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Effect of dispersant on the rheological properties and slip casting of concentrated sialon precursor suspensions

Xin Xu, Marta I.L.L. Oliveira, Renli Fu, José M.F. Ferreira*

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

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Abstract

The ability of Hypermer KD1 to disperse high solids loading reaction sialon suspensions for slip casting has been characterised. It has been found to be a very effective dispersant in organic media of 60-vol.% MEK and 40-vol.% Ethanol, yielding fluid and highly homogeneous suspensions. The effects of added amounts of KD1 have been observed through adsorption data, sedimentation tests and rheology measurements. KD1 imparts low viscosity and stability to the suspension. It has been found that 3-wt.% addition of KD1, based on the weight of reaction sialon powders, results in a very stable and high flowable suspension with near Newtonian flow behavior. Less amounts of dispersant lead to unstable suspensions with obvious shear thinning flow behaviors, while adding excessive dispersant leads to high viscosities, especially at high solids loading. Measuring the pore size distribution of green bodies from different suspensions has proved the effects of dispersant amounts on dispersing the slurries and on slip casting performance.

Keywords: Porosity; Rheology; Sialon; Slip casting; Suspensions

1. Introduction

Sialon ceramics have attracted an increasing interest in the development of structural ceramics due to their unique combination of excellent properties.[1] However, the reliability and the cost of sialon ceramics have not been improved enough to a level, which could be accepted by the industry area, thus preventing seriously the further development of sialon ceramics.

Low reliability can be attributed to the defects remaining in the final products. Many defects originate from the production process before sintering. For instance, large pores are the most common defects in sintered ceramics and they are mostly related to defects in grains such as pores, dimples and void spaces between granules. As the defects in the green bodies grow during the sintering process, the microstructure should be controlled in the green bodies to minimize the size of defects as well as to achieve a uniform and dense microstructure.[2]

Slip casting is known to be a suitable and inexpensive compaction process to produce material with high green densities and microstructural homogeneity, even for complex geometries.[2,3] Therefore, it would be advantageous if sialon ceramics could be shaped by using the low-cost slip casting method, which would promote the wide spread use of sialon ceramics and the stride forward industrialisation.

Slip casting of sialon powder in aqueous media has been studied by many authors.[4–6] However, little effort has been made on obtaining green bodies composed of Si_3N_4, Al_2O_3, Y_2O_3 and AlN through slip casting.[7] Reaction sialon powder suspension should be stabilized by steric repulsive forces in organic media because of the hydrolysis of the AlN in aqueous environments. The optimization of colloidal suspensions in order to reach a low viscosity, Newtonian flow behavior and stability is the first step in order to produce homogeneous, defect free pieces. The kind and amount of dispersant have great effect on the preparation of homogeneous, high concentrated ceramics suspensions with low viscosity.[8–10]

An investigation on the slip casting reaction sialon powder is presented in this work. The key point is the preparation of a concentrated suspension with optimised

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

E-mail address: jmf@cv.ua.pt (J.M.F. Ferreira).

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flow behaviour suitable for slip casting. For this, the effects of dispersant amount on the flow behaviour and slip casting performance of the suspensions have been studied.

2. Experimental procedure

The starting powders used to prepare the sialon ceramics were α-Si_3N_4 (H.C. Stark, Germany, $d_{50}=0.38$ μm), Al_2O_3 (Alcoa Chemicals, USA, $d_{50}=0.38$ μm), AlN (H.C. Stark, Germany, $d_{50}=2$ μm) and Y_2O_3 (H.C. Stark, Germany, $d_{50}=0.75$ μm). Weighed batches of 76.92-wt.% Si_3N_4 + 13.46-wt.% AlN + 5.77-wt.% Y_2O_3 + 3.85-wt.% Al_2O_3 powder mixtures were planetary milled for 4 h in 2-butanol, using Al_2O_3 jars and Si_3N_4 balls. After milling, particle size distribution was measured using a Coulter LS230 particle size analyser (Coulter, UK), the mixed slurries were dried in an oven at 40 °C for 48 h. The powders were then deagglomerated in an agate mortar, sieved through an 80 μm sieve, and used as starting powder to prepare the suspensions. Fig. 1 shows a photograph of the starting powders, while Fig. 2 displays the particle size distribution. The main features of the particle size distribution are an average particle size with the main population centred at about 0.35 μm, mainly derived from the finer α-Si_3N_4 and Al_2O_3 components, with some contribution from Y_2O_3, especially for the right hand side of the main peak, and a smaller and coarser population centred at about 1.8 μm, derived from the coarser AlN component. These features are in good agreement with the SEM analysis (Fig. 1) and with the above indicated average particle sizes of different components as given by the suppliers.

