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Effect of homogenizing procedures on the slip casting of reaction sialon suspensions

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Abstract

Reaction sialon suspensions were prepared using 3-wt.% KD1 (a polyester/polyamine condensation copolymer) as dispersant in organic media of 60-vol.% methyletheylketone and 40-vol.% ethanol. Different homogenizing procedures were used and compared, such as: high energetic planetary milling, low energetic ball milling and ultrasonic disaggregation. The effect of different homogenizing routes and solids loading on the rheology of suspensions and on the properties of slip casting green bodies has been studied. The differences observed among the various mixing procedures could be attributed to the different degrees of disaggregation and therefore to different fractions of surface coverage of the reaction sialon powders by the dispersant.

Keywords: A. Slip casting; A. Suspension; A. Milling; B. Porosity; D. Sialon

1. Introduction

Sialon ceramics are considered as the most promising materials with great potential for advanced structural applications due to their unique combination of excellent properties [1]. However, the wide spread use of sialon ceramics and the stride forward industrialization have been limited by the low reliability, difficulty in machining and high manufacturing costs of components, especially when parts with complex shapes are to be fabricated.

The use of the relatively low-cost slip casting process for ceramics manufacture has been proved to provide more homogeneous materials with controlled microstructure and increased reliability [2]. Slip casting requires homogeneous stable suspension with high solids loading and low viscosity. A well-dispersed suspension can be obtained by choosing suitable dispersant, solvent, particle size distribution, etc. Most studies to date have focused primarily on the selection of suitable a dispersant [3–5]. However, the mixing procedure is also of crucial significance for the final performance of ceramics [6–9], as it may destroy particle agglomerates, modifies the surface structure of the powders, reduces the particle size, drives the mixture to a more homogeneous distribution of the components and influences the interparticle interaction forces.

When dispersed in a liquid phase, particles have a natural tendency to agglomerate under the action of two different kinds of attractive forces: Van der Waals forces and capillary forces [10,11]. An efficient break down of agglomerates directly influences the rheological behaviour of suspensions. During mixing process, three requirements should be achieved: breaking up the agglomerates already exiting in the dry powder, homogenization of the different kinds of raw powders, and most importantly, preventing further agglomeration after mixing.

The objective of this study is to investigate the influence of mixing procedure on the preparation of stable suspensions, and further on the properties of slip casting green bodies.

2. Experimental procedures

2.1. Powder characterization

The raw powders used in the present work are listed in Table 1, as well as the characteristics of the powders, as

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Table 1
Characteristics of the powders used, as provided by the suppliers

Powder	Grade	Supplier	d_{50} (μm)
Si_3N_4	M11	H.C. Stark, Germany	0.38
AlN	C	H.C. Stark, Germany	1.06
Y_2O_3	C (fine)	H.C. Stark, Germany	0.75
Al_2O_3	A16SG	Alcoa Chemicals, USA	0.38

provided by the suppliers. The solvent chosen in this study was the azeotropic mixture of 60-vol.% methylethylketone (MEK) (Riedel-de Haën, Germany) and 40-vol.% ethanol (E) (Merck, Germany). The dispersant, KD1 belongs to a kind of polyester/polyamine condensation copolymer with a molecular weight of about 10,000 g/mol, it contains both acidic and basic sites, where the base functionality probably consists of some type of amine group. It has been proved to be an efficient additive for dispersing reaction sialon powders in organic media [12]. The optimal KD1 addition is 3-wt.% (based on the weight of reaction sialon powders), which corresponds to the maximum adsorption density [13].

To eliminate the influence of particle size and hard agglomerates, the reaction sialon powder mixture (76.92-wt.% Si_3N_4 + 13.46-wt.% AlN + 5.77-wt.% Y_2O_3 + 3.85-wt.% Al_2O_3) was first prepared as follows: weighed batches of raw powder mixtures were planetary milled at a speed of 180 rpm for 4 h in 2-butanol, using Al_2O_3 jars and Si_3N_4 balls. After milling, the mixed slurries were dried in an oven at 40 °C for 48 h. The powders were then sieved through an 80 μm sieve, and used as starting powder to prepare the suspensions through different homogenizing procedures.

The size distribution of the starting powders' mixture, dispersed in the 60M/40E solvent, was measured using a Coulter LS130 particle size analyser (Coulter Corporation, USA) equipped with a small cell (25 ml), assuming the refractive index of the silicon nitride (1.97).

