obtain pieces with high green strength in a few seconds. The green density of the casts is 58.2% of theoretical and after sintering at 1500°C/2 h a final density of 98% is reached. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; Carrageenan; Gel processing; Near net shaping; Rheology; Suspensions

1. Introduction

As has been demonstrated elsewhere, better ceramics can be obtained through colloidal processing.[1,2] The colloidal approach to ceramics has led to more uniform microstructures with smaller defects size and population and to the development of toughened materials with increased reliability.[3,4] Furthermore, colloidal forming methods are suitable for manufacturing complex shaped parts.[5,6] On the basis of well established methods such as slip casting, pressure casting or injection molding, much research is being performed to develop new processes for the direct consolidation of powders. The final objective is to reduce the costs of the shaping procedure and to reduce or avoid the machining step.[7]

Consolidation of ceramic parts through binder gelation have the potential to avoid the foregoing problems. On one hand the costs of forming operations can be significantly reduced because consolidation only requires a few seconds, in contrast with slip casting that needs several hours. Furthermore, the moulds cost much less and have a longer mean life than those used for pressure casting or high pressure injection molding. On the other hand, gelling additives provide very strong green bodies that can be easily handled and machined.[8–10]

Researchers at the Oak Ridge National Laboratory have developed the gelcasting process in which a concentrated powdered slip in a solution of organic monomers is poured into a mould and then polymerized by means of a catalyst.[11,12] Besides the chemical gelation another approach to ceramic processing is to promote thermal gelation through polymer solutions that gelate under suitable temperature conditions. The most common gelling agent in ceramics is agarose.[13–15] Very low concentrations of agarose, like 1 wt.% referred to solids, provide a high gel strength to form a complex shaped green part. However, the use of agarose presents several disadvantages. The first is the very high cost of this additive. The second refers to the fact that it must be added to the ceramic slurry at a temperature above 80–90°C in order to dissolve it completely. At this temperature the suspending liquid evaporates rapidly promoting agglomeration and flocculation, which strongly increase the slip viscosity.

Many researchers are currently studying new additives that could replace agarose, as gelatine, starches,

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PII: S0955-2219(01)00283-7

etc. However, most of these recently proposed additives have poorer gelling properties so that larger concentrations are required to form a rigid gel network.

In this work a new family of gelling additives namely carrageenans is proposed as a suitable binder for gel forming of ceramics into simple or complex shapes.[16]

2. Carrageenans structure and characteristics

Carrageenans constitute a family of hydrocolloids that are obtained from red seaweed of the Euchema order, and are extensively used in the food industry to gel, thicken and stabilise food systems. They are sulfonated polysaccharides, polymers of D-galactose. The monomers are derivatives such as semi-ester sulfates in positions C_2, C_4 or C_6 or doubly sulfated as in C_2 and C_6. The polymer is made up of repeating monomers joined by alternating α-(1,3) and β-(1,4) glycosidic linkages. Various naturally occurring arrangements create the different types of carrageenan, referred to as mu (μ), nu (ν), lambda (λ), xi (ξ), kappa (κ), iota (ι) and theta (θ). The fractions μ, ν and λ are known as precursors and they transform into terminal fractions κ, ι, and θ in the algae by enzymatic action through a sulfatase by transformation of D-galactose-6-sulphate in 3,6-anhydro-D-galactose. Moreover, industrial carrageenans do not only contain pure terminal fractions, but some quantity of precursor is still present.[17] The presence of hybrid fractions, such as κ–ι, and others is also common. The existence of other fractions, such as α, β, δ, or π has been also reported.

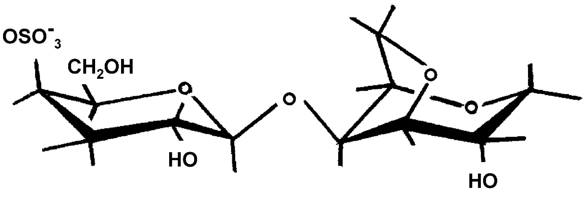
The most interesting carrageenans from an industrial point of view contain the fractions κ, ι and λ, whose structures are shown in Fig. 1.

