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Cordierite-based glass-ceramics processed by slip casting

Sen Mei, Juan Yang, J.M.F Ferreira *

Department of Ceramics and Glass Engineering, UIMC, University of Aveiro, 3810-193, Portugal

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Abstract

In this research work, cordierite-based glass ceramics were prepared by slip casting from slurries with different solids loading. The amount of dispersant imposed different influence on the rheological behaviour of the cordierite–glass suspensions at different solids loading. A shear thinning behaviour was observed in the lower solids loaded suspensions (50 wt.%) with different amounts of dispersant within the whole range of shear rate. As the solids loading increased (60, 70 wt.%), the rheological behaviour of the suspensions gradually changed to shear thickening at higher shear rates. An optimal amount of dispersant for the cordierite–glass suspensions was found, which could lead to green bodies with homogeneous microstructures and to the smallest pore diameters. The sintered bodies prepared by slip casting exhibit higher density and microstructural homogeneity than those obtained by dry pressing. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Cordierite; Dispersant; Glass ceramics; Rheology; Slip casting

1. Introduction

Cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) and cordierite-based glass-ceramics are promising materials as substrates in the microelectronic application because of their excellent dielectric properties (~5 at 1 MHz, with low dielectric loss). For example, they can be co-fired with copper at low temperatures (below 1000° C) to form electronic substrates, and match silicon in thermal expansion characteristics ($1\text{–}2\times10^{-6}$/K from 25 to 1000° C).[1–3] However, cordierite is difficult to densify without sintering additives. Relatively poor mechanical properties, which have prevented its widespread application,[4] were usually encountered. In order to realise the full potential application of cordierite, low softening point glass powders (usually borosilicate glass) have been added to the stoichiometric cordierite to decrease the sintering temperature and obtain a denser body.[5] A relatively low sintering temperature is also essential for circuit materials, since higher temperatures would cause the circuit materials to be oxidised.

Slip casting has been proved to be a reliable and simple technology to produce homogeneous and dense green bodies,[6,7] especially for multi-component systems or composites.[8] The homogenisation and the rheological behaviour of the suspensions has been shown to play a significant role on the slip casting processing, and in turn, on the microstructure and properties of the final products.[9] A well dispersed slurry can be obtained by choosing a suitable dispersant, a critical concentration of this dispersant and a proper pH value.[10] The dispersant is usually absorbed on the surface of the ceramic particle up to a critical concentration. Beyond this concentration, the dispersant would remain in solution and interferes with the stabilisation of the suspensions. The effects of electrolyte dispersant concentration on the surface charge were investigated by Bohuslav Doobiá et al.[11] It was found that the surface charge depended not only on the pH value but also on the concentration of dispersant and nature of the specifically adsorbing and indifferent ions. A screening effect of dispersant concentration was also observed due to repulsion between charges that were already absorbed, and newly arriving ions.[11]

Solids loading also affects the properties of the suspensions. In some particle systems, green densities could initially show an increase to a maximum, followed by a decreasing trend with increasing solids loading.[12–14] A linear increase in packing density with solid loading was also observed in some other suspensions.[15–17] However,

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* Corresponding author. Tel.: +351-234-370242; fax: +351-234-425300.

E-mail address: jmf@cv.ua.pt (S. Mei).

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no relationship between solids loading and green density was found in other systems.[18–20]

Colloidal processing techniques (such as slip casting, pressure casting, tape casting and infiltration casting) have been widely used for preparing cordierite ceramics or glass-ceramics.[21] Among all the colloidal processing techniques, tape casting is the one most prevalently used for the preparation of cordierite ceramics. For example, SiC aligned fibres reinforced cordierite matrix composites were fabricated with the tape casting and lamination technique. The final product showed improved mechanical strength over monolithic specimens.[22] Cordierite as substrate materials were obtained by laminating the green tapes of cordierite together with low softening point glasses and sintering into a single substrate. On the contrary, relatively less work has been done concerning the slip casting preparation of cordierite ceramics and glass ceramics. The present work presents a systematic investigation on the slip casting processing of cordierite and earth–alkaline–borosilicate glass powders. As a comparison, the microstructure and sintering behaviour of green bodies obtained by dry pressing is also studied.

2. Experimental procedure

2.1. Preparation of powders

A commercial alumina powder (A16 SG, Alcoa Chemicals, USA), with a BET specific surface area of 11 m^2/g, $Mg(NO_3)_2 \cdot 6H_2O$ (Merck KgaA, Germany) and silica powder (Aldrich Chemical Company, Inc., USA) were used to synthesise a stoichiometric cordierite powder. The raw materials were mixed together in absolute ethanol and then milled for 6 h in a planetary ball mill. The mixtures were completely dried in an oven at 110°C and then calcined at 1300°C for 2 h to obtain the cordierite powder. The calcined cordierite was placed in a mortar jar for planetary milling for 12 h to obtain desired particle size.