2.2. Suspension preparation

All the suspensions (diluted and concentrated) were prepared by adding the powders' mixture to the solution of the dispersant in the solvent and mixing the raw powders, dispersant and solvent according to different homogenization routes, as follows:

- Route 1: Planetary ball milling. An alumina jar with Si_3N_4 balls was used for planetary milling the starting powder mixture at a speed of 150 rpm, which is more energetic than routes 2 and 3 and could produce some milling effect.
- Route 2: Ball milling. A plastic polyethylene bottle with silicon nitride balls was used as ball mill. With this method, the mixing energy is low and little milling takes place.
- Route 3: Ultrasonic mixing. The disaggregation was carried out by ultrasonication (power: 360 W; frequency: 50 Hz).

Steady shear measurements of the suspensions were carried out using a rheometer (Carri-med, CSL 500, UK) at a constant temperature of 20 °C. The adopted measuring configuration was a cone and plate. Before beginning the measurements, pre-shearing was performed at a high shear rate ($1000\,s^{-1}$) for 1 min to transmit the same rheological history to the whole sample being tested.

The particle size distributions of powders dispersed by the different mixing routes were measured using a Coulter LS130 particle size analyser, assuming the refractive index of the silicon nitride (1.97). The measuring suspension was dropped into the 60M/40E solvent in a small cell (25 ml) to dilute it to a suitable concentration for the measurement.

2.3. Adsorption measurements

In order to determine the amount of dispersant adsorbed onto the surface of particles/agglomerates, green bodies were consolidated from suspensions prepared by the different mixing routes by pouring the 10-vol.% suspensions with 3-wt.% added KD1 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 analyzed 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.

2.4. Slip casting and characterization of green bodies

The concentrated suspensions were poured into plastic ring moulds based on an absorbent plaster plate. The consolidated bodies were removed from the mould after 24 h and dried slowly in air for 24 h at room temperature and then at 60 °C for further 48 h.

The pore size distributions of green samples were measured using mercury porosimetry (PoreSizer 9320, Micromeritics, USA). The density of green bodies was measured according to the Archimeds' principle by the mercury immersion method.

3. Results and discussion

Fig. 1 shows the size and morphology of mixed reaction sialon powders, while Fig. 2 plots the particle size distribution of the same reaction sialon powders' mixture. As can be seen from the SEM micrograph and particle size distribution, the powders are very fine but partially agglomerated, although some particles' interconnections do not seem to be strong enough to classify the whole system as a hard agglomerated powder. The agglomerated nature of the powders' mixture is clearly evident in the particle size distribution (Fig. 2), which shows a larger average particle size (~2.25 μm) in comparison with that already measured in water (~0.35 μm) for the same powders' mixture also in

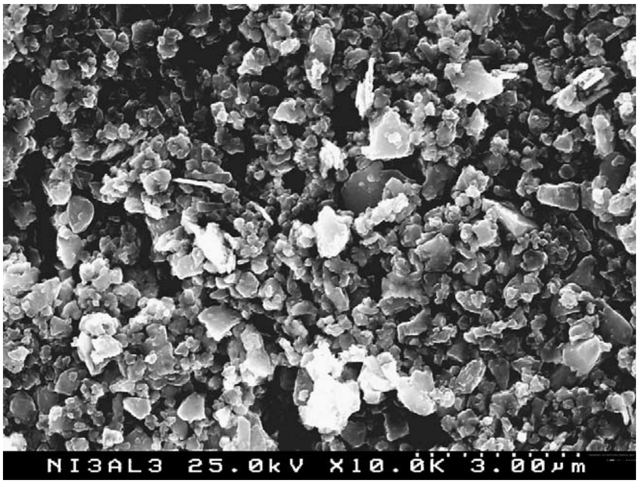

Fig. 1. SEM micrograph of the starting reaction sialon powder mixture.

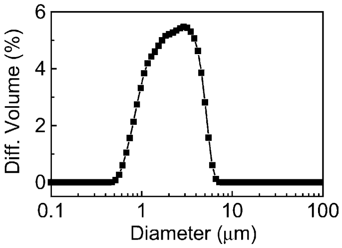

Fig. 2. Particle size distribution of starting reaction sialon powder mixture.

absence of a dispersant [13]. Such differences might be due to the hydrolysis reaction of AlN when dispersed in water, which causes the pH to increase, thus creating transient conditions that might favor the dispersion of the main component (Si_3N_4) in the formulation.