An azeotropic mixture of 60-vol.% methylethylketon (MEK) (Riedel-de Haën, Germany) and 40-vol.% ethanol (Merck, Germany) was selected as the solvent. Hypermer KD1 (Imperial Chemical Industries PLC, UK) was used as dispersant.

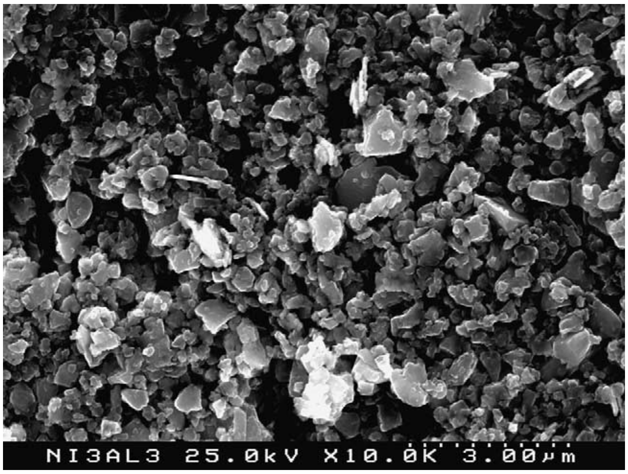

Fig. 1. SEM of the starting reaction sialon powder mixture.

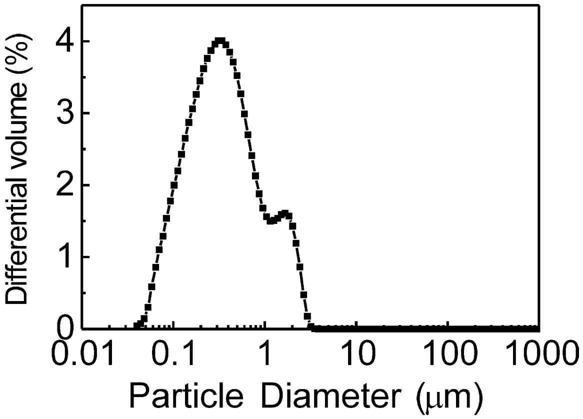

Fig. 2. Particle size distribution of the starting reaction sialon powder mixture.

A series of 10-vol.% reaction sialon suspensions with different dispersant additions, based on the weight of sialon powders, were prepared for sedimentation tests and adsorption measurements. The sedimentation tests were performed by putting the suspensions into graduated 10 ml cylinders and allowed them to stand undisturbed for more than 1 month. In order to determine the amount of dispersant adsorbed, green bodies were consolidated by pouring the 10-vol.% suspensions with different dispersant additions into plastic rings placed on a plaster plate. After drying at 80 °C, both the slip cast bodies and the raw reaction sialon powders were analysed by thermal gravimetric analysis (TGA) (Labsystem STA, Setaram, France) at a heating rate of 5 °C/min up to 600 °C in air atmosphere, The differences of weight losses were used to determine the amount of KD1 adsorbed on each sample.

More concentrated suspensions with different dispersant additions were prepared by planetary milling, using Al_2O_3 jars and Si_3N_4 balls. Rheological properties of the suspensions were evaluated using a rheometer (Carri-med, CSL 500, UK) at temperature of 20 °C.

Slip casting experiments were made by pouring the slips into plastic rings set on absorbent plaster blocks. After drying, the pore size distribution of green samples was measured using mercury porosimeter (PoreSizer 9320, Micromeritics, USA).