An earth–alkaline–borosilicate glass powder (Schott Glass Package, Germany) was used to decrease the sintering temperature of cordierite. The composition of glass powder, as given by the supplier, is shown in Table 1.

2.2. Preparation of suspensions

The suspensions were prepared by mechanically mixing cordierite and glass powders with the proportion of 50:50 (wt.%) into a solution of polycarboxylic acid, Dolapix CE 64 (Zschimmer & Schwarz, Germany) in distilled water. The solids loading used were 50, 60, 70 wt.%. The compositions of the samples are shown in Table 2. After being stirred for 30 min for uniform distribution of the components, the as-obtained slurries were deagglomerated in polyethylene bottles using ZrO_2 balls for 24 h. A de-airing and conditioning step was then performed for further 24 h by rolling the slips in the milling container without balls.

Table 1
Compositional ranges (wt.%) for the glass powder, as given by the supplier

Oxide components	B_2O_3	MgO	Al_2O_3	SiO_2	CaO	Sb_2O_3	BaO
Content range (wt. %)	1–10	1–10	10–50	> 50	10–50	< 1	1–10

Table 2
The solids loading (wt.%) and dispersant concentrations (wt.% based on solids) used, and the respective samples code

Amount of dispersant (wt.%)	0.20	0.40	0.60	0.80	1.00
Solids loading (wt.%)	Samples code				
50	D1-50	D2-50	D3-50	D4-50	D5-50
60	D1-60	D2-60	D3-60	D4-60	D5-60
70	D1-70	D2-70	D3-70	D4-70	D5-70

2.3. Preparation of green and sintered bodies

The green bodies were consolidated by pouring the suspensions into plastic moulds (diameter = 13.5 mm, height = ~5 mm) placed on a plaster plate. Before sintering, the green samples were completely dried in an oven at 110°C. The sintering schedule included a initially heating rate of 5°C/min up to 300°C, then a heating rate of 3°C/min between 300 and 500°C to burn out organic dispersant inside the green bodies, followed by a heating rate of 10°C/min up to different desired temperatures. The samples were hold at each temperature for 2 h; followed by natural cooling by switching-off the power.

To compare the effect of different shaping processes on the green body, compacts were also shaped by uniaxial pressing (about 20 MPa) in a die and then isostatic pressing (about 200 MPa). The heat treatments of the pressed compact were the same as for the slip casting samples.

2.4. Characterisation techniques

The particle size distributions and mean particle sizes of obtained cordierite and glass powders were measured using a Coulter LS230 instrument (Coulter Electronics Limited, UK). The morphology of the powders was observed by scanning electron microscopy (SEM) (4100-1, Hitachi, Japan). Rheological properties of the suspensions were determined with a rotational control stress rheometer (Carri-med 500 CSL, UK) after the suspensions were de-aired. The measurements were performed at a constant temperature (20°C). The adopted measuring configuration was a cone and plate, and steady measurements were conducted at shear rates from about 0.01 to 1000 s^{-1}. A pre-shearing was performed at the higher shear rate for 1 min before measurement, followed by an equilibrium time for 30 s to transmit the same rheological history to the whole tested suspensions. Pore-size distribution was examined by Hg-intrusion porosimetry (Poresizer 9320, Micromeritics, USA). The microstructural evolution of green bodies and sintered bodies was also observed using scanning electron microscopy (SEM). The green and sintered densities were measured by the Hg immersion method.

3. Results and discussion

3.1. Characterisation of powders

Fig. 1 shows the evolution of particle size distribution of cordierite powders with milling time. The particle size decreases initially with the milling time. Further increase in milling time from 12 h (D_{50} = 1.157 μm) to 20