Since each homogenizing procedure should have its own limitations in terms of deagglomeration kinetics and maximum achievable deagglomeration degree, it seems advisable to firstly define the optimum homogenization time for each deagglomeration route prior to making the comparison of the rheological behaviour of the suspensions. Table 2 shows the apparent viscosity values measured at $100\,s^{-1}$ as a function of mixing time for the different homogenizing routes. It can be seen that the three suspensions present similar trends with the increase of deagglomeration time: viscosity firstly decreases down to a minimum value at the end of a given period, and then tends to slightly increase with further deagglomeration time. Thus, the optimal deagglomeration times have been fixed at 4, 48 h and 20 min, according to routes 1, 2 and 3, respectively.

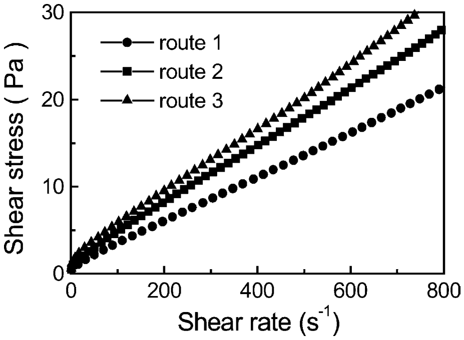

Fig. 3. Influence of the mixing route on the flow curves of 40-vol.% suspensions.

Fig. 3 plots the flow curves of suspensions containing 40-vol.% solids deagglomerated for time periods corresponding to the optimized deagglomeration times determined for each dispersing procedure. It can be seen that all three deagglomeration routes result in near-Newtonian flow behaviours with very small yield stress values, which correspond to a high degree of dispersion in the suspensions. Fig. 3 also shows that the suspension prepared by planetary milling exhibits the lowest viscosity values over the entire shear rate range, while that submitted to ultrasonication presents the highest viscosity values. This can be understood since the planetary milling route is more prone to destroy hard agglomerates existing in the starting raw powders, the breakdown of the agglomerates will release the entrapped solvent from intra-agglomerate regions and will expose new surface areas to the dispersion media where the dispersant can readily adsorb. This interpretation is also supported by the results reported elsewhere [12,13], which reveal the high affinity of the anchoring groups of the dispersant KD1 to the surface of the reaction sialon particles, imparting to this system a very good dispersing ability when the optimal amount of KD1 is added. Excess amounts of KD1 in the solution will increase the viscosity by different mechanisms (chain entanglements, association of the high solubility part of KD1 with solvent molecules, which will not be available for flowing).

Fig. 4 shows the particle size distributions of 40-vol.% solids suspensions obtained from different mixing procedures. As can be seen, planetary milling leads to some milling effect, and completely breaks down the

Table 2
Evolution of the apparent viscosity measured at $100\,s^{-1}$ with mixing time for the different mixing procedures

	Route 1				Route 2			Route 3		
	Mixing time									
	1 h	2 h	4 h	8 h	24 h	48 h	72 h	10 min	20 min	30 min
η (mPa s)	43.8	40.8	37.0	37.5	56.1	48.2	51.2	64.1	58.3	58.9

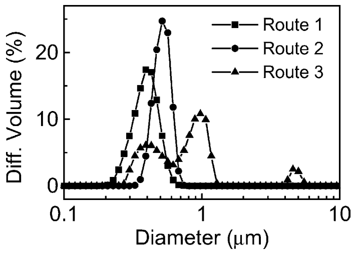

Fig. 4. Particle size distributions of 40-vol.% suspensions according to different dispersing procedures.

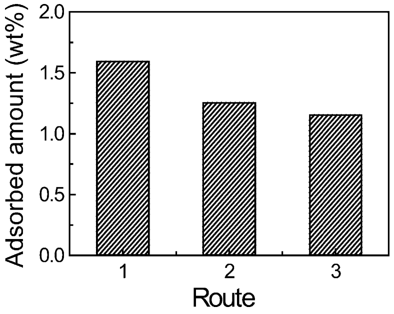

Fig. 5. Influence of the homogenizing procedure on the amount of dispersant adsorbed from 10-vol.% suspensions.

agglomerates existing in the starting powders. Fig. 5 shows that the amounts of dispersant adsorbed from 10-vol.% suspensions dispersed with 3-wt.% KD1 decrease with the decreasing efficiency of the deagglomeration method according to the following sequence: planerary milling > ball milling > ultrasonication. The results presented in Figs. 4 and 5 are consistent with the previous discussion regarding the influence of mixing route on flow curves. The most energetic mixing procedure promotes a more efficient deagglomeration and leads to the formation of more adsorption sites at the particles surface resulting in a higher adsorption of dispersant. Thus, a highly stable suspension with low viscosity is obtained.