Since the fraction λ is a precursor it is only present at low concentration in commercial carrageenans and usually in combination with its terminal fraction θ.

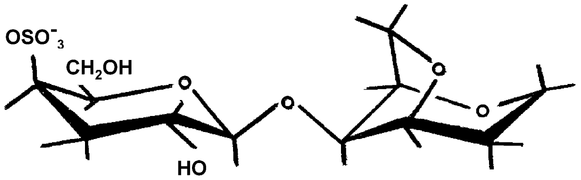
Variations in the components significantly influence gel strength, solubility, synergism, melting temperature and gelling temperature, and hence, the gelling mechanisms can be quite different.

The proportion of sulfates oscillates from 24.9% in a pure κ fraction (minimum content) to 52.2% for a theoretically pure λ fraction, being 41.3% for an ι-carrageenan.

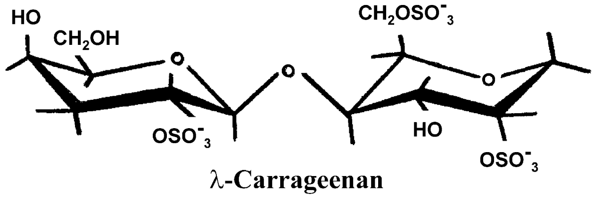
The behavior of carrageenans largely depends on the effect of different cations that can link to semi-ester sulfate groups. In the series $Na^+ \rightarrow Ca^+ \rightarrow K^+$ the effect is to reduce the solution viscosity while gelling properties are enhanced. When considering the series of carrageenans λ → ι → κ the gelling properties increase and viscosity decreases. Hence a sodium λ-carrageenan will have the maximum viscosity whereas a potassium κ-carrageenan will have the maximum gelling power.[18]



κ-Carrageenan



ι-Carrageenan



λ-Carrageenan

Fig. 1. Structure of the most important industrial carrageenans.

These substances are soluble in hot water between 40 and 70°C depending on the concentration and the presence of cations. They have a good stability at pH $\geqslant 7$ which decreases at acidic conditions, especially at high temperatures. For low pH the polymer hydrolysis decreases and gelling properties decrease. However, when the gel is formed it maintains stable for a year at pH = 3.5.[19]

According to this, a maximum gelling efficiency will be obtained using a κ-carrageenan with potassium ions at neutral or basic pH. If acidic pHs are necessary the carrageenan should be added on the acidic slip after heating separately the slip and the carrageenan solution. In such cases it is desirable also to reduce the processing time, including mixing and consolidation. For a pH 4 a maximum time of 30 min is recommended at a temperature of 80°C.[19] As gelation does not occur above 60°C the processing time can be increased for hours even at lower pHs.

Gelation occurs by formation of double helix structures by means of hydrogen bonding.[20] The cation linked to the sulfate groups as counterion determines the angles between monomers, K^+ being the one that provides a more compact structure with antiparallel double helices. Hydrogen bonding is conditioned by the presence of caotropic agents trapping protons, such as urea, guanidine or salts like KI, NaSCN, that difficult or impede gel formation. Fig. 2 shows the gelation mechanism of carrageenans, which takes place on cooling and is reversible.

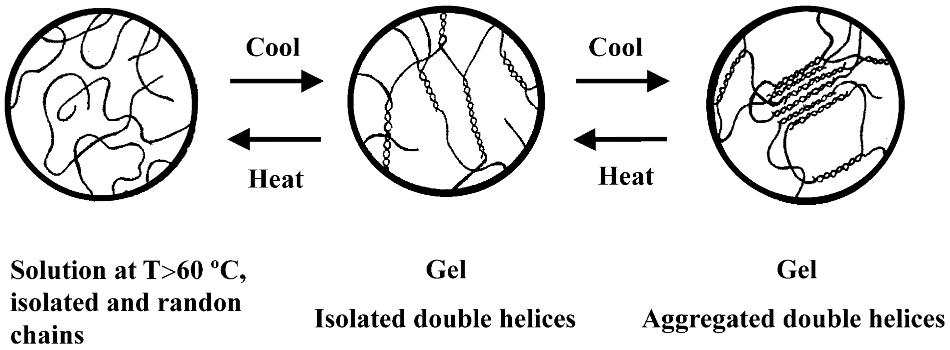


Fig. 2. Gelation mechanism of carrageenans.