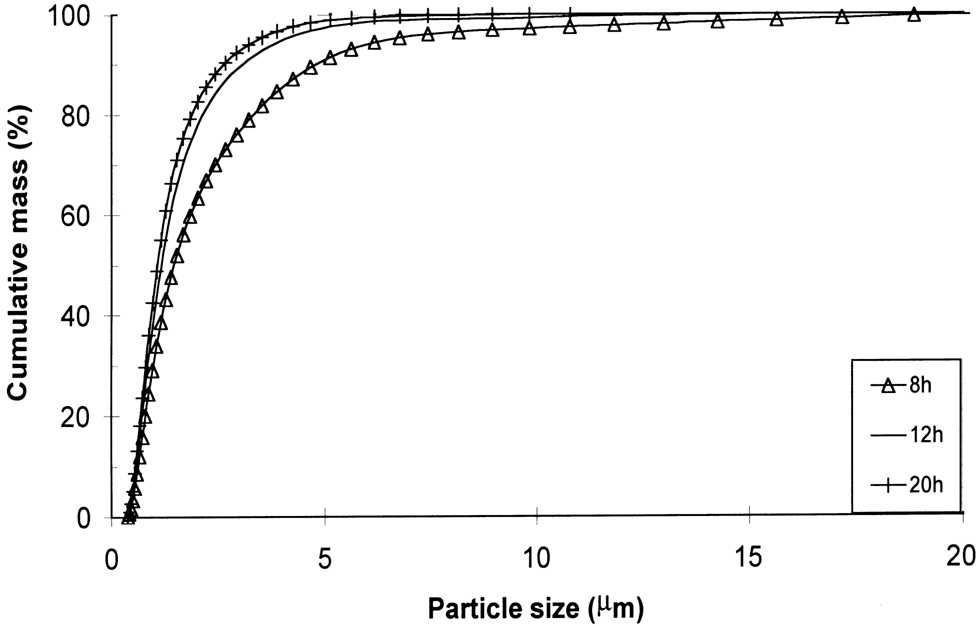
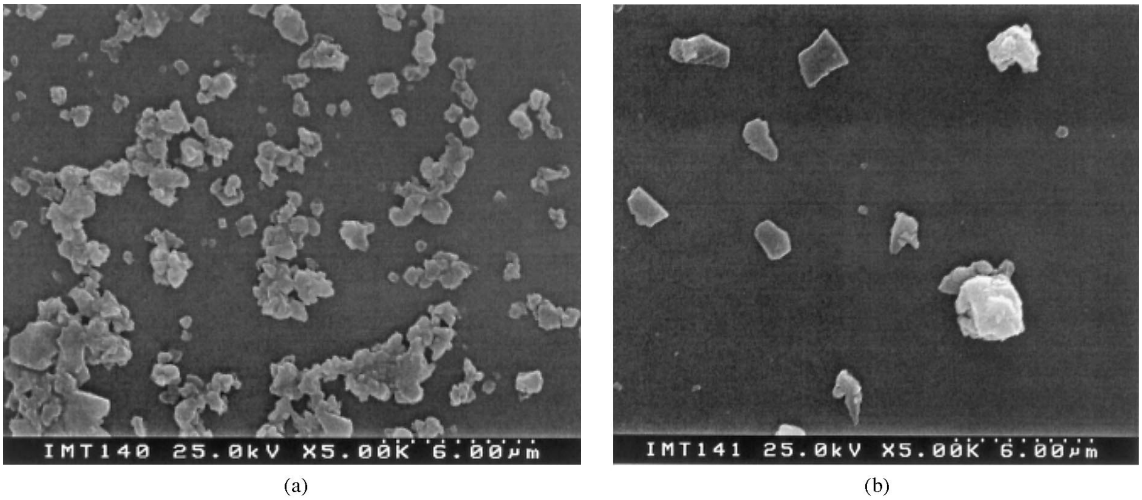


Fig. 1. Particle size distribution of cordierite powders after milling for different time periods (cumulative mass).



(a) (b)

Fig. 2. The morphology of (a) cordierite powder after 12 h-milling and (b) glass powder as supplied.

h (D_{50} = 1.065 μm) could not cause significant decrease in particle size of cordierite powders. Indeed, the cumulative curves (12 h and 20 h) in Fig. 1 are almost superimposed. Therefore, a milling time of 12 h were chosen for slip casting processing of the cordierite powders. The morphologies of these two powders are shown in Fig. 2a and b, respectively. It can be seen that agglomerate formation occur in the cordierite powders due to the fine size of the primary particles, while dispersed particles are observed in the case of glass powders.

3.2. Characterisation of suspension

The evolution of the rheological properties of the suspensions containing 50, 60 and 70 wt.% solids with the amount of the dispersant is reported in Figs. 3–5, respectively. At the lower solids loading (50 wt.%, Fig. 3), the amount of the dispersant does not greatly influence the properties of the suspensions, which could be characterised by a shear thinning behaviour at low shear rates followed by a trend to constant viscosity levels at high shear rates. Along the entire testing range of shear rates, the viscosity decreases by more than three orders of magnitude. At low shear rates, the inter-particle forces dominate the interactions between the suspended particles and hydrodynamic forces become dominant as shear rate increases. As the solid loading increases (60 wt.%, Fig. 4), the effect of dispersant concentration on the rheological properties of the suspensions becomes more obvious. The shear-thinning behaviour is still observed at lower dispersant concentration (D1-60, D2-60), however, the suspensions change their rheological behaviour from shear thinning at low shear rate, to shear thickening at high shear rate, for higher concentrations of dispersant (D3-60, D4-60 and D5-60). The viscosity of the suspension decreases sharply as the dispersant concentration increases up to D3-60. Further increase in the dispersant concentration would increase the viscosity of the suspension (D4-60). Therefore, 0.6 wt.% of Dolapix seems to be the optimum concentration for the cordierite–glass system, which gives the lowest viscosity. For dispersant concentrations higher than the optimum amount, the dispersant in excess remains in solution and acts as a free electrolyte, increasing the ionic strength. The electrostatic forces among particles will be disturbed and hence the viscosity will increase, as reported by Briscoe et al.[10] The reason why the viscosity increases as dispersant concentration further increases could be explained by the screening effect excerted by the excess dispersant in solution that would result in a compression of the electrical double layer around the dispersant covered particles. When the solids loading was further increased to 70 wt.% (Fig. 5), shear thickening behaviour was observed in the whole dispersant concentration range. An optimum point for the dispersion concentration seems to be 0.6 wt.% of Dolapix (D3-70). The dispersant concentration is the same as that of D3-60 (0.6 wt.%). The shear-thickening behaviours occurring in the suspensions with 60 and 70 wt.% solids are due to hydrodynamic interactions and increasing frequency of collisions among the particles. Furthermore, at these high solids loading, particles have to approach each other up to short distances while at rest. In order for a system under these conditions to flow, particles have to pass over each other, increasing their average distance. However, capillary forces oppose

