

Influence of varied suspension properties on properties of spray-dried granules

S. Eckhard*, M. Fries, S. Höhn, C. Rödel

Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Winterbergstraße 28,
01277 Dresden, Germany

Susanna.Eckhard@ikts.fraunhofer.de, Manfred.Fries@ikts.fraunhofer.de,

Soeren.Hoehn@ikts.fraunhofer.de, Conny.Roedel@ikts.fraunhofer.de

Abstract

Within this study the effect of various suspension parameters on the suspension viscosity and resulting granule properties like internal granule structure and fracture behaviour was studied. The varied suspension parameters included solid content within the suspensions, primary particle size and surface charge of the primary particles via pH modification.

All suspension modifications influenced the resulting suspension viscosities.

From the investigated granule samples it was shown, that the suspension viscosity alone is not always the decisive parameter affecting the resulting internal granule structures after spray-drying and therewith the resulting mechanical properties of the granules. In some cases the parameter, which was responsible for the changed suspension viscosity, showed a predominating influence on the resulting internal granule structures and therewith mechanical properties.

Introduction

Ceramic primary particles often show a poor flowability that negatively influences the handling behaviour of the material. An agglomeration step is essential to improve the properties of the material. Spray-drying is one of the most common processes to produce ceramic material mixtures with specific tailored properties from water or solvent based suspensions as press bulk material. By varying the granule properties like granule density, size, shape, internal or external structure it is feasible to adjust the produced bulk to the following processing steps.

From literature and own investigations it is known, that the granule properties can be influenced by various parameters as suspension properties and spray-drying conditions [1-6]. Especially in industrial applications it is essential to generate constant granule product qualities and to be able to modify the product qualities in a well defined way. Therefore it is important to know, which influence the change of single suspension or single spray-drying parameters has on the resulting product properties as single granule strength or internal structure.

Within this study, the investigation of the effect of changed single suspension parameters on the resulting suspension viscosity as well as on the resulting granule properties like fracture strength and internal granule structure after spray-drying was done. The modification of suspension viscosity by different parameters like primary particle size, primary particle surface charge and solid content in the suspension enabled the investigation, if specific viscosity levels always result in comparable internal structures, independent of the parameter that was used for viscosity modification.

Besides other factors, the internal granule structure has a strong effect on the resulting mechanical properties of the granules like fracture strength and fracture deformation. The characterization of the internal granule structure is necessary to fill the gap between cause (changed suspension parameter) and effect (changed mechanical properties of the granules) and to be able to explain / influence selectively the resulting internal granule structures and mechanical granule properties. Necessary for these investigations is a quantitative way for structure characterization. State of the art is the subjective comparison of internal granule structure [7] often accompanied with porosity measurements. Several approaches concerning structure quantification can be found in literature [8, 9]. As this is not satisfying for evaluating and quantifying porous internal granule structures a previously published method for internal structure preparation and quantification is used. [10, 11]

* Corresponding author: Susanna.Eckhard@ikts.fraunhofer.de

Experimental

Five suspensions were prepared from Al₂O₃ primary particles. For the investigation of the influence of varied primary particle sizes on the resulting suspension and granule properties, two different alumina particles were chosen: “fine” (Nabalox NO 713-10 ($d_{50}=0.5\mu\text{m}$), Nabaltec AG) and “coarse” (Nabalox NO 625-10 ($d_{50}=2.5\mu\text{m}$) Nabaltec AG).

First the particles were stirred in water and additives were added. Afterwards the suspensions were stirred again for at least 60 min to guarantee a homogeneous distribution of all ingredients within the suspensions. For the improvement of stability of the green body after pressing a polyvinyl alcohol binder was added (Mowiol 4-88, Clariant). The added amounts were 1 and 3 wt% respectively (see Table 1). To be able to generate suspensions with high solid contents, Batches 3 to 5 were produced using an additional dispersant with an average molar weight of 8000 g/mol (Sodium Polyacrylate NaPA, Sigma Aldrich).