3. Results and discussion

The adsorption isotherms of Hypermer KD-1 at the reaction sialon surface are shown in Fig. 3. The straight line shows 100% adsorption. It can be seen that KD1 displays a strong affinity isotherm being completely adsorbed at low concentrations. Adsorption reaches a plateau value when large amounts of KD1 are added.

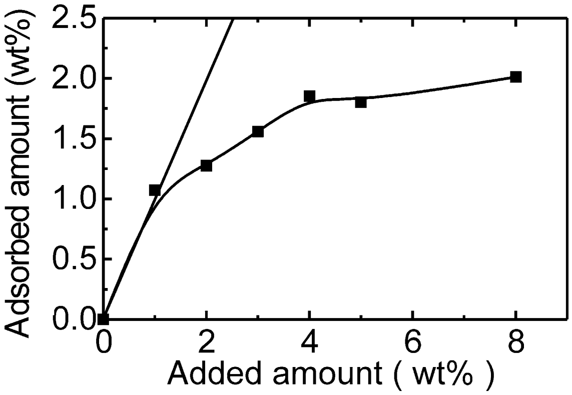

Fig. 3. Adsorption isotherms from 10-vol.% suspensions dispersed with different added amounts of KD1.

The plateau value is about 1.8-wt.%, which would depend on the density of active sites existing at the surface of reaction sialon powders.

According to the technical information provided by the supplier, Hypermer KD1 consists of a polyester/polyamine polymer with an estimated MW of about 10,000. It is composed of an anchoring group, which is absorbed onto the particle surface, and a polymeric chain with a chemical structure designed to have a good solvency in the dispersion medium used and give optimum steric stabilisation to the dispersion. The oligomeric nature of the anchoring groups makes that there will be always one or more anchors attached to the surface of the particles, which makes it stick better to the surface.

Slurry stability was evaluated by measuring the settling of powder (sediment height as a percentage of the total suspension height) for different added amounts of the dispersant. Sedimentation testes were carried out using the whole composition, since previous measurements made on each separate powder revealed quite similar behaviour.[11] Fig. 4 shows the sediment volume of 10-vol.% reaction sialon suspensions with varying additions of KD1. It can be seen that increasing the amount of dispersant makes the sediment volume to first decrease gradually up to a minimum value observed for 3-wt.% dispersant, followed by a slight increase for further additions. These results are in close agreement with the measurements made before on the individual powders[11] and indicate that a more consolidated structure is progressively formed up to the optimal amount (3-wt.%), followed by a small decrease in sediment packing density due to an over deflocculation effect.

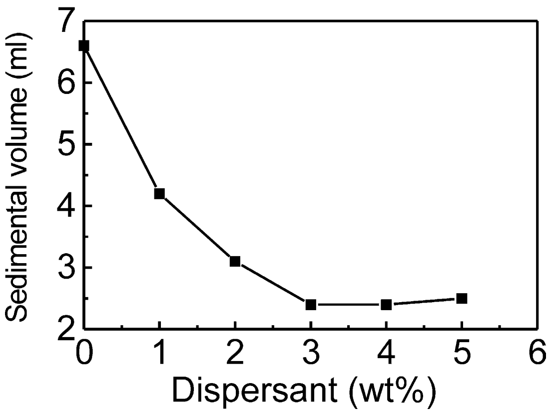

Fig. 4. Sediment volume of reaction sialon against KD1 additions.

The viscosity versus shear rate curves of the suspensions with solids loading of 40- and 50-vol.% in the presence of different added amounts of dispersant are presented in Fig. 5a and b, respectively. As can be seen in Fig. 5a, at the lower solids loading (40-vol%) the amount of the dispersant does not greatly influence the rheological properties of the suspensions. The suspensions can be characterized by a shear-thinning behaviour at low shear rates followed by a trend to constant viscosity at high shear rates. With increasing solids loading to 50-vol% (Fig. 5b), the rheological properties of the suspensions became more sensitive to the added amount of dispersant. The suspensions with 1 and 2-wt.% dispersant show obvious shear-thinning behaviours, with the shear thinning character decreasing as the amount of dispersant increases. In the presence of 3-wt.% dispersant, the suspension exhibits nearly constant viscosity and could be fitted to near-Newtonian flow behaviour with only a slight degree of shear thinning.