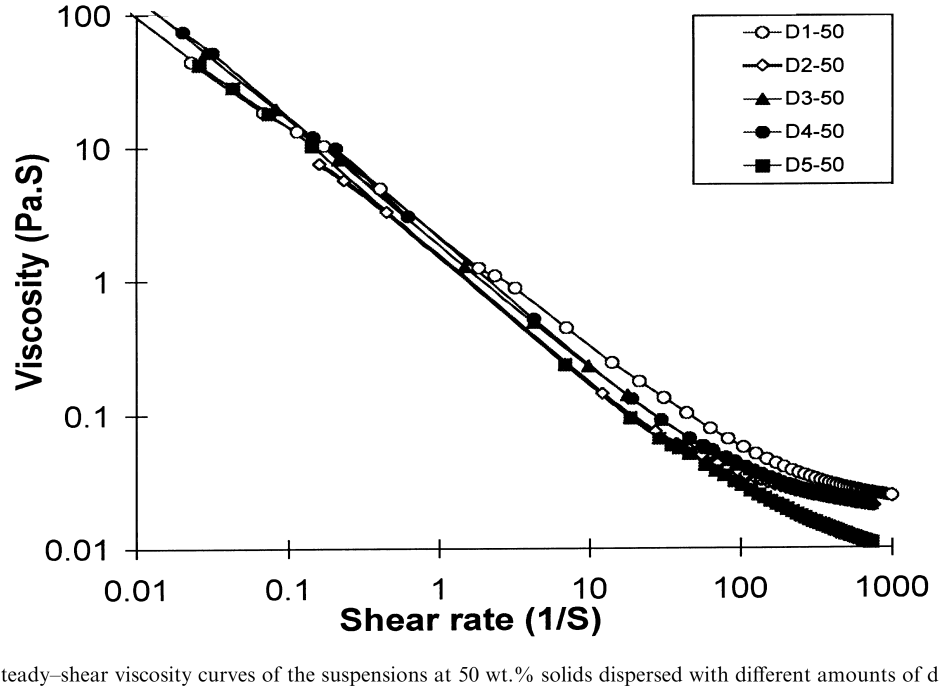


Fig. 3. Steady–shear viscosity curves of the suspensions at 50 wt.% solids dispersed with different amounts of dispersant.