The solids loading of suspensions for colloidal processing of ceramics should be as high as possible, while compatible with a suitable viscosity level. Fig. 6 shows the viscosity (shear rate $= 100\,\mathrm{s}^{-1}$) of suspensions prepared by the different mixing procedures as a function of solid volume fraction. It can be clearly seen that route 1 always gives lower viscosity values, which permits the highest maximum solids loading.

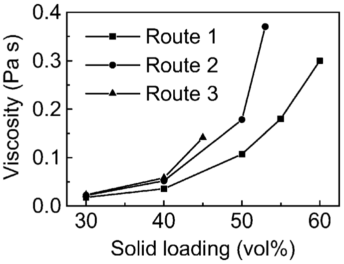

Fig. 6. Influence of solids loading and homogenizing procedure on viscosity of suspensions.

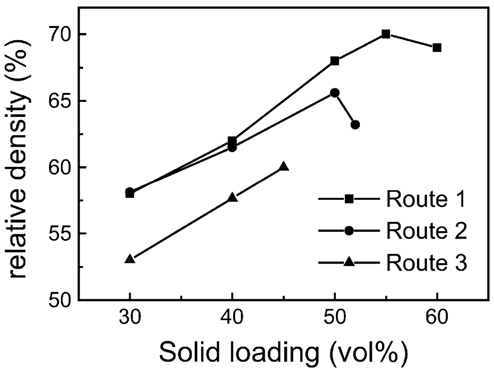

Fig. 7. Relative density of green bodies from different homogenizing procedures.

At low solid loading, the average magnitude of Van der Waals forces would be small due to the relatively larger distance between suspended particles. So a small adsorption of dispersant could lead to enough steric force to counterbalance Van der Waals forces [10]. Thus, at low solids loading, the differences of rheological properties among the suspensions with different homogenizing routes are less obvious. 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 available, under which conditions Van der Waals forces will dominate the interaction between suspended particles, leading to poor dispersion. So it is easy to understand why route 1 leads to the largest maximum solids loading.

Figs. 7 and 8 show, respectively, the relative densities and average pore diameters of green bodies obtained from different suspensions. It can be seen that route 1 always gives higher relative densities and smaller pore diameters, especially at high solids loading, which is consistent with the viscosity measurements. Particles in low viscosity near-Newtonian suspensions have more freedom to promote particle rearrangements during the deposition stage and also to segregate [14,15]. However, this freedom is gradually lost as solids loading and the concomitant viscosity of the suspensions increase, while at the same time,

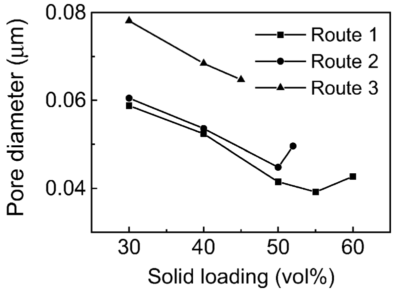

Fig. 8. Average pore diameter of green bodies from different homogenizing procedures.

the probability for some air bubbles to become entrapped either in the suspension as well as in the green bodies also increases. This explains why the green densities plotted in Fig. 7 show increasing trends with increasing solid loading in the suspension, reaching maximum values for 50 and 55-vol.%, when the suspensions were prepared according to routes 2 and 1, respectively, decreasing for higher solids concentrations. These results show that there will be a complex balance among the factors that play the most relevant roles in the slip casting process, pointing out to the need of searching for the optimal processing conditions.

4. Conclusions

For slip casting operations, higher solid loadings are preferred. Since these suspensions exhibit a slightly shear-thinning behaviour, the viscosity decreases with increasing rotation speed. Under these conditions, the planetary milling route is clearly the better mixing procedure for the preparation of stable and well-dispersed suspensions of the reaction sialon powder mixture with high solids loading. Using this procedure, a concentrated suspension up to 60-vol.% solids with near-Newtonian flow behaviour could be obtained, leading to green bodies with high relative densities and low average pore sizes. These results could be attributed to the higher degree of deagglomeration and a more suitable partition of the dispersant between the particle surface and the solution.

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