Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 36 (2010) 385–390
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Short communication

The influence of solid loading in suspensions of a submicrometric alumina powder on green and sintered pressure filtrated samples

M. Michálková [a,*], K. Ghillányová [b], D. Galusek [a,b]

[a] Vitrum Laugaricio, Joint Glass Center of the IIC SAS, TnU AD, FChFT STU and RONA a.s., Študentská 2, 911 50 Trenčín, Slovak Republic
[b] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 84536 Bratislava, Slovak Republic

Received 6 April 2009; received in revised form 27 April 2009; accepted 26 July 2009
Available online 25 August 2009

Abstract

The present work deals with preparation of stable suspensions of a submicrometre alumina powder with different contents of solid for pressure filtration. The optimum dispersant content (2.2 wt.% of Darvan C-N) was determined by sedimentation tests and viscosity measurements. By modification of the solid loading and dispersant content two kinds of aggregation were observed. One type of aggregates is related to the use of excessive solid loading in suspension. In samples prepared from these suspensions only minor effect on sintered microstructure was observed, which increased with increasing volume fraction of hard aggregates. In case of excess dispersant addition weak aggregates formed as the result of depletion flocculation. Weak aggregates had stronger negative effect on green microstructure, with consequent negative impact on sinterability.

Keywords: Aggregate; Alumina; Suspension

1. Introduction

Colloidal techniques in the manufacturing of ceramics provide considerable benefits for the control of packing uniformity of consolidated powder forms. Compared to powder consolidation in dry or semi-dry state (e.g. pressing in a die), colloidal methods can lead to better packing homogeneity in the green body, which in turn leads to better microstructure control during firing [1–3]. The quality of products formed by wet processing is determined primarily by the state of the dispersion. Dispersion of the particles and the stability of the suspension, therefore, are the key factors for the successful production of a large number of industrial products [4].

Many recently developed ceramic processing techniques including spray drying, slip casting, pressure casting, tape casting, and gel casting employ well-dispersed suspensions with very high levels of solid loading. For these forming techniques, the concentration of suspension influences the green density of the formed ceramic material.

Pressure filtration (PF) is separation of suspension into a green cast and a pure filtrate liquid. The green cast is formed at a porous filter which is impermeable for the particles but permeable for the liquid. The driving force is a static pressure difference either accomplished by applying vacuum on the backside of the filter (vacuum casting) or by applying a high pressure on the suspension. Using a constant filtration rate instead of constant pressure, a constant growth rate of the cake is induced, which provides homogeneous particle incorporation into the growing cake surface. Therefore, particle packing structure is independent of cake thickness so that gradient-free green compacts are formed. Owing to increasing flow resistance the applied pressure has to be continuously increased with cake thickness [5]. Green compacts of high density are usually produced by PF techniques of highly concentrated (about 49 vol.%) powder suspensions [5], but high relative green density up to 60% can be achieved also from suspensions with only 20 vol.% [6] and 30 vol.% of solid [7].

A number of works deal with the influence of the solid loading and dispersion state of suspension during PF, and their relation to green microstructure [6,8–10], but only a few is focused at the properties of sintered material prepared from these suspension [11,12]. Uchikoshi et al. [12] prepared compacts from two suspensions: well-dispersed and insufficiently dispersed suspensions of fine zirconia powder. Green sample consolidated from the well-dispersed suspension

* Corresponding author.
E-mail address: uachmimi@savba.sk (M. Michálková).

0272-8842/$36.00
doi:10.1016/j.ceramint.2009.07.032

showed a good sinterability, while CIP treatment at 400 MPa was needed to increase the sintered density of the compact consolidated from the insufficiently dispersed suspension. Garrido and Aglietti in their work compare [11] the pressure filtration and slip casting of mixed alumina–zircon suspensions. Pressure filtrated bodies were slightly less dense than the compacts prepared by slip casting and relative green density increased with increasing the degree of dispersion of the particles. After sintering 2 h sintering at 1600 °C a clear relation between the green and the sintered density for all compositions was observed, showing that the high green density gave the highest sintered density.

