Powder Technology 258 (2014) 252–264

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Modification of the mechanical granule properties via internal structure

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ARTICLE INFO

Article history:
Received 4 November 2013
Received in revised form 22 February 2014
Accepted 1 March 2014
Available online 12 March 2014

Keywords:
Granule structure
Mechanical properties
Granule fracture
Compression strength
Porosity
Shell thickness

ABSTRACT

Disadvantageous mechanical properties of ceramic granules for die pressing applications, such as too high compression strength or too low ductility, may cause imperfections within the resulting component structure. To avoid these inhomogeneities, the granules have to show optimized mechanical properties.

The correlation between internal structure parameters and resulting mechanical properties of ceramic granules was investigated systematically by spray-drying of varied α-Al_2O_3 suspensions. Nine granule samples with different internal structures were produced. The mechanical properties were characterized using a compression test of single granules. Internal granule structures were quantified using image analysis techniques. To detect structure parameters responsible for changed mechanical granule properties, the internal structure parameters were divided in micro- and macrostructure parameters and their influence on resulting mechanical properties was studied individually.

The variation of additive type or amount overlaid the effect of changed internal granule structure parameters on the resulting granule compression strength and strain. If the additive type and amount were kept constant and suspension parameters like solid content, primary particle size, particle surface charge or width of the primary particle size distribution were modified, a clear influence of changed internal granule structure parameters on the resulting mechanical granule properties were measured.

Increased shell thickness (macrostructure) and reduced microporosity (microstructure) caused a granule strength increase. The effects of micro- and macrostructure parameters on mechanical granule properties can be added up. For the investigated samples a dominant influence of the microstructure on the resulting mechanical properties compared to the macrostructure effect was found.

1. Introduction

The processing properties of spray-dried ceramic granules are decisively influenced by their flow behavior and the mechanical granule properties. Disadvantageous mechanical properties of granules for die-pressing applications such as too high fracture strength or too low ductility may cause imperfections like voids or inhomogeneities within the structure of the final die-pressed ceramic components. These imperfections are often permanent as they cannot be cured by further sintering. The quality of the final component is strongly negatively influenced. To avoid this, a systematic adjustment of mechanical granule properties is necessary [1–4].

The mechanical properties of spray-dried granules like single granule fracture strength and strain can be tailored by the specific selection of type and amount of additives to the suspensions or by the modification of the internal granule structure. With regard to the internal structure, the influence of size distribution and location of pores within a granule on resulting granule strength is already reported in literature [5]. Hotta et al. documented the effect of varied granule size distributions and structures on the resulting compression behavior of the granule bulk [1]. Walton and Mumford classified different granule fracture types and related these to the particle structure. The porosity of an agglomerate is decisive for the resistance against deformation and the amount of produced fragments. Parallel the agglomerate strength can be modified by the addition of various additives — e.g. binding agents can increase the strength of granules [6]. Especially if the used additives are very expensive, covered by patent rights or the suitable additive selection is limited, desired changes of mechanical granule properties according to further handling and processing steps have to be done via internal granule structure modification.

For a systematic modification of mechanical granule properties via internal granule structure, the correlations between internal structure parameters and the resulting change of mechanical properties have to be known. These effects are still an area of investigation. Reasons for this are the limited possibilities to quantify the internal granule structure. First attempts to quantify the internal structure were described by several authors [7–11]. The characterization of the internal granule structure via mercury intrusion porosimetry is an established method. As this technique only delivers integral values without any information

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http://dx.doi.org/10.1016/j.powtec.2014.03.016
0032-5910/

concerning the internal structure distribution, this method is not suitable for the attempt to study the effect of structure changes on the mechanical property modifications. In another experimental approach Saad et al. evaluated the internal porosity by the determination of volume and weight of defined granule samples [11]. With this approach integral values were achieved, but no information about internal porosity distribution was available [11]. Alternative methods like liquid immersion technique are often not usable for all granule types as various requirements on the granule structures and the immersion medium have to be met. Image analysis on prepared surfaces as alternative method seems to be a promising technique to determine differential structure parameters. The preparation of porous granule structures is a challenging task as break-outs of particles on the surface or smearing of organic additives might result in unsuitable surfaces for further structure quantification via image analysis. Walker et al. [7], Bertrand et al. [9] and Mahdjoub et al. [10] tried to evaluate the internal structure via embedding, mechanical polishing and SEM visualization of granules and documented different granule morphologies (hollow, homogeneous). Besides the exemplary determination of the volume fraction of large macrospores also first attempts to determine the shell thickness were documented and correlations between suspension stabilization and resulting internal structures were found [7,9,10]. Soottitantawat et al. visualized internal structures via fracture surfaces and determined a ratio of macro-pore volume to granule volume and the amount of hollow and homogeneous granules via counting [8]. A threshold value to separate hollow and homogeneous granules was not defined [8].