The modification of particle surface charge was done using nitric acid (Merck). During preliminary tests, the change of the zeta potential with varied pH value of an aqueous suspension of fine Al₂O₃ particles without additives was measured (Figure 1). By adding a small amount of nitric acid, the original pH value of the ceramic suspension and therewith the surface charge of Al₂O₃ particles was modified to generate a sample suspension close to the isoelectric point (Batch 1, pH = 7.7). Further addition of nitric acid resulted in further reduction of the pH value and therewith positive surface charges. Because of the repulsive forces, the primary particles were mobile during drying step; the suspension was stabilized electro-statically and showed a low viscosity (Batch 2, pH = 3.8).

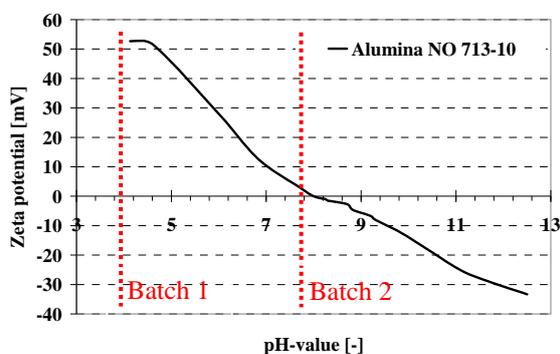


Figure 1 Zeta potential evolution over varied pH values for fine alumina particles (713-10)

After homogenization all suspensions were characterized concerning solid content (HR83 Halogen Moisture Analyzer, Mettler Toledo), suspension density (gravimetric), viscosity (Viskosimeter VT550, Haake) and pH-value (pH-Meter CG 840, Schott) as presented in Table 1.

To investigate the effect of changed pH value and therewith surface charge modification, the suspensions and resulting granules of Batches 1 and 2 are compared. The analysis of the effect of primary particle size on suspension viscosity and granule properties was done using suspensions and granules from Batches 3 and 4. Granules and suspensions of Batches 4 and 5 were compared to investigate the influence of changed solid content.

All granules were spray-dried in mixed flow pattern. Granules of Batches 3 to 5 were produced using a spray dryer in laboratory scale (Mobile Minor, GEA Niro). For granules from Batches 1 and 2 a larger spray-dryer (Production Minor, GEA Niro) was used. As there were no cross comparisons done, these changes in drying equipment can be neglected. For all suspensions a two component nozzle with compressed air as spraying gas was chosen. The drying medium was air. Drying parameters like inlet and outlet temperature, drying gas rate and nozzle pressure were kept in comparable ranges for the directly compared batches to minimize the influence of drying conditions on resulting granule properties. As a result of e.g. different suspension viscosities the suspension mass flow was varied.

Slight differences in the outlet temperature are also a result of changed suspension properties. As for the further strength and structure characterization specific size fractions were sieved, these differences can also be neglected.

Table 1 Suspension composition and suspension properties

		Batch 1	Batch 2	Batch 3	Batch 4	Batch 5
Binder	wt%	1.0	1.0	3.0	3.0	3.0
Dispersant	wt%	-	-	0.3	0.3	0.3
Nitric Acid	wt%	0.1	0.5	-	-	-
Particle Size	µm	0.5	0.5	2.5	0.5	0.5
Spray-Drying Conditions						
T Inlet	°C	200	200	190	185	185
T Outlet	°C	85	83	104	100	89
Susp. Mass Flow	kg/h	3.2	3.5	18.7	18.4	11.2
Drying Gas Mass Flow	kg/h	74	76	254	243	247
Nozzle Gas Mass Flow	kg/h	4.5	4.5	5.4	7.4	5.3
Suspension Properties						
Solid Content	wt%	48.5	48.6	68.4	68.2	39.7
pH	-	7.7	3.8	9.7	10.6	10.5
Viscosity (240 s ⁻¹)	mPa s	133.4	10.4	47.8	135.3	7.1
Suspension Density	g/cm ³	-	1.5	1.9	1.9	1.4

The granule size distribution after spray-drying was measured using static laser diffraction (Malvern Mastersizer MS2000, Malvern Instruments Inc.).