The main objective of this work is the investigation of the influence of different solid loadings on the properties of suspensions prepared from a submicrometric alumina powder, specifically focused on the influence of aggregates at high solid contents. The effect of solid loading on density and porosity of pressure filtrated green samples is also examined. The effect of the excess of a Darvan C-N dispersant on green body is observed and analyzed. The impact of the suspension properties on sintering and final microstructure is discussed.

2. Experimental

High purity 99.99% commercial alumina powder (TAIMICRON TM-DAR, Taimei Chemicals Co., Ltd., Tokyo, Japan) with primary particle size of 150 nm and specific surface area 13.7 $m^2\ g^{-1}$ was used as a starting material. To find out the optimal concentration of dispersant five different concentrations of Darvan C-N (R.T. Vanderbilt Company, Inc., Norwalk, USA) were used: 1.8, 2.0, 2.1, 2.2 and 2.4 wt.% relative to the weight of alumina, respectively, in a 40 vol.% of alumina suspension. The suspensions were prepared in three steps: mixing of distilled water with dispersant, addition of alumina powder, and mixing for 24 h on rollers with alumina milling balls. The rheological properties of the suspensions were examined by viscosity measurements, which have been carried out using a Rheometer AR 2000 (TA Instruments) with Plate/Plate geometry (Peltier plate + 40 mm Steel Plate). The measurement conditions: pre-shear = 100 s^{-1} during 60 s and than 60 s equilibration, duration of measurement = 60 s, shear stress = 0.01–100 Pa, temperature 25 °C.

The sedimentation tests were also used for the optimization of the dispersant content. For the test, 0.75 ml of the 40 vol.% alumina suspension with different contents of dispersant was mixed with 24.25 ml of distilled water. The suspensions were first stirred thoroughly for 10 min in a beaker and then transferred to the measuring cylinder where they were allowed to stand undisturbed for 48 h. The suspension density was measured by pipetting out 5 ml of the cloudy suspension from a predetermined height (corresponding to a volume of 15 ml) from the top of the cylinder. It was then dried and weighed in order to determine the weight of suspended particles in the 5 ml of the suspension. The volume of suspension containing dispersed particles above the settled mass at the bottom was calculated after subtracting the space covered by the sediment. The total amount of solid remaining in suspension was then estimated from the total volume of suspension over the sediment bed. The remaining solid was assumed to have been reported in the sediment, the volume of which is read directly at the bottom of the graduated cylinder. The relative density of the sediment was then estimated from the ratio of the density of the sediment to the true density of the solid.

To determine the optimal concentration of alumina in suspension in order to optimize the properties of green body six different concentrations were used: 20, 30, 40, 45, 46 and 47 vol.% of alumina (denoted as A20–A47 in the following text), respectively. In addition, a suspension with 40 vol.% of alumina with 5 wt.% of dispersant (A40DC) was also prepared. The suspensions were used for particle size analysis (LS 230 Laser Diffraction Particle Size Analyzer, measured in EMPA, Duebendorf, Switzerland).

Green samples were prepared by vacuum–pressure filtration (constant consolidation rate 0.4 mm/min, maximal consolidation pressure 5.795 MPa) of suspensions with different solid loadings. Vacuum was applied during the whole process of consolidation. Samples were than dried in drying chamber at 120 °C for 2 h. Green samples were used for porosity measurements (PASCAL 140 and 440, measured in EMPA Duebendorf).

The sintering was carried out in an electrical furnace (NETZSCH GmbH, Selb, Germany) with $MoSi_2$ heating elements in air. During the sintering process the specimens were heated at 20 °C/min up to the maximum temperature 1250 and 1275 °C with 10 min and 1 h of isothermal dwell, respectively, and then cooled down to room temperature. Density was measured by the Archimedean method in mercury. Sintered microstructures were examined by scanning electron microscopy (Zeiss EVO 40 HV, Germany), at fracture surfaces. For the determination of the average grain size linear intercept method was used.