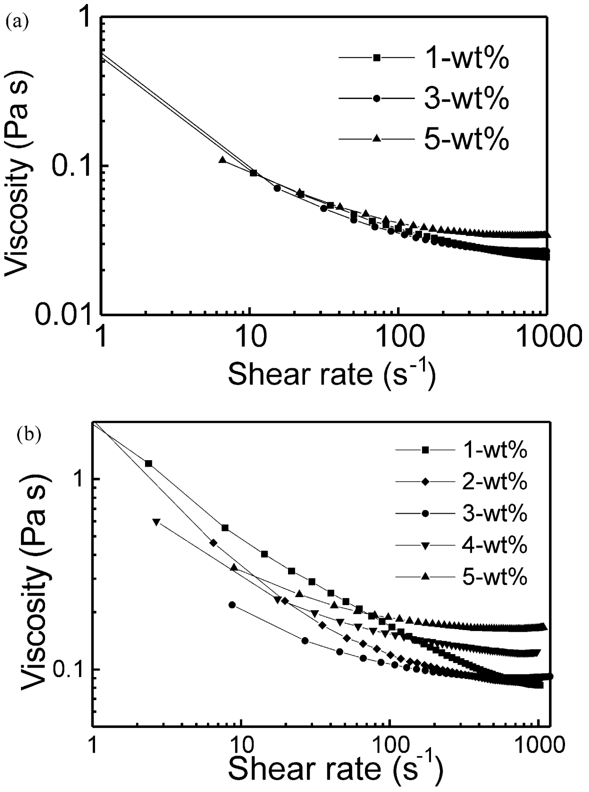

Fig. 5. Viscosity curves of the suspensions dispersed with different additions of KD1: (a) 40-vol.%; (b) 50-vol.%.

With further increasing the added amount of dispersant, the suspensions still show near-Newtonian behaviour, but the viscosity level also increases.

At low solids loading, the magnitude of the average Van der Waals forces would be small due to the relatively large distance between suspended particles. So, a small addition of dispersant could lead to repulsion forces with enough magnitude to counterbalance Van der Waals forces,[12] and the frequency of the collisions between separate particles (due to Brownian motion) is lower. This explains why the rheological properties of the suspensions are almost unaffected by the amount of dispersant at low solids loading. However, it should also be pointed out that due to insufficient surface coverage at low dispersant additions, the balance between Van der Waals forces and steric forces is not completely stable, and agglomerates would easily form through the uncovered surface sites due to Brownian motion, as sedimentation tests show.

With increasing solids loading, the importance of Van der Waals forces also increases due to the shorter distances between suspended particles. Therefore, agglomerates will readily form if insufficient amount of dispersant is added, under which conditions Van der Waals forces will dominate the interaction between suspended particles, and significant shear shinning will be observed due to the breakdown of agglomerates because of the applied shear.[13]

Fig. 3 suggests that a maximum adsorption plateau of about 1.8-wt.% KD1 occurs for an added amount of dispersant of about 4-wt.%, which would correspond to a monolayer coverage. Considering that one part of the oligomer dispersant molecules has a high affinity to the solvent, while the anchoring groups have a high affinity to the surface of particles, the equilibrium concentration between adsorbed and dissolved proportions of the dispersant would depend on solids loading. This means that increasing solids concentration would enable to achieve the condition of monolayer coverage at lower add amount of dispersant. In fact, Fig. 5 shows that the best dispersion conditions at high solids loading (50-vol.%) are obtained in the presence of 3-wt.% dispersant, while a transient and not yet well defined situation seems to occur at 40-vol.% solids. Adding excess amounts of KD1 would increase its proportion in the solution, therefore degrading the dispersion properties. This explains why the viscosity of the suspensions dispersed with 3-wt.% KD1 exhibit minimum viscosity values at high solids loading. Although the suspension still remains relatively stable for KD1 $>$ 3-wt.%, the viscosity increases also due to the higher amount of liquid associated with the adsorbed polymer chains, not available for flowing, and thus increasing the thickness of the adsorbed layers, as well as due to entanglements among the excess dispersant molecules in solution.