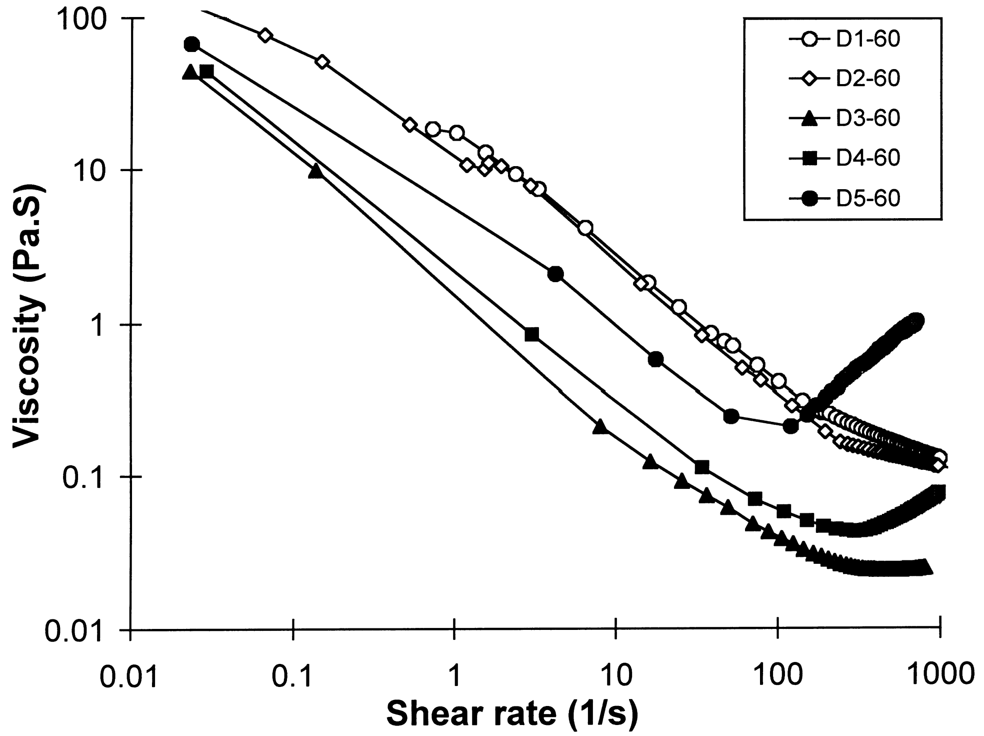


Fig. 4. Steady–shear-viscosity curves of the suspensions at 60 wt.% solids dispersed with different amounts of dispersant.

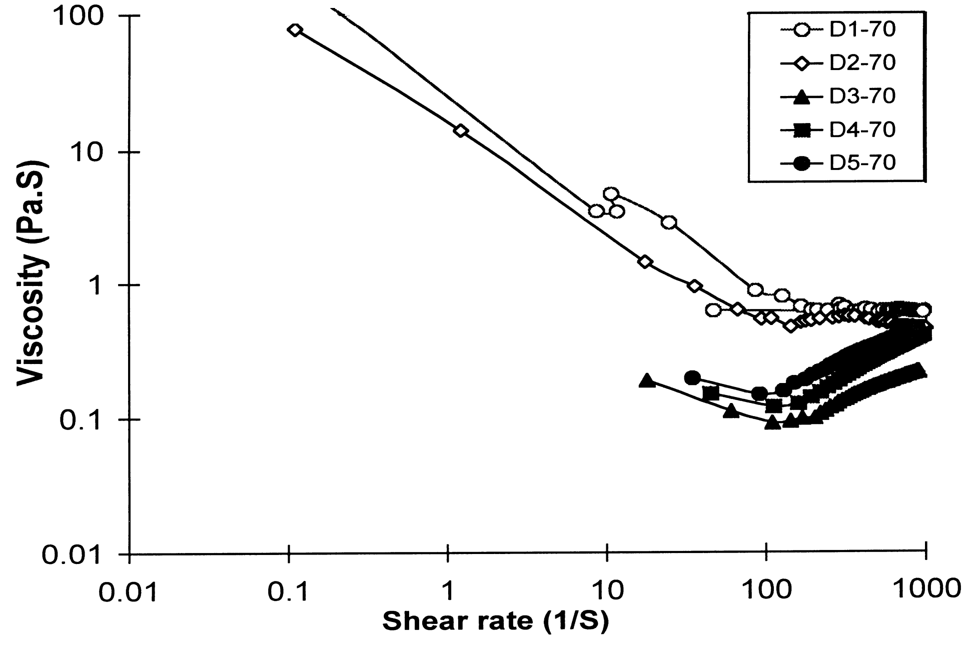


Fig. 5. Steady–shear viscosity curves of the suspensions at 70 wt.% solids dispersed with different amounts of dispersant.

to this expansion of the system. The combination of all of these interactions would lead to the observed increase of viscosity in the higher shear rate regime.

All of these results show that the influence of dispersant on the rheological behaviour is particularly noticeable for the high solids-loaded suspensions in which the particles have to approach each other up to short distances at which electrosteric repulsions become active. For the lower solids loading system (50 wt.%), the average distances among suspended particles might be larger than those at which the steric contribution for the stabilisation enters into play and dispersion should occur mainly through the electrostatic contribution. On the other hand, the amount of liquid phase is high enough to make the suspension fluid.

3.3. Characterisation of green bodies

Fig. 6 shows the relative density of the green bodies of different samples. The density reaches the maximum value when the concentration of dispersant is 0.6 wt.% for all solids loadings. The evolution of pore size distribution of the green bodies with solids loading for 0.2 wt.% dispersant is reported in Fig. 7. All the samples show relatively narrow pore size distributions, which favour the densification of the samples, but the pore volume fraction and the average size of pores decrease as solids loading increase. The effect of different amounts of