The analysis of the mechanical properties of the granules was done using a single granule compression test (Etewe GmbH). The increasing force accompanied by further granule deformation was plotted and saved. An example graph is shown in Figure 3. For every measurement procedure, parameters like fracture force F_{Break} and fracture deformation D_{Break} were determined and averaged for the whole sample. The specific fracture load σ_{Break} was calculated by using the detected granule diameter $d_{Granule}$ at the beginning of the compression test and by assuming a spherical granule shape.

$$\sigma_{Break} = \frac{F_{Break}}{\frac{\pi}{4} d_{Granule}^2} \quad (1)$$

For the visualization and quantification of internal granule structures the granules were sieved into a close size fraction of 45-63 µm that was comparable to the investigated size fraction for the determination of mechanical properties. The granules were embedded in epoxy resin and polished mechanically to visualize the internal structures. For the generation of homogeneous surfaces without artefacts an ion polishing step was added (RES 101, Baltec). Images of the internal structures were generated at different magnifications using a field emission scanning electron microscope (NVision, Zeiss). The image analysis for structure quantification was done using a commercial image analysis tool (AnalySIS FIVE, Olympus) in accordance to a method described by Höhn et al. [10, 11].

All determinable parameters are shown in Figure 2 and can be separated into micro and macro structure parameters. The macro structure quantification included the determination of the amount of hollow, homogeneous and intersection granules per sample as well as macro porosity within each granule. For the characterization of the granule micro structure the parameter micro porosity, that describes the void volume between the primary particles within the granule shell, was chosen.

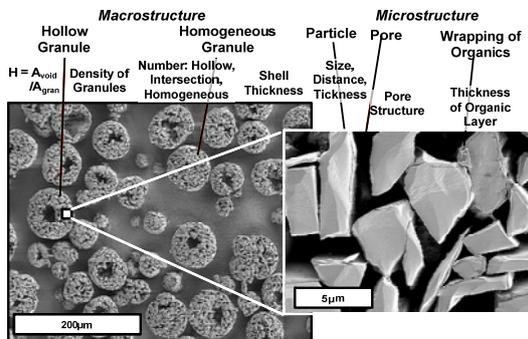


Figure 2 Micro and macro structure parameters

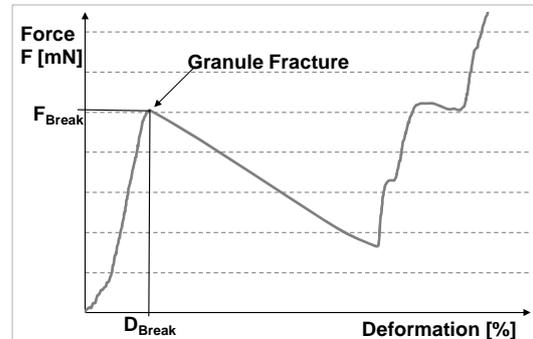


Figure 3 Example force deformation graph, single granule compression test

Results and Discussion

The characteristic granule diameters d_{10} , d_{50} and d_{90} as results of the analysis of granule size distribution and the resulting mechanical granule properties as well as internal structure parameters are presented in Table 2.

Table 2 Granule sizes, structure parameters and mechanical granule properties

		Batch 1	Batch 2	Batch 3	Batch 4	Batch 5
Binder	wt%	1.0	1.0	3.0	3.0	3.0
Dispersant	wt%	-	-	0.3	0.3	0.3
Nitric Acid	wt%	0.1	0.5	-	-	-
Particle Size	μm	0.5	0.5	2.5	0.5	0.5
Granule Structure Parameters						
Amount Hollow	%	4.0	11.8	6.3	50.0	54.7
Amount Homogeneous	%	85.2	71.3	57.0	20.0	17.6
Amount Intersection	%	10.8	17.0	36.7	30.0	27.7
Macro Porosity (Void)	%	0.2	0.7	0.5	3.7	7.9
Micro Porosity (Shell)	%	49.4	45.5	41.5	37.6	37.3
Total Porosity	%	49.4	45.9	41.8	39.9	42.2
Granule Size Distribution						
d_{10}	μm	24	23	42	34	28
d_{50}	μm	47	49	87	77	56
d_{90}	μm	95	106	160	148	105
Mechanical Properties						
Fracture Force	mN	2.2 ± 0.4	2.4 ± 0.4	9.3 ± 2.6	10.7 ± 3.4	5.4 ± 2.0
Fracture Deformation	%	9.0 ± 2.4	11.2 ± 3.0	8.4 ± 2.3	7.3 ± 1.4	7.8 ± 2.7
Specific Fracture Load	MPa	1.1 ± 0.2	1.1 ± 0.2	4.0 ± 1.1	4.9 ± 1.4	2.8 ± 1.2