Adsorption of polymeric chains with some associated solvent would result in an increase of their effective volume, Φ_{eff}, which can be qualitatively defined as:

$$\Phi_{\text{eff}} = V_{\text{solid}} + V_{\text{polymer}} + V_{\text{solvent}} \tag{1}$$

Assuming that all of the adsorbed species form a layer of thickness, δ, around a spherical particle of diameter a, the effective volume of the particle would be expressed by:

$$\Phi_{\text{eff}} = \left(1 + \frac{\delta}{a}\right)^3 \tag{2}$$

Thus, thicker adsorbed layers would result in a more significant increase of the apparent size of the dispersed particles, i.e. in a higher effective solids volume fraction.[14] This means that suspensions will not behave as hard sphere systems, with the collisions between particles being mediated by the adlayer thickness, which in turn depends on the dispersion conditions (the relative affinity of the anchoring groups to the surface, the solvency of the protruding part of the oligomer in the media and the adsorbed amount, solids loading, etc.). All of these factors are strongly interrelated and determine the rheological response of the suspensions. Based on this relationship, the steady shear viscosity of different solids loaded suspensions measured at a given shear rate is usually adopted to estimate the adlayer thickness by using the modified Krieger–Dougherty model.[15,16] However, in the present case the estimation of the adlayer thickness by this method is much more complicated because, as stated above, the adlayer thickness would change with solids loading, since a higher fraction of solvent will be associated with the dispersant molecules at lower solids volume fractions. Because of that, some authors have used surface force apparatus to directly measure the thickness of adsorbed layers at glass surfaces,[17] or at silicon nitride powder surfaces.[18] Bergström, et al.[17] found adlayer thicknesses of approx. 9–15 nm for compressed layers, depending on dispersant concentration, whereas a thickness of approx. 23–24 nm, independent of polymer concentration, was estimated for undisturbed layers. From the comparison between the measured interaction lengths with previous layer thickness estimates based on rheological studies they concluded that the polymer layers are compressed in concentrated suspensions.

It could be concluded that solids loading has a stronger effect on viscosity in the case of flocculated suspensions than it does on well-stabilized suspensions of particles with an optimum surface coverage by the dispersant. As the solids loading increases, stabilization of the suspensions becomes more critical. In the present system, the preparation of 55-vol% solids suspensions with 1- or 5-wt.% KD1 addition for rheological measurements

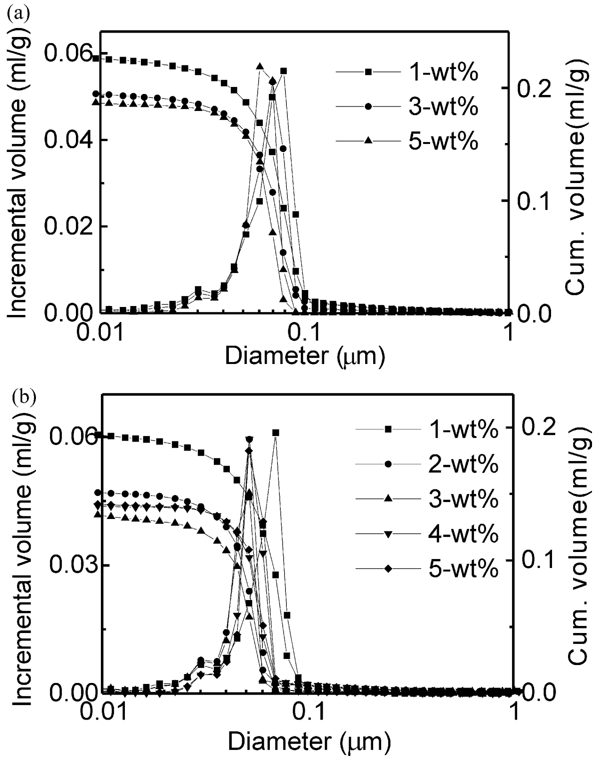

Fig. 6. Pore size distributions of the green bodies as function of KD1 additions: (a) 40-vol.%; (b) 50-vol.%.

was impossible, while 3-wt.% revealed to be the optimal amount of dispersant in the high solids volume fraction range up to 60-vol.%,[18] which is more or less the maximum achievable solids loading in this system. It has been reported [19] that the required amount of dispersant to yield optimum dispersion increases with the increase of solid loading, while in the present study, the optimum dispersant addition could be fixed to 3-wt.% at high solid loading, which might be due to the high affinity of the anchoring groups of dispersant to the surface of the particles, further additions would increase the free dispersant concentration in the solvent.