3. Experimental

A commercial Al_2O_3 powder was used (Condea HPA05, Germany) with a mean particle size of 0.35 μm and a specific surface area of 9.5 m^2/g. Aqueous suspensions were prepared by ball milling for 6 h with an alumina jar and balls. As deflocculant an ammonium salt of polyacrylic acid (Duramax D3005, Rohm & Haas, USA, 35 wt.% active matter) was used. The dispersing conditions were studied for concentrations of the polymer solution ranging from 0.5 to 1.5 wt.% referred to dry solids. The suspensions were prepared to a solid loading of 80 wt.% (50 vol.%). These suspensions were shaken in closed flasks for 24 h prior to binder addition in order to reach an adequate surface equilibrium.[21]

The rheological behaviour of the slurries was studied using a rheometer (Haake RS50, Germany) operated at control rate mode. Measurements were performed with a double-cone and plate system (60 mm in diameter, cone angle 2°) at temperatures ranging from 25 to 92°C. Zeta potential measurements were performed on slurries diluted to a concentration of 20 wt.%, using a mass transport analyser (Micromeritics, USA). Particle size distribution was determined for each suspension using a laser analyser (Mastersizer S, Malvern, UK).

As gelling agent a potassium κ-carrageenan (Secogel TC, Hispanagar, Spain) was used. According to supplier specifications it has a gel strength of 900–1200 g/cm^2 at 20°C for a concentration of 1.5%, and a sulfate content below 30%. Aqueous solutions of carrageenan were prepared to concentrations of 1, 2, 3 and 4 wt.% by mechanical stirring in water and further heating up to 92°C in order to allow the complete dissolution of the powdered binder. The resulting pH of the solutions was 10. The mixtures were then introduced in the measuring vessel of the rheometer and a constant shear rate of 100 s^{-1} was applied. At these conditions a probe of temperature allowed the continuous determination of viscosity both on heating and subsequent cooling.

The casting slips were prepared by heating the dispersed slips above 60°C, and then adding the required quantities of each carrageenan solution up to a total concentration of gelling matter of 0.25 wt.% referred to solids. Casting was performed on metallic moulds cooled by flowing water to obtain test bars. The cavity dimensions were 60×10×10 mm. Residence times of the slurries in the moulds were 10–20 s. After this time a consistent gel is obtained that easily flows through the mould cavity. The wet bars were supported on Mylar films in order to avoid deformation. The as-cast parts were left in air to dry for 24 h. Green densities were measured by Hg immersion. Linear shrinkage was evaluated from geometrical measurements. Sintering was performed in air at 1500°C for 2 h Microstructural observations were made by scanning electron microscopy on fracture surfaces, as well as polished and thermally etched surfaces.

4. Results and discussion

4.1. Rheological behavior of carrageenan solutions

Fig. 3 shows the variation of viscosity on heating for solutions prepared at 1, 2, 3 and 4 wt.% carrageenan. Obviously the viscosity increases with concentration so that for 4 wt.% the torque of the rheometer is overloaded. In all cases a strong increase in viscosity is registered corresponding to the dissolution of solid