Comparing Batches 1 and 2, where the effect of changed surface charge of the primary particles via pH modification was studied, effects on the suspension properties were found: At comparable solid contents and primary particle sizes the viscosity increased while the pH value was moved in the range of the isoelectric point of the material within Batch 1 ($\text{pH} = 7.7$). Following the theory of DLVO, were the acting force between two entities results from attractive and repulsive forces between these particles, particles at the isoelectric point of the suspension showed no repulsive forces between each other. A reason can be found in the balanced negative and positive surface charges. At $\text{pH} = 7.7$ the mainly acting force was the attractive van der Waals force, that led to agglomeration of the particles within the suspension. High suspension viscosities were a result [12, 13]. Because of the increased viscosity of the suspension of Batch 1 the determination of the suspension density was not possible.

An increase of the surface charge of the primary particles by further addition of nitric acid and therewith reduction of pH-value resulted in a low viscous suspension (Batch 2). Because of the positive surface charges of the particles, the attractive van der Waals forces were predominated by the repulsive forces. The particles were kept in distance and agglomeration was prevented.

As an effect of changed suspension viscosities the internal granule structures showed differences: The low viscous suspension resulted in a higher amount of hollow granules within the batch (see Table 2). This theory was already published by Walker et al. and others who correlated the mobility of the primary particles within a suspension to the resulting granule shape and structures [8]: Mobile primary particles of well stabilized suspensions, as they were present for the granules of Batch 2, were able to move with the evaporating liquid to the shell of the drop/granule during the drying process. Higher amounts of hollow granules were formed as can be seen in Figure 5. This was also quantified via structure analysis. Additionally these particles of low viscous suspensions were able to move closer together and form denser packed structures/shells. Because of the surface charge of the primary particles a reorganisation during the drying process enabled the development of denser packed particle arrangements. A lower micro porosity was a result, which was determined via image analysis for the granules of Batch 2 in comparison to the granules of Batch 1. Examples are shown in Figures 4 and 5, right. [6, 14-17]

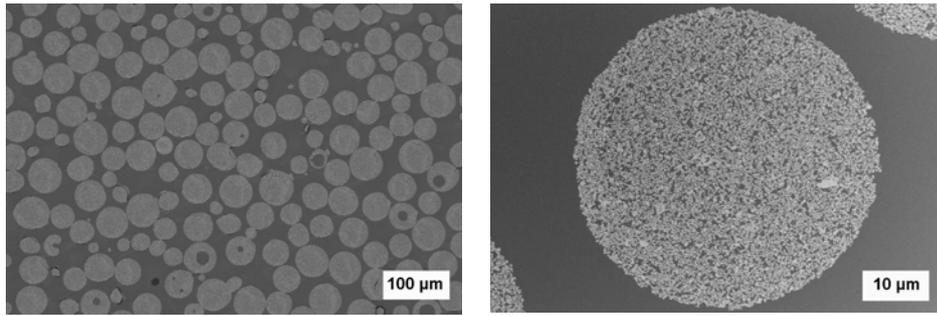


Figure 4 Internal structures of granules of Batch 1

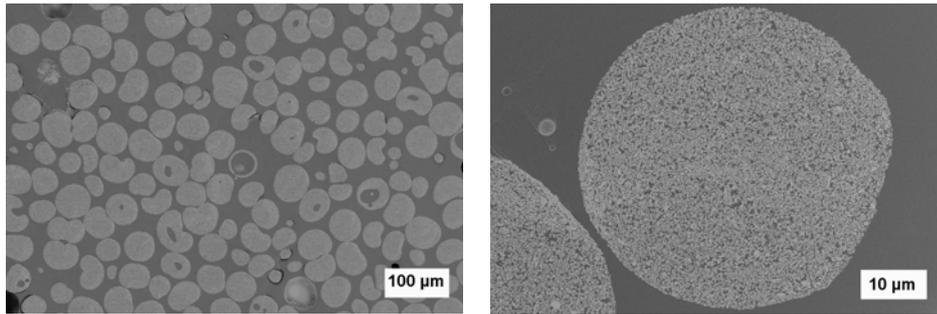


Figure 5 Internal structures of granules of Batch 2

The changed internal granule structures showed no effect on the determined specific fracture loads that were comparable for both batches. Slight differences were measured concerning the determined fracture deformation values.