3. Results and discussion

3.1. Content of dispersant

To obtain a ceramic suspension with high solids content that can be successfully processed, relatively low viscosity must be achieved and stability must be maintained. This requires efficient dispersant added in optimal amount. Lower dispersant concentration results in insufficient degree of dispersion (not all particles are dispersed) whereas too high addition can result in depletion flocculation [13]. In both cases the agglomerates present in suspension increase the suspension viscosity.

Fig. 1 shows the viscosities plotted against the shear rate of 40 vol.% alumina suspensions with five different additions of the dispersant. The lowest addition of dispersant (1.8 wt.%) results in the highest viscosity. With increasing amount of the dispersant the viscosity gradually decreases up to the content 2.2 wt.%. After that, higher dispersant concentration results in higher viscosity again.

The stability of suspensions was evaluated also by sedimentation tests. The effect of different additions of dispersant on relative density of sediment is shown in Fig. 2.

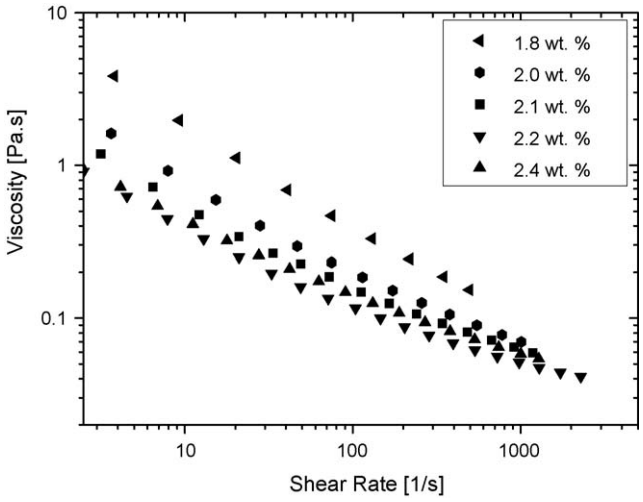

Fig. 1. Viscosity of 40 vol.% alumina suspensions with different amounts of dispersant Darvan C-N.

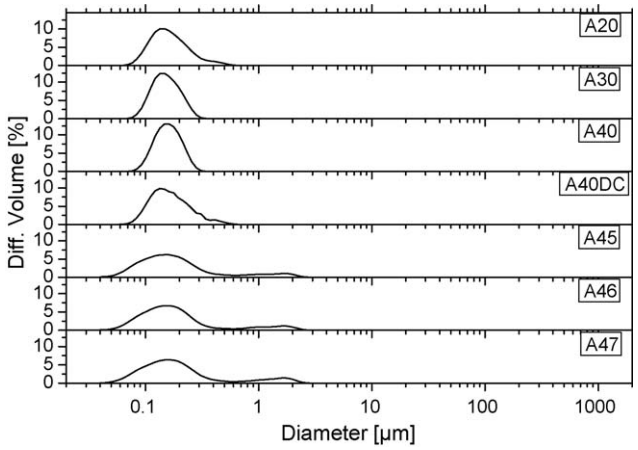

Fig. 3. Particle size analysis of alumina suspensions with different solid loadings.

It is well known that well-dispersed suspensions are characterized by slow sedimentation, a cloudy supernatant, and a higher sediment density [14]. In this case the highest density of sediment was reached at dispersant concentration of 2.2 wt.%, which is in good agreement with the results of viscometry measurements (Fig. 1): the addition of the dispersant 2.2 wt.% was therefore selected for further experiments.