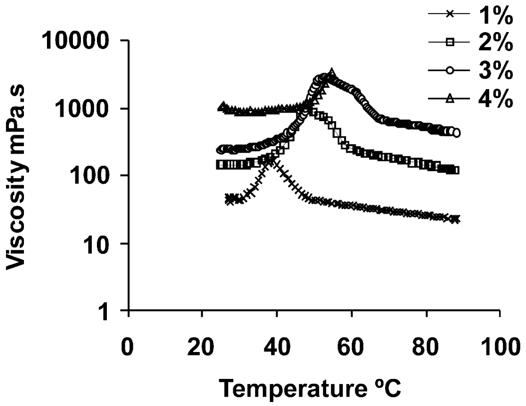


Fig. 3. Evolution of viscosity on heating of carrageenan aqueous solutions.

carrageenan. Once dissolution has been completed the viscosity linearly decreases for increasing temperatures. The temperature at which the maximum locates increases with the solution concentration. This fact must be considered for an adequate control of the gel forming process. When adding the carrageenan solution to the powdered slurry it is useful to have the highest possible concentration in order to reduce the quantity of water to be added to the slurry. However, the higher is the concentration the higher are the viscosity and the dissolution temperature, which result in a worse control of the processing conditions.

According to Fig. 3 the dissolution is complete for temperatures of 50, 65 and 70°C for concentrations of 1, 2 and 3 wt.%, respectively.

The viscosity on cooling for those concentrations is plotted in Fig. 4. When cooling from 90°C the viscosity values in the down curve are nearly the same than those of the up-curve. The viscosity slightly increases on cooling and the variation maintains the linearity. However, the variation of viscosity is higher than that expected for the relative viscosity, because the polysaccharide molecules interact each other. On arriving to a certain temperature a sharp increase in viscosity takes place that corresponds to the gelation process. The gelling point defines the temperature at which gelation starts and depends also on the concentration. Fig. 5 plots the variation of both the dissolution temperature and the gelling point as a function of carrageenan concentration. Gelation starts at 32.5, 42.2 and 48.5°C for 1, 2 and 3 wt.% carrageenan, respectively. According to this plot, the gelation hystheresis of carrageenans is not too large, because the differences between the dissolution and gelation peaks are maintained below 20°C, much lower than the gelation hystheresis reported for agars which maintains higher than 45°C.[22] The advantages for a direct application to ceramic processing are that the slurries can be heated only at around 60°C if the additive has been previously dissolved, and that gelation occurs above 35°C, so it is not necessary to use freezing systems.

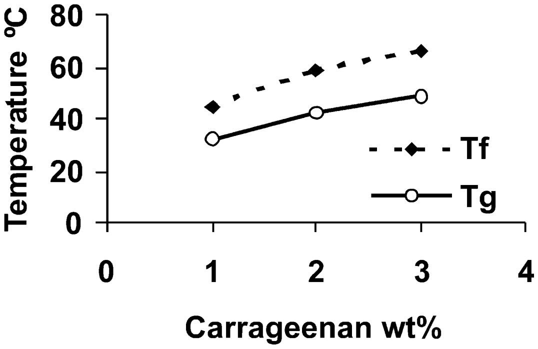


Fig. 5. Hystheresis cycle of carrageenan solutions.

4.2. Rheological behavior and gel-forming performance of ceramic slurries

The dispersing conditions of concentrated slips of the alumina powders used in this work have been reported in other previous works.[21,23] Well-dispersed slips can be prepared at a solid loading of 80 wt.% (50 vol.%) and a concentration of polyelectrolyte solution of 0.8 wt.%, (0.28 wt.% active matter). The resulting pH was 9.3±0.1 for the studied range of concentrations. Fig. 6 shows the variation viscosity of 80 wt.% slips at different deflocculant concentrations. The mean particle size and the zeta potential are also shown and are in good agreement with the variation of viscosity. Particle size distribution was measured by adding drops of the concentrated suspension into the measuring unit of the laser analyser. Zeta potentials were measured by diluting the so-prepared suspensions to a solid concentration of 20 wt.%.