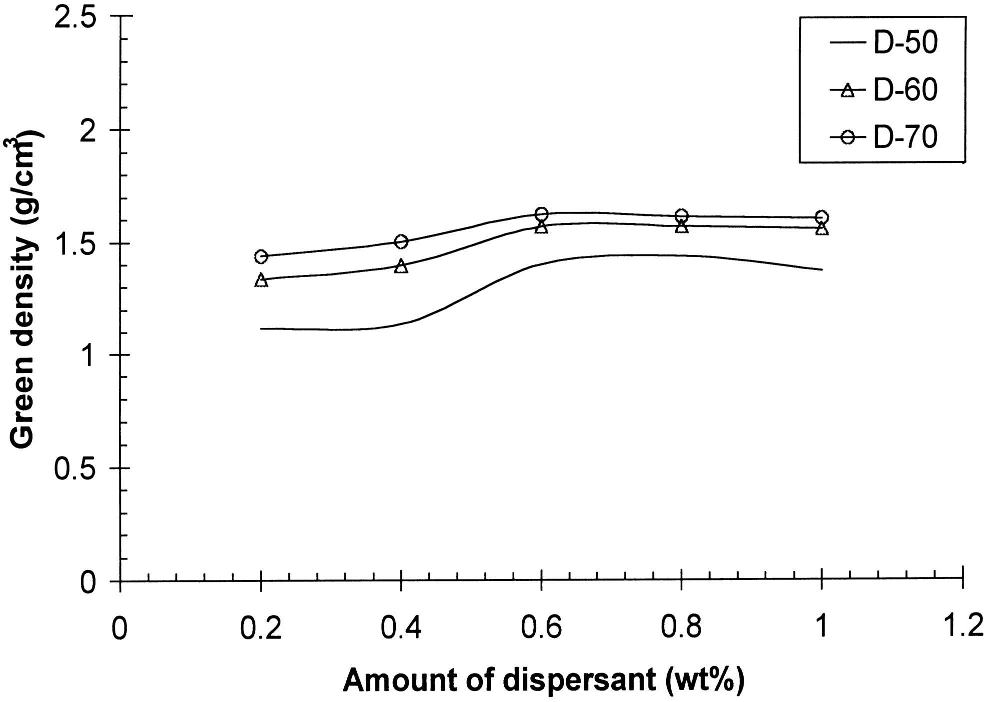


Fig. 6. The effect of solids loading on green densities for different dispersant concentrations.

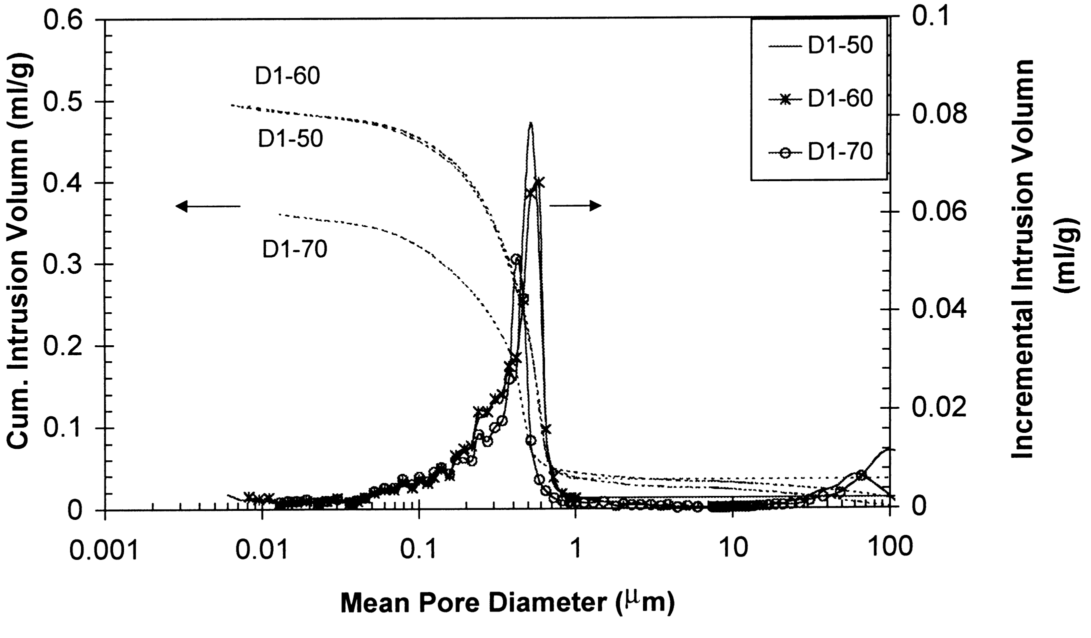


Fig. 7. The pore size distribution in sample D1 with different solids loading.