3.2. Suspensions

Efficient dispersion of powder particles in suspension is prerequisite for all slurry based forming processes. In spite of optimal dispersant addition, at high solid loading the agglomerates can form as a result of deficient space or else too close particle–particle contacts [15]. Since the occurrence of agglomerates has deteriorating effect on both suspension and green body characteristics it seems to be crucial to find out at which solids concentration the degree of dispersion decreases.

Fig. 3 shows particle size distribution at different solid loadings of alumina suspensions. The suspensions with 30 and 40 vol.% of alumina exhibit relatively narrow particle size distribution without any distinguished aggregates. A certain amount of aggregates and also wider particle size distribution was observed in suspensions with 45, 46 and 47 vol.% of alumina, which hints at insufficient homogenization during preparation due to too high solid content.

The suspension denoted as A40DC is the modified suspension A40 prepared with the excess of dispersant (5 wt.% of dispersant with respect to alumina). The presence of aggregates is the result of so-called ‘‘depletion flocculation’’ [13].

3.3. Green body

To find the correlation between the suspension and green body properties the relative density, and pore size distribution of green samples prepared by pressure filtration were measured. Fig. 4 shows the relation between the relative green density of the samples and the solid loading of the suspension. Generally, relative green density increased with the increase of solid loading in the suspension. Even though suspensions with 45, 46 and 47 vol.% of solid phase contain agglomerates, samples prepared from these suspensions have

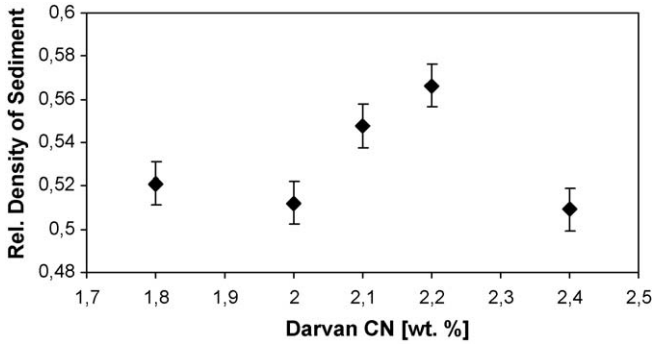

Fig. 2. Relation between relative density of sediment and the content of dispersant.

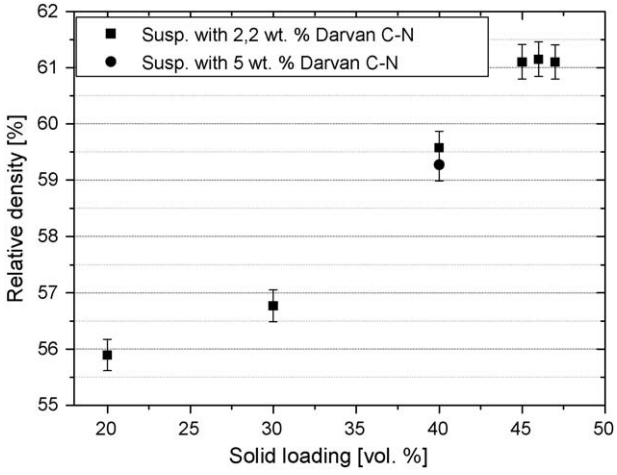

Fig. 4. Relative density of green body as a function of different solid loadings of suspensions.

higher relative green density compared with the effectively dispersed ones (20–40 vol.%).

In this case the presence of the aggregates seems to have positive influence on the green density. This effect could be explained by the following consideration. It can be supposed that the suspensions with too high solid loading consist both of dispersed particles, and aggregates formed in primary minimum (''strong aggregates''), as schematically shown in Fig. 5b [15]. In this type of aggregates the particles touch each other, with dispersed individual particles filling interagglomerate voids, resulting in higher green densities. The reason for the formation of strong aggregates lies probably in insufficient distribution of polymer dispersant molecules due to high viscosity of suspension with high solid loading. The molecules of the dispersant therefore do not completely cover all alumina particles and coagulation takes place.