For Batches 1 and 2 correlations between changed suspension viscosity and internal granule structures were found. By the modification of the suspension pH value, the defined modification of internal granule structures is possible. High viscous suspensions lead to loose packed structures, whereas well stabilized suspensions result in denser packed structures and higher amounts of hollow granules within the batch. For the two investigated samples no defined effect of changed internal micro and macro structures on the mechanical granule properties was found. The spray-drying and structure investigation of further samples is part of actual studies.

The modification of the primary particle size resulted at comparable solid content in the starting suspensions in changed primary particle numbers. Identical suspension densities were measured. A high number of particles within the suspension of Batch 4 resulted in increased particle surfaces, that had to be wetted by the same amount of water (approx. 31.6 wt%). Less liquid medium was available for the motion of the particles within the suspension of Batch 4 what resulted in an increased viscosity of 135.5 mPas. For the suspension from coarse primary particles, a lower viscosity was determined, that was an effect of the reduced primary particle surfaces.

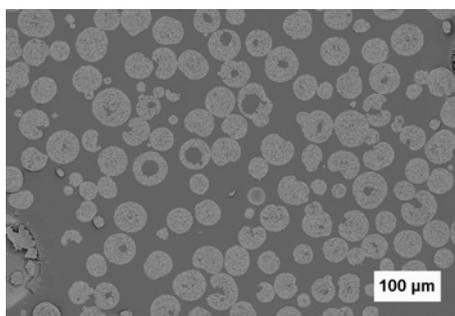


Figure 6 Internal macro structure, Batch 3



Figure 7 Internal macro structure, Batch 4

Different internal granule structures were quantified for the granules from Batches 3 and 4. Example images can be seen in Figures 6 and 7.

For the granules of Batch 3, produced from low viscous suspensions containing coarse primary particles, high micro porosities were determined, even if from theory high packing densities were expected from low viscous suspensions [8]. In this case the developed internal granule structures were mainly affected by the parameter that was used for suspension viscosity modification: primary particle size. For the granules of Batch 3 it was not possible to generate dense packed shells during the drying process because of the size of the particles and

their mutual obstruction during the drying and packing process. Because of the high porosity of the granule shell, evaporation of the liquid medium during the drying process was not hindered and continuous shrinking was allowed. Higher amounts of homogeneous granules within Batch 3 were formed. This was in accordance to the structure analysis data within Table 2.

For granules from Batch 4 (fine particles but higher viscosity) the measured micro porosity was reduced. The dense packed shells were accompanied by a high void volume (macro porosity) what was also an effect of the drying behaviour of the suspension with fine primary particles. Even if the mobility of the primary particles was reduced because of the increased viscosity, denser packed structures were formed because of size and shape of the particles. During the drying process the dense packed shells hindered the mass transfer of the liquid medium – shrinking was prevented and ballooning of the droplets during the drying process was assumed. Higher measured amounts of hollow granules within Batch 4 confirm this theory. A further reason could be found in the packing density of the primary particles within the suspension at the beginning of the drying process: It can be assumed, that even at the beginning of the drying process the particles were already closer together in suspensions of Batch 4 compared to suspensions of Batch 3.

For the investigated Batches 3 and 4 the viscosity effect on the resulting internal granule structures was superimposed by the effect of the changed primary particle size, the suspension parameter used for viscosity modification.

As a result of varied internal structures, lower specific fracture loads were determined for granules of Batch 3. Higher micro porosities and therewith distances between the coarse particles as well as reduced contact numbers were responsible for reduced specific fracture strengths. Reduced micro porosities as well as increased contact numbers within the structure of granules of Batch 4 were responsible for increased fracture strengths. The low micro porosities were a result of the reduced primary particle size. Additionally these denser packed structures showed a higher resistance against deformation as it was determined for Batch 4 in comparison to Batch 3.

A defined effect on the shape of the granules can be seen in Figures 6 and 7 – high viscous suspensions supported the drying of spherical granules (Batch 3). A reduced suspension viscosity resulted in a reduced sphericity of the granules (Batch 4).