Fig. 7 shows the flow curves of the well-dispersed slurry at different temperatures up to 55°C. According to them no agglomeration effects could be detected when heating up to that temperature. However, for

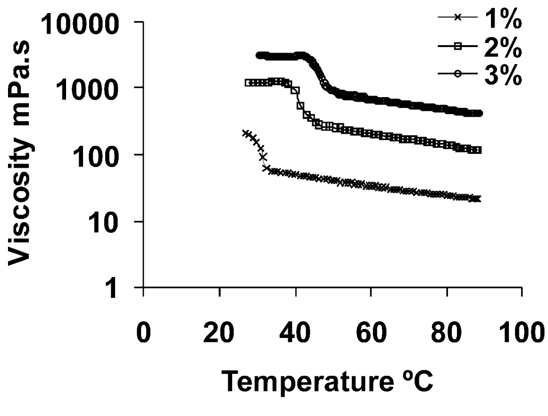


Fig. 4. Evolution of viscosity on cooling of carrageenan aqueous solutions.

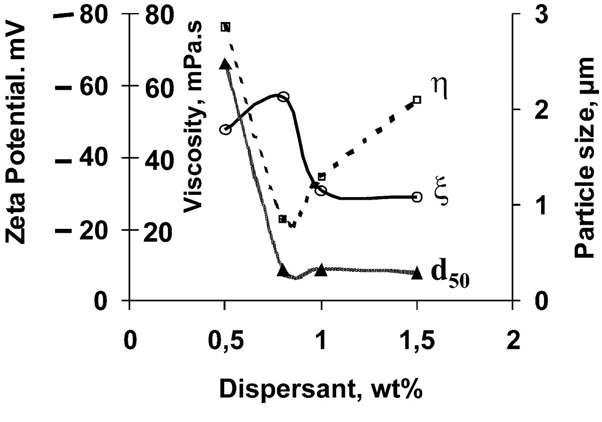


Fig. 6. Variation of mean particle size, zeta potential and viscosity of alumina slips as a function of polyelectrolyte concentration.

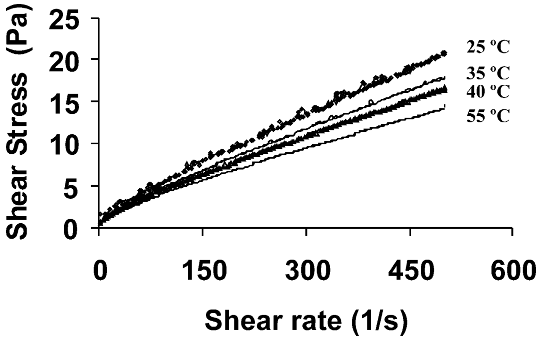


Fig. 7. Flow curves of 50 vol.% alumina slips with 0.8 wt.% deflocculant at different temperatures.

temperatures higher than 65°C the viscosity tended to increase, thus indicating heterogeneity caused by either water evaporation or polymeric bridging.

Carrageenans should be added to the slip at a temperature of 65°C or less, where viscosity is low enough and control is still possible. Carrageenan solutions (2 wt.%) were added to the ceramic slurry up to a final concentration of gelling matter of 0.25 wt.% referred to solids (1.0 wt.% with regard to the total quantity of water). After the binder addition, the total solid loading of the slip becomes 72.7 wt.%. As gelation occurs through the formation of a network structure through the water molecules the behavior of the mixture will mainly depend on the arrangement of the helices and the formation of double helices on cooling, as they are the responsible for gelation. Nevertheless, the interaction of the polysaccharides with the ceramic particles can have some influence on the viscosity of the mixture. This topic is now under study. When expressed the carrageenan content in relation to total solids the concentration of carrageenan is lower than 0.25 wt.%, much lower than any other gelling additive described before in the literature. Fig. 8 shows the evolution of viscosity on cooling for the 80 wt.% alumina slip containing 0.25 wt.% carrageenan (referred to solids) at a shear rate of 100 s^{-1}. In this plot the gelling process starts at a temperature of 33°C, and the viscosity of the gel is twice than that of the hot slurry (2.0 Pa.s at 27°C).