The excess of added dispersant (the sample A40DC) also results in lower green density than in green bodies prepared from suspensions with very high solid loading. Also, the A40DC sample prepared from 40 vol.% alumina suspension with 5 wt.% of dispersant had lower relative green density than the suspension A40 with optimal 2.2 wt.% of the dispersant. The explanation resides in different characters of formed aggregate types, Fig. 5c. The aggregates formed as a result of the excess dispersant consist of non-touching particles randomly linked by polymer chains so these ''aggregates regions'' have lower density than the well-dispersed ones. This is then the reason of lower green density compared to samples prepared from suspension with optimal dispersant addition.

Fig. 6 summarises the pore size distributions of pressure filtrated samples prepared from suspension with different alumina contents. In green bodies prepared from well-dispersed suspension (20, 30 and 40 vol.% of alumina) the pore size decreases with increasing solid loading. Provided that green body prepared from dispersed suspension has homogenous microstructure the decrease of the pore size is logically linked to increasing green density at higher solid loading.

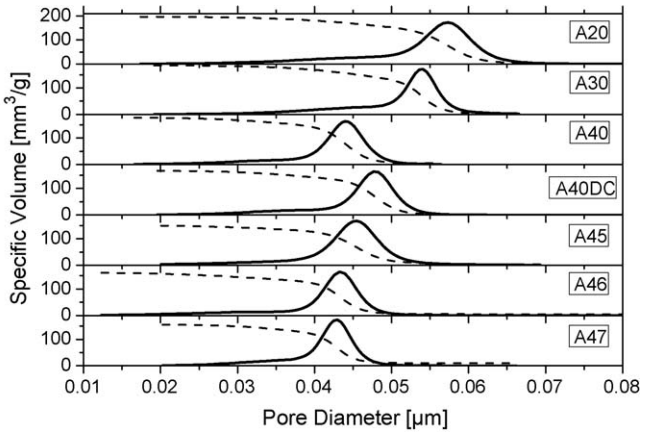

Fig. 6. Pore size distribution in green bodies prepared from suspensions with different solid loadings.

The pore size distribution of green body prepared from the suspension with higher solid content containing the strong aggregates does not differ from those prepared from the suspension A40. This result is in good agreement with the results of Smith et al. [16] who demonstrated that mercury intrusion porosimetry did not provide a pore size that could reflect filtration behaviour of slips with different degrees of dispersion – measured pore sizes in samples prepared both from poorly and well dispersed suspensions were identical. It is important to point out that poor dispersion of the particles in cited work was attained by insufficient dispersant addition, which caused the coagulation in primary minimum forming strong aggregates. The situation is therefore in principle comparable to suspensions with high solid loading in this study.

However, if excess dispersant was added into the suspension, a significant shift to higher mean pore size value and also broader pore size distribution is observed in comparison to alumina suspension with the same solid loading but with optimum amount of the dispersant. Hence the detrimental effect of the excess dispersant addition resulting in depletion