The results about optimization of the amount of added dispersant also suggest that evaluating the effect of dispersant, based merely on the measurement of apparent viscosity at a fixed shear rate, may be misleading in some cases, because of the viscosity changes as a function of shear rate. It would be better to assess the dispersion ability through flow behaviour rather than through apparent viscosity measurements.

Table 1
Effects of solids loading and added amount of dispersant on green density

Solids loading (vol.%)	Added amount of KD1 (wt.%)	Relative green density (%)
30	3	57.3
40	1	56.6
	3	60.8
	5	61.1
50	1	60.3
	2	66.1
	3	68.3
	4	67.7
	5	67.4
55	3	69.7

Table 1 shows the effects of solids loading and added amount of dispersant on density of green bodies obtained from slip casting different suspensions, while Fig. 6a and b show the pore size distributions of the greens derived from 40- and 50-vol.% solids loaded suspensions. All the samples show relatively narrow pore size distributions, which favour the densification of samples. Table 1 and Fig. 6 confirm that the best dispersion conditions at 50-vol.% solids would have been obtained with 3-wt.% KD1 addition since this amount of dispersant led to the higher value of packing density, lower pore volume fraction and narrower pore size distribution, while at 40-vol.% solids the optimal amount of dispersant is still not well defined yet. These results confirm that there is a close agreement between the rheological results shown in Fig. 5, (low viscosity and near ideal Newtonian-like behaviour), which would favour the packing ability of particles due to the less tendency for suspension structuration, and the homogeneity and packing degree of slip cast bodies. On the other hand, Table 1 also reveals the great influence of solids loading on green density in the presence of a fixed amount (3-wt.%) of added dispersant. The relative green density changes from 57.3% at 30-vol.% solids to 69.7% at 55-vol.% solids, i.e., a difference of more than 12%! This means that both solids loading and suspension structure govern the packing efficiency, and that under the optimal amount of dispersant, the solids loading plays a significant role in the packing efficiency. These results can be understood since increasing the number of particles per unit volume would lead to a more favourable polymer configuration at the particles' surface and approach particles up to shorter average distances at which the efficiency of the steric stabilisation mechanism would be enhanced.

As can be observed in Fig. 5a, the flow curves of 40-vol.% suspensions with different amounts of dispersant are similar; however, the packing efficiency of 1-wt.% suspension is obviously worse than the two others, which could be attributed to the lower degree of suspension stability. During slip casting process, the distance between particles decreases with the removal of solvent, and then agglomerates would easily form due to insufficient steric forces developed between particles, resulting in worse packing efficiency.

In the present study, the relative green density from optimized suspension is near 70% ρ_{th}. Since references dealing with slip casting of reaction sialon suspensions were scarce, a comparison with Si_3N_4[3,20] or Sialon[4,7,21] is opportune. Our values of green density are about 10% ρ_{th} higher than those in references, indicating the suitability of KD1 to disperse reaction sialon powders.

4. Summary

Dispersant KD1 was used successfully to deflocculate concentrated reaction sialon suspensions. KD1 imparts stability through steric repulsion forces among the particles. Since steric interactions involve short range forces, which become efficiently active when particles with adsorbed KD1 molecules approach up to close distances, the effect of the amount of dispersant on viscosity level and flow behaviour of the suspensions only became salient at high solids loadings ($\geqslant$50-vol.%). Under these conditions, an optimum dosage of 3-wt.% of KD1 relative to the weight of reaction sialon powders was found, which led to very stable suspensions that exhibited a near Newtonian flow behavior. Accordingly, the packing efficiency revealed to be a complex function of solids loading and suspension structure being maximised at 3-wt.% KD1 and with increasing solids loading. These conditions also led to increasing degrees of homogeneity, lower pore volume fractions and narrower pore size distributions, which will enhance the reliability of the final products.

Acknowledgements

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