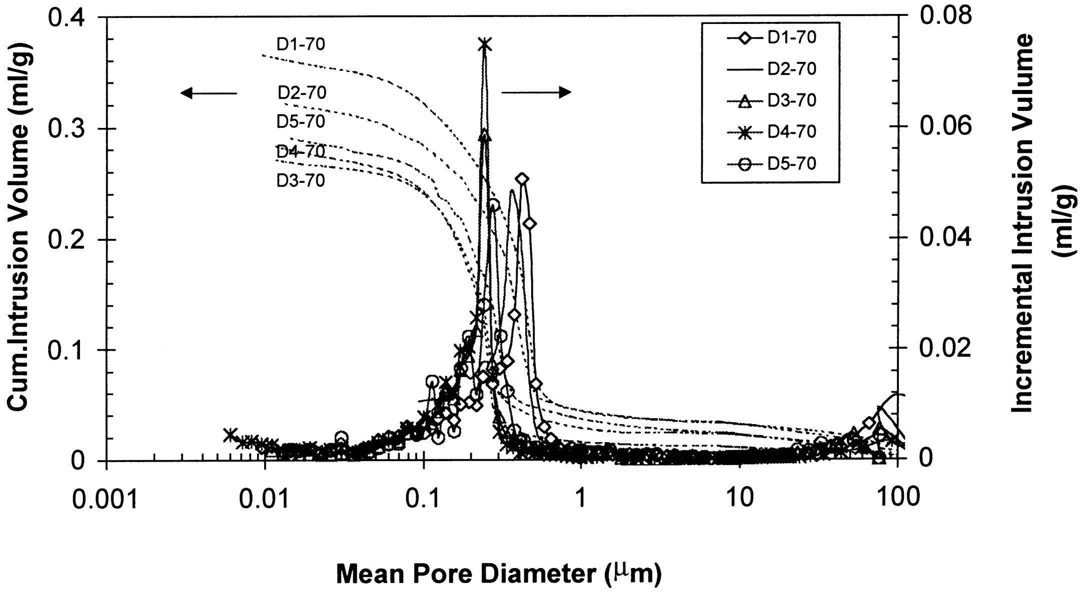
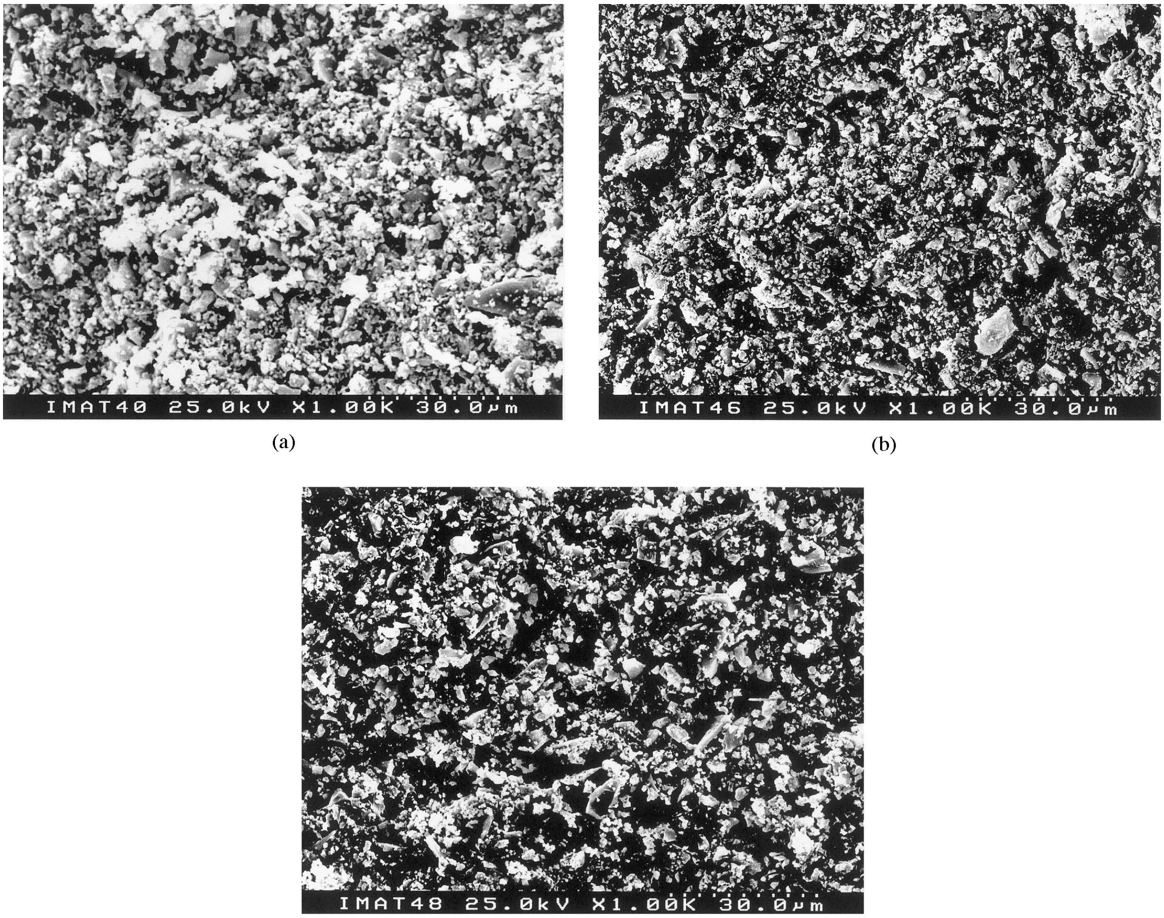


Fig. 8. The pore size distribution of the green bodies (70 wt.% solids loading) for different dispersant concentrations.