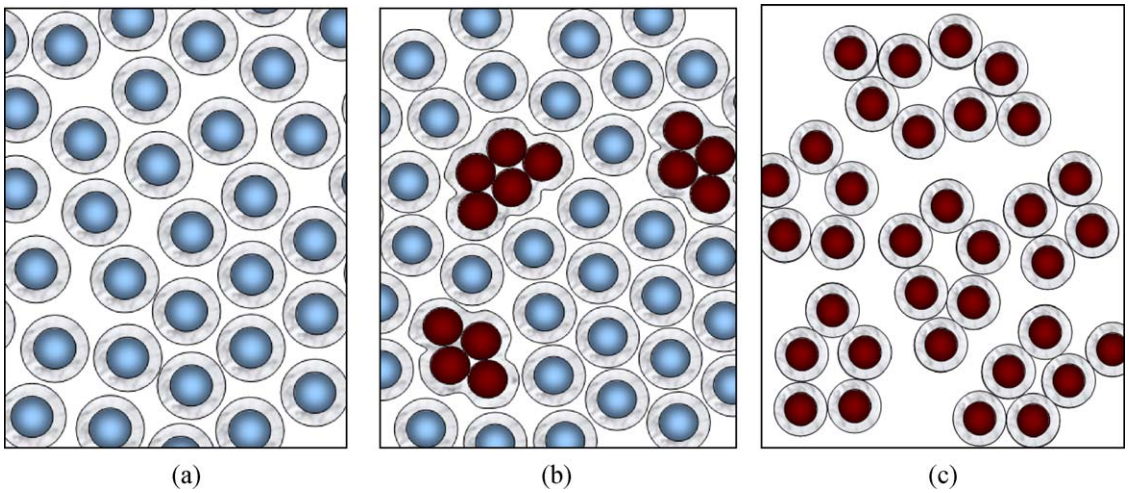

Fig. 5. Schematic drawing of (a) dispersed suspension; (b) suspension with strong aggregates; (c) suspension with weak aggregates formed as the result of depletion flocculation.

flocculation (the presence of weak aggregates) was confirmed on both the suspension and green body characteristics. This result is related to different characters of the pores. The strong aggregates, formed in restricted space in suspension with too high solid loading and inhomogeneous distribution of the dispersant, would be denser with relatively smaller intraagglomerate pores. This means that the negative effect of such aggregates will not be manifested by the shift of the pore size distribution to higher values. The presence of such aggregates is not expected to result in any problems until the sintering stage. On the other hand, weak aggregates formed by depletion flocculation contain larger pores/voids than between well-dispersed particles, which then results in higher pore size measured by the mercury porosimetry.

3.4. Sintering and final microstructure

It is generally accepted that the properties of final ceramic bodies are closely related to the properties of green body, which are in turn controlled by suspension characteristics. To study these relations sintered densities and the mean grain sizes of specimens sintered under various conditions were determined. Fig. 7 represents relative density and grain size of sintered samples as a function of different solid loadings of initial suspensions. Two sintering regimes were used. In the first regime the samples were sintered for 10 min at the temperature of 1250 °C. The relative density of samples increased with increasing solid loading in the suspension up to the compacts A45. This trend follows the green density – solid loading dependence. However, the samples A46 and A47 show lower relative density and higher average grain size compared to the others, which could be related to the presence of aggregates in the suspensions as mentioned above. Such aggregates were found also in the 45 vol.% suspension but in the A45 the detrimental effect on density and sintered microstructure was not observed.

The particle size analysis could be helpful in explaining this effect. Fig. 8 shows the detailed part of the particle size measurement of the suspensions A45–A47, which were found

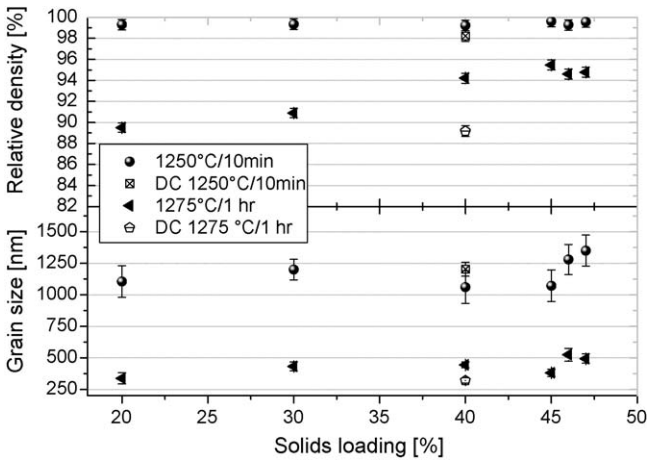

Fig. 7. Relative density and grain size of sintered samples as a function of solid loading in alumina suspensions.