For Batches 3 and 4 the change of the primary particle size showed a measurable effect on the resulting suspension viscosities. The resulting internal granule structures caused varied mechanical granule properties. The effect of the suspension viscosity for Batches 3 and 4 on the resulting internal granule structures was not comparable to the investigated effects of Batches 1 and 2. For the suspension viscosity modification via particle size the parameter primary particle size superimposes the effect of the changed viscosity during the structure generation process. Loose packed structures were generated from low viscous suspensions from large primary particles whereas dense packed structures were generated from high viscous suspensions of fine primary particles.

A variation of the solid content at comparable primary particle size and additive combination also resulted in changed suspension viscosities (Batches 4 and 5). The lower the solid content was, the lower viscosities were determined, what was an effect of reduced numbers of primary particles and therewith reduced particle surfaces. The pH value was not affected. The determined suspension density was reduced as the amount of added solid content was also reduced (Batch 5).

A change in the solid content resulted in changed mechanical properties of the granules: At high solid content high specific fracture loads were measured accompanied by slightly decreased fracture deformation values. These differences were explained with the determined internal granule structure parameters which were a result of the modified suspension viscosity: As the primary particle size was comparable, also comparable micro porosities were determined: 37.6 % for Batch 4 and 37.3 % for Batch 5. The packing density of both granules was comparable. Differences were found concerning the macro porosity, which decreased with increasing solid content: For granules of Batch 5 (low solid content) a lower amount of primary particles was available within the droplet during drying process. Therewith a lower amount of particles was moving during the drying process to the shell of the droplet/granule – thinner shells were formed (higher macro porosity) and the amount of homogeneous granules decreased. Example granules are shown in Figures 8 and 9.

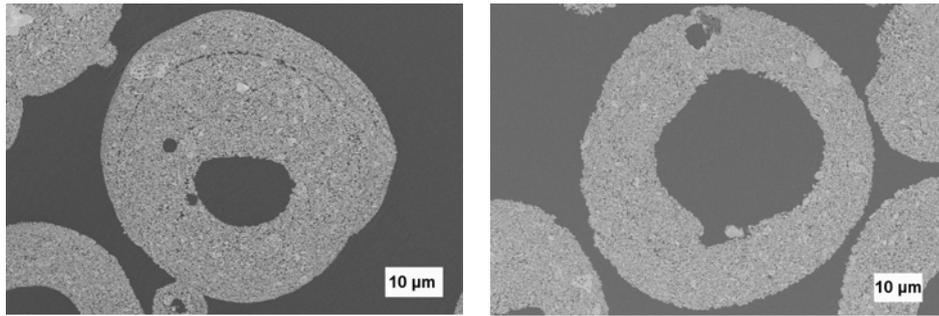


Figure 8 Internal macro structure, Batch 4 **Figure 9** Internal macro structure, Batch 5

Changing the solid content affected the suspension viscosities: A higher solid content caused a high suspension viscosity as the particle number and therewith particle surface was increased. The suspension viscosity influenced the resulting internal granule structures. High viscous suspensions resulted in thicker shells whereas the packing density was not affected. The modified internal granule structures were used to explain the different mechanical properties of granules of Batches 4 and 5. As the micro porosity was comparable the macro structure (shell thickness, macro porosity) was the decisive structure parameter.

Summary and Conclusions

Within this work the effects of exemplary changed single suspension parameters like solid content, primary particle size or surface charge of the primary particles on the resulting suspension viscosities, internal granule structures as well as on the resulting mechanical properties of spray-dried ceramic granules were studied.

An increase of solid content within the suspension resulted in increased suspension viscosities. During the drying step of a droplet, these higher number of primary particles of high viscous suspensions formed thicker granule shells – the amount of homogeneous granules increases. The packing density of the primary particles (micro porosity) was not modified. The increased shell thickness was responsible for the determined fracture strength increase of the granules, produced from suspension with higher solid content and therewith higher viscosity.

A reduction in primary particle size from 2.5 µm to 0.5 µm at comparable solid content resulted in a noticeable increase of particle number. Because of the therewith higher surfaces, the suspension viscosities increased by the reduction of the particle size. The changed suspension viscosity did not influence the resulting internal granule structures as strong as the modified drying behaviour of the droplets because of changed primary particle sizes: Smaller particles from high viscous suspensions formed denser packed granule structures (reduced micro porosity) with increased number of contacts because of size and shape of the particles. The determined increased specific fracture strengths confirmed this theory. Because of their shape and size, larger primary particles were not able to move as close together as the small particles, even if the reduced suspension viscosity would promote this effect. The resulting thicker but more porous shells were weaker.