(a)

(b)

(c)

Fig. 9. The microstructures of fracture surfaces of the green bodies (70 wt.%) for different dispersant concentrations. (a) D1-70; (b) D3-70; (c) D5-70.

dispersant on the pore size distribution of the green bodies is also reported in Fig. 8 for suspensions containing 70 wt.% solids. The main peak shifts to smaller pore size and becomes narrower with increasing the dispersant concentration from D1-70 to D4-70, showing an opposite trend for further addition of dispersant. The peak of D5-70 shows about the same average pore size as D3-70, but increases in intensity. This indicates that the addition of 0.6 wt.% of the dispersant into the suspensions with 70 wt.% could lead to a green body with smallest pore diameter and more uniform pore size distribution. These results are in good agreement with those of green density.

Fig. 9 shows the microstructures of fracture surfaces of the green bodies (70 wt.%) with different dispersant concentrations. Clear differences in the homogeneity could be observed among these samples. Serious agglomerates and larger pores exist in the green body prepared from D1-70 (Fig. 9a), indicating that this amount of the Dolapix is not enough to correctly disperse the powders. At the intermediate dispersant concentration (D3-70, Fig. 9b), a well-defined and more uniform microstructure can be observed. Some flocculation among the particles can be observed again when the dispersant concentration further increases (D5-70, Fig. 9c). Moreover, the pores could be easily observed again in this sample.

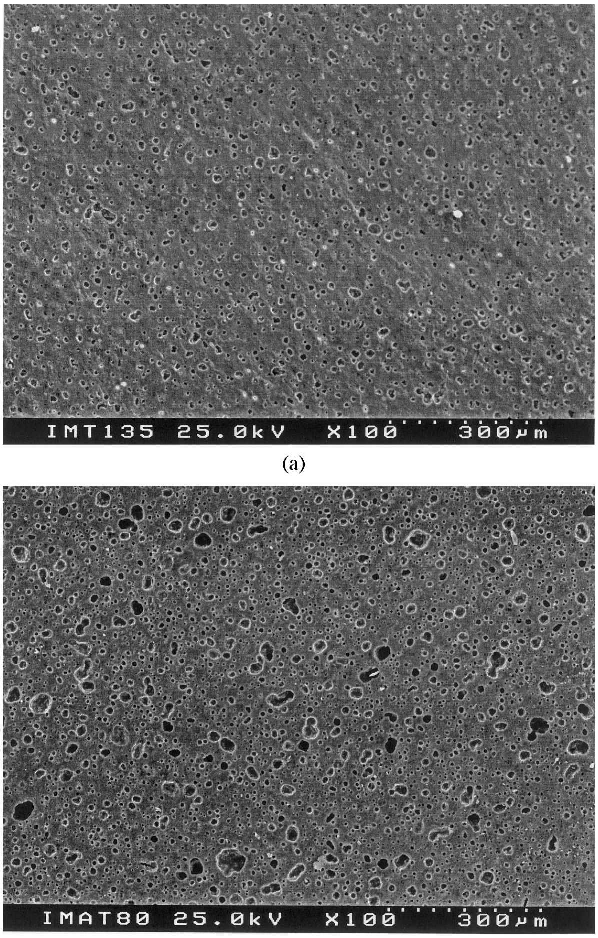


Fig. 10. The microstructures of samples heated at 1200°C for 2 h, prepared by different consolidation methods. (a) slip casting; (b) dry pressing.

3.4. Characterisation of sintered bodies

Fig. 10 compares the microstructures of slip cast (a) and dry pressed (b) samples heated at 1200°C for 2 h. The pore size of the sintered sample prepared by slip casting is smaller than that obtained by dry pressing. A more uniform pore size distribution can be observed in the slip cast sample. The maximum sintered densities for the different consolidation methods, slip casting and dry pressing, are 92.2 and 84.3%, respectively. Therefore, slip casting proves to be a more suitable technique to prepared cordierite glass-ceramic with homogeneous microstructure.

4. Conclusions

1. The rheological measurements show that both the amount of dispersant and solids loading play important roles on the rheological behaviour of the cordierite-glass suspensions. At low solids loading (50 wt.%) shear-thinning behaviour was observed, irrespective of the amount of dispersant, within the whole range of shear rate. As the solids loading increased (60, 70 wt.%), the suspensions became shear thickening in the higher shear rate range, especially for dispersant concentrations that gave the minimum viscosity values.
2. For all solids loading, green densities increase with increasing amounts of dispersant up to an optimal value, decreasing afterwards. On the other hand, the size of pores decrease and the pore size distribution becomes more uniform with increasing amounts of dispersant up to the optimal level, while the volume fraction of pores tends to increase for further amounts of dispersant.
3. Slip casting proves to be a more efficient processing technique to prepare dense and homogeneous cordierite-based glass–ceramic composites, compared to the dry pressing technique.

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