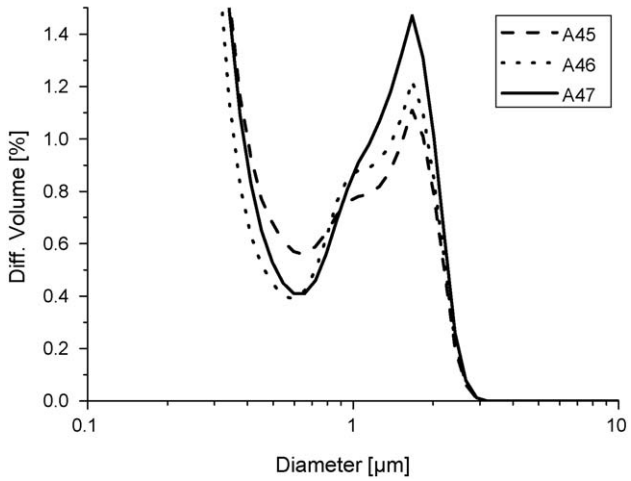

Fig. 8. Increasing volume fraction of hard aggregates in suspensions with increasing solid loading.

to contain certain amount of hard aggregates. The scale is adjusted to emphasise the differences between the suspensions. As can be seen in the figure, the suspension A45 contains the smallest amount of the large aggregates ($D > 1$ μm). The volume fraction of large aggregates increases with increasing solid content. From the conjunction of all mentioned results (sintered density, microstructure and particle size distribution) it can be concluded that if the fraction of strong aggregates is kept under certain level, their presence does not necessarily have to have any observable negative effect on the sinterability and final microstructure.

After sintering for 1 h at 1275 °C the relative densities of all samples were nearly identical. Also the mean particle sizes were comparable, except of the compacts A46 and A47, where the presence of aggregates results in microstructure coarsening.

Even though A20 and A30 differed significantly in terms of their green densities and pore size distributions in comparison to specimens prepared from more concentrated suspensions, all these samples could be sintered to nearly full density under the same conditions. Moreover, the sintered microstructures were nearly identical, except of the already mentioned A46 and A47. This suggests that it is mainly the homogeneity of the green body, and to much smaller extent the green density and the pore size, that affect the final microstructure of dense ceramics.

In comparison, the samples prepared from the A40DC suspension clearly show that the excess of dispersant results in decrease of relative density after sintering in both sintering regimes. This decrease is the result of depletion flocculation effect creating different types of aggregates, which retard the sintering. Hence, complete densification of samples prepared from flocculated suspensions requires higher sintering temperature and naturally results in coarser microstructure. Similar results were reported for reaction sintering of transparent YAG samples prepared by slip casting of aqueous Al_2O_3–Y_2O_3 suspensions [17].

4. Conclusions

The influence of different solid loadings of alumina suspensions on the properties of suspensions, green compacts and their sinterability was investigated. Viscometry measurements together with sedimentation tests confirmed that the 2.2 wt.% (related to alumina) of the dispersant Darvan C-N is optimal amount for stabilization of the suspension of the used submicrometre alumina powder.

Sintering of samples with different solid loadings and optimal concentration of dispersant and at the temperature of sintering 1275 °C did not result in any significant differences in relative density or particle size of sintered compacts, despite the fact that the suspensions with higher solid loading contained strong aggregates. Small negative effect is visible at higher volume fractions of aggregates.

The excess of dispersant resulted in the formation of weak aggregates in suspension as the result of depletion flocculation. The presence of weak aggregates had negative effect both on green and sintered microstructure. These samples did not sinter to full density under the applied sintering conditions, and anticipated higher temperature and longer sintering times required to attain fully dense materials are expected to result in significant microstructure coarsening.

Acknowledgements

The financial support of this work by the grant APVV 0485-06, and by the grant agency VEGA under the contract number 1/0603/09 is gratefully acknowledged.