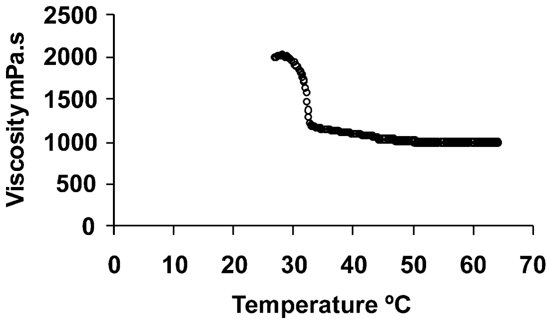


Fig. 8. Evolution of viscosity on cooling of alumina slips with 0.25 wt.% carrageenan.

This slip with 0.25 wt.% carrageenan was cast on a steel mould cooled with flowing water. Samples were removed and left in air for drying for 48 h. After drying, the wet cast becomes a rigid body, showing a weight loss of 26.5% and a linear shrinkage of 14%. The green density of the casts was 2.32 g/cm^3, that is 58.2% of theoretical density. This value is high compared with those found in the literature and comparable to the obtained by colloidal filtration routes. Fig. 9 shows a general view of the microstructure obtained by SEM on a fracture green surface. The microstructure is uniform, with a homogeneous distribution of the particle size and shape, and no evidence of agglomerated regions or big pores that could be associated to binder agglomerates.

After sintering at 1500°C/2 h a final density of 3.90 g/cm^3 (98.2% of theoretical) is obtained. The SEM microstructure of fracture and polished sintered surfaces is shown in Fig. 10 (a) and (b), respectively. Besides the high uniformity, the absence of bigger residual porosity confirms that the binder was homogeneously distributed and completely dissolved. Some intragranular porosity still remains, as a consequence of trapped pores formed at the triple points, which are retained during the final sintering stage where grain growth occurs. This phenomenon is typically found in alumina. Higher sintering temperatures led to exaggerated grain growth with no significant improvement of density.

The complete dissolution of the gelling additive and an efficient homogenization with the ceramic particles are essential to reach higher packing densities, necessary to improve the gel forming consolidation methods. It has been also demonstrated that carrageenan are efficient gelling additives for ceramic processing with two important characteristics: the capability to produce strong gels, and the reduced cost in comparison with other more known additives, like agarose.

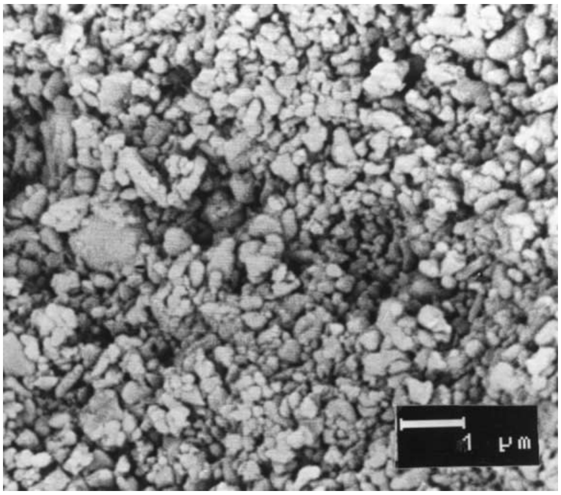


Fig. 9. Green microstructure of a fracture surface of the gel cast alumina.