The difficulty of the evaluation of different internal granule structures is known in the literature. A systematic method for a complete internal structure characterization based on image analysis techniques has not been documented yet but is necessary for the investigation of further correlations between internal structure and resulting mechanics or internal structure and suspension properties.

Our study is based on our previous work [12] where different mechanical properties of investigated granule batches were found. For these granules also different internal granule structures were detected with experimental methods and image analyzing techniques on prepared surfaces. The granule batches were separated in hollow and homogeneous batches and the varied mechanical properties were assigned to the different internal structures. The internal structures were not characterized systematically concerning defined structure parameters. Therefore the changed mechanical properties could not be assigned to single structure parameter changes. Within this study the correlations are studied systematically. Internal structure parameters are divided into micro- and macrostructure parameters and their influence on resulting single mechanical properties are studied individually. As starting point for the change of internal structures, the effect of varied suspension formulation on resulting granule structures was investigated. The solid content was changed as well as primary particle size and size distribution or additive kind and amount. Besides our own investigations, various authors [13,14] discussed the influence of some suspension properties on the resulting structures of spray-dried granules.

The different granules with modified internal granule structures were produced by spray-drying and characterized concerning resulting internal structures and mechanical properties. For the quantification of internal granule structures an alternative way to experimental structure characterization was developed by Höhn et al. [15,16]. Image analysis of specially prepared granule cross sections was used. The mechanical properties were measured using a single granule compression test.

2. Material and methods

2.1. Material

The investigated granules were spray-dried from varied aqueous suspensions. The used primary particles were α-alumina particles with different particle sizes. The particles 'Al_2O_3 coarse' (Nabalox NO 625-10, Nabaltec AG) showed an median particle size of $d_{50} = 2.5$ μm ($d_{10} = 1.2$ μm, $d_{90} = 4.8$ μm) whereas the particle fraction 'Al_2O_3 fine' (Nabalox NO 713-10 MF, Nabaltec AG) showed the characteristic particle sizes of $d_{10} = 0.1$ μm, $d_{50} = 0.4$ μm and $d_{90} = 3.5$ μm. The primary particle sizes were measured using laser diffraction (Mastersizer 2000, Malvern). The granules of sample G3 were produced from a weight equivalent mix of the two primary particle samples 'Al_2O_3 coarse' and 'Al_2O_3 fine'. The generated primary particle batch 'Al_2O_3 mix' showed an median primary particle size of $d_{50} = 2.2$ μm that was between 'Al_2O_3 coarse' and 'Al_2O_3 fine'. Additionally this primary particle material showed a wider size distribution ($d_{10} = 0.2$ μm, $d_{90} = 6.8$ μm) compared to the two other particle batches.

After suspending the particles in water by stirring, the specific additives polyvinyl alcohol Mowiol PVA 4-88 (Clariant), polyethylene glycol PEG 400 (Merck) or sodium polyacrylate NaPA 8000 (Sigma Aldrich) were added to the suspension following Table 1. These additives can be separated in surface-active (NaPA) and surface-inactive additives (PVA, PEG). After this the suspensions were homogenized for 60 min by stirring. The suspensions were characterized regarding pH (pH Meter, Schott), density of the suspension (measuring cylinder), solid content (halogen moisture analyzer, Mettler Toledo) and viscosity (rotational viscosimeter, Haake). The suspensions were spray-dried (Production Minor, GEA Niro A/S) under comparable thermal conditions with air as drying medium. In all cases a two fluid nozzle

Table 1
Suspension formulation modification to achieve varied internal granule structures.

Granule Sample		G1	G2	G3	G4	G5	G6	G7	G8	G9
Suspension properties										
Binder (PVA, surface-inactive)	wt%	3.0	3.0	3.0	3.0	1.0	-	3.0	3.0	3.0
Lubricant (PEG, surface-inactive)	wt%	-	-	-	-	-	3.0	-	-	-
Dispersant (NaPA, surface-active)	wt%	-	-	-	-	-	-	0.3	0.3	0.3
Solid content	wt%	39.6	68.1	39.8	39.9	39.9	39.9	39.9	39.7	68.2
Average primary particle size $d_{PP,50}$	μm	2.5	2.5	2.2 (mix)	0.4	0.4	2.5	2.5	0.4	0.4
Studied effects	**Comparing**									
Solids content [wt%]	**G1 & G2**	39.6	68.1							
	G8 & G9								39.7	68.2
Average primary particle size [μm]	**G1, G3 & G4**	2.5		2.2 (mix)	0.4					
	G7 & G8							2.5	0.4	
Additive amount (surface-inactive) [wt%]	**G4 & G5**				3.0	1.0				
Additive type [-]	**G1 & G6**	PVA					PEG			
Additve amount (surface-active,	**G1 & G7**	0.0						0.3		
dispersant) [wt%]	**G4 & G8**				0.0				0.3	