The authors wish to express their thanks to Daniela Jochec-Mošková from the Institute of Polymers of the Slovak Academy of Sciences for viscosity measurements and to Jakob Kübler from EMPA Swiss Federal Laboratories for Materials Testing and Research for providing the facilities for porosimetry and particle size measurements.

References

[1] F.F. Lange, Powder processing science and technology for increased reliability, Journal of the American Ceramic Society 72 (1989) 3–15.

[2] J. Yang, F.J. Oliveira, R.F. Silva, J.M.F. Ferreira, Pressureless sinterability of slip cast silicon nitride bodies prepared from coprecipitation-coated powders, Journal of the European Ceramic Society 19 (1999) 433–439.

[3] D.-M. Liu, Influence of pore structure in green compacts on the densification of $SiC–Al_2O_3–Y_2O_3$, Ceramics International 22 (1996) 403–406.

[4] O.O. Omatete, M.A. Janney, S.D. Nunn, Gelcasting, from laboratory development toward industrial production, Journal of the European Ceramic Society 17 (1997) 407–413.

[5] P. Greil, U. Gruber, N. Travitzky, M. Kulig, Pressure filtration of silicon nitride suspensions with constant filtration rate, Materials Science and Engineering A 151 (1992) 247–254.

[6] B.V. Velamakanni, F.F. Lange, F.W. Zok, D.S. Pearson, Influence of interparticle forces on the rheological behavior of pressure-consolidated alumina particle slurries, Journal of the American Ceramic Society 77 (1) (1994) 216–220.

[7] E. Fair Geoff, F. Lange Fred, Effect of interparticle potential on forming solid, spherical agglomerates during drying, Journal of the American Ceramic Society 87 (1) (2004) 4–9.

[8] R. Joray, B. Yu, F. Lange, J. Pollinger, Optimization of an aqueous, commercial silicon nitride slurry for colloidal isopressing, Journal of the European Ceramic Society 22 (2002) 1061–1066.

[9] P. Maarten Biesheuvel, Henk Verweij, Influence of suspension concentration on cast formation time in pressure filtration, Journal of the European Ceramic Society 20 (2000) 835–842.

[10] S. Raha, K.C. Khilar, P.C. Kapur, Pradip, Regularities in pressure filtration of fine and colloidal suspensions, International Journal of Mineral Processing 84 (2007) 348–360.

[11] L.B. Garrido, E.F. Aglietti, Pressure filtration and slip casting of mixed alumina–zircon suspensions, Journal of the European Ceramic Society 21 (2001) 2259–2266.

[12] T. Uchikoshi, Y. Sakka, K. Ozawa, K. Hiraga, Pressure filtration and sintering of fine zirconia powder, Journal of the European Ceramic Society 18 (1998) 669–674.

[13] A.U. Khan, B.J. Briscoe, P.F. Luckham, Interaction of binders with dispersant stabilised alumina suspensions, Colloids and Surfaces A: Physicochemical and Engineering Aspects 161 (2000) 243–257.

[14] L. Wang, W. Sigmund, F. Aldinger, Systematic approach for dispersion of silicon nitride powder in organic media. II. Dispersion of the powder, Journal of the American Ceramic Society 83 (4) (2000) 697–702.

[15] J.A. Lewis, Colloidal processing of ceramics, Journal of the American Ceramic Society 83 (10) (2000) 2341–2359.

[16] P.A. Smith, H. Kerch, S. Krueger, G.G. Long, J. Keller, R.A. Haber, Pore sizes and filtration rates from two alumina slips, Journal of the American Ceramic Society 77 (1994) 1777–1782.

[17] K.A. Appiagyei, G.L. Messing, J.Q. Dumm, Aqueous slip casting of transparent yttrium aluminum garnet (YAG) ceramics, Ceramics International 34 (2008) 1309–1313.