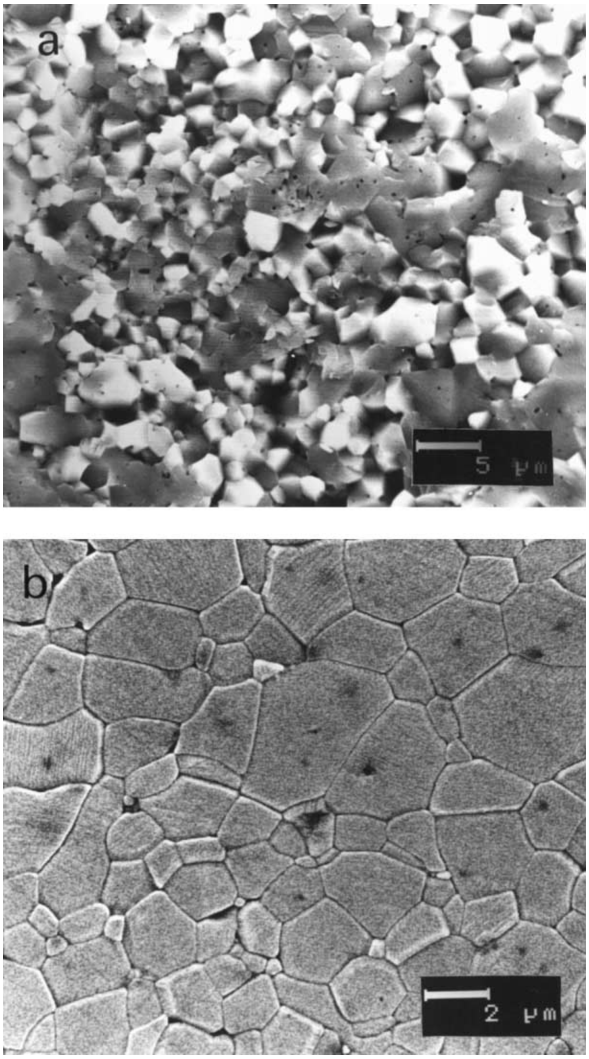


Fig. 10. SEM microstructure of sintered gel cast alumina samples, (a) fracture surface and (b) polished and thermally etched surface.

5. Conclusions

Carrageenans constitute a family of possible processing aids in ceramics. The fraction κ-carrageenan in the presence of potassium promotes thermal gelation on cooling and the gel strength is very high (nominally higher than 1000 g/cm^2 for a test gel prepared from a 1.5 wt.% solution in water, measured by a load application pin or indenter in a testing machine).

Connecting a probe of temperature to the rheometer it is possible to continuously determine the variation of viscosity with temperature. Aqueous solutions of carrageenan at different concentrations have been characterized so that a hystheresis curve can be plotted and the dissolution and gelation temperatures can be accurately determined. Both temperatures increase with carrageenan concentration. Within the studied range (1–3 wt.%) the carrageenan is completely dissolved below 65°C, and the gel is completely formed at 30°C. These are clear advantages with respect to other additives that need higher temperatures to completely dissolve (even more than 80°C). Furthermore, the potassium concentration in the carrageenan is low (below 1 wt.%). As the carrageenan is added in a concentration of 0.25 wt.%, this means that the final concentration of potassium introduced in the shaped body is negligible.

Alumina aqueous slips were prepared at a solid loading of 80 wt.% (50 vol.%) by adding a polyelectrolyte. The slips remain stable up to temperatures of 55–60°C. Consequently, they can be homogeneously mixed with the gelling additives avoiding flocculation of particles or binder agglomeration. A concentration of carrageenan as low as 0.25 wt.% referred to solids is enough to allow gel casting into simple or complex shapes providing strong gels. As gelation occurs through the water molecules the better results will be obtained when the concentration of liquids decreases.

Gelling time for test bars was within 10–20 s and the green density was higher than 58% of theoretical. After sintering at 1500°C/2 h the relative density was higher than 98%.

All this demonstrates the suitability of carrageenan for gel forming processes. The process is fast, no binder out is required as only 0.25 wt.% binder is used, and the cost of this additive is at least one order of magnitude lower than that of agarose.

Acknowledgements

This work has been supported by CICYT (Spain) under contract (MAT97-0676). The authors thank D. Rafael Armisen (Hispanagar S.A., Spain) for agarose supply and helpful discussions. A.J. Millán thanks CONICIT (Venezuela) for the concession of a grant.

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