A change in the surface charge of the primary particles showed an effect on the suspension viscosity as well as the resulting internal granule structures: High surface charges resulted in well stabilized low viscous suspensions that promoted the generation of hollow granules and slightly denser packed shells. Low surface charges resulted in agglomerated particles within the suspension and therewith increased suspension viscosity. Loose packed particle structures were generated.

From the investigated samples within this study it can be seen, that the suspension viscosity alone is not the decisive parameter for the developed internal structures of granules during the drying process. The suspension parameter responsible for the viscosity change also affects the drying behaviour of the suspension. In some cases, e.g. for primary particle size as shown here for Batches 3 and 4, an overlaying of the effect of the influencing parameter over the viscosity effect can be found and resulted in modified internal granule structures. Within future tasks the effect of more parameters like suspension temperature or additive kind and amount on the resulting suspension viscosity as well as the resulting granule properties and internal structures will be studied to extend the presented exemplary effects.

Acknowledgements

The authors would like to thank the German Research Foundation DFG for the financial support of the project within “Schwerpunkt Programm 1423 - Prozess-Spray”.

References

- [1] Walton, D.E., Mumford, C.J., *Chemical Engineering Research and Design* 77 Part A: 442-460 (1999)
- [2] Subero, J., Pascual, D., Ghadiri, M., *Chemical Engineering Research and Design* 78 Part A: 55-60 (2000)
- [3] Tanaka, S., Chia-Pin, D., Kato, Z., Uematsu, K., *Journal of the European Ceramic Society* 27: 873-877 (2007)
- [4] Antonyuk, S., Tomas, J., Heinrich, S., Mörl, L., *Chemical Engineering Science* 60: 4031-4044 (2005)
- [5] Salman, A.D., Reynolds, G.K., Tan, H.S., Gabbott, I., Hounslow, M.J., *Granulation - Volume 11 of Handbook of Powder Technology*, Elsevier, 2007
- [6] Fries, M., *Produktgestaltung keramischer Sprühgranulate für die uniaxiale Pressverdichtung zu großformatigen Bauteilen*, Fraunhofer Verlag, 2009
- [7] Hotta, T., Nakahira, K., Naito, M., Shinohara, N., Okumiya, M., Uematsu, K., *Journal of the European Ceramic Society* 21: 603-610 (2001)
- [8] Walker, W.J., Reed, J.S., Verma, S.K., *Journal of the American Ceramic Society* 82-7: 1711-1719 (1999)
- [9] Soottitantawat, A., Peigney, J., Uekaji, Y., Yoshii, H., Furuta, T., Ohgawara, M., Linko, P., *Asia-Pacific Journal of Chemical Engineering* 2: 41-46 (2007)
- [10] Höhn, S., Eckhard, S., Fries, M., Matthey, B., Herrmann, M., Michaelis, A., *Journal of Ceramic Science and Technology* 02-02: 75-88 (2011)
- [11] Höhn, S., Eckhard, S., Fries, M., Nebelung, M., *Spray 2010 - 9. Workshop über Sprays, Techniken der Fluidzerstäubung und Untersuchungen von Sprühvorgängen*, Heidelberg 2010
- [12] Derjaguin, B., Landau, L., in *Acta Physico Chemica URSS*. 14: 633 (1941)
- [13] Verwey, E. J. W., Overbeek, J. T. G., *Theory of the stability of lyophobic colloids*, Elsevier, 1948
- [14] Bertrand, G., Filiatre, C., Mahdjoub, H., Fossy, A., Coddet, C., *Journal of the European Ceramic Society* 23: 263-271 (2003)
- [15] Bertrand, G., Roye, P., Filiatre, C., Coddet, C., *Chemical Engineering Science* 60: 95-102 (2005)
- [16] Tsubaki, J., Yamakawa, H., Mori, T., Mori, H., *Journal of the Ceramic Society of Japan* 110-10: 894-898 (2002)
- [17] Tsetsekou, A., Agrafiotis, C., Leon, I., Miliadis, A., *Journal of the European Ceramic Society* 21: 493-506 (2001)