Quantification of internal structures of spray-dried granules

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1 Introduction

In the production process of ceramic, metallic and hard metal powders, the solids are mixed with aqueous or organic solvents, milled and spray-dried after the addition of chemical agents. The granule structure has a direct or indirect influence on the properties of the single granules, the bulk material and of the formed end products. Therefore the understanding of the shaping process of granules structure is essential for optimized suspensions, spray parameters and bulk material properties.
In this paper an artifact free preparation technique based on ion beam preparation and SEM visualization is reported. The quantitative characterization of the spray granules structure constitutes the basis for a correlation with the process parameters. Using model granules, the quantification of macroscopic as well as microscopic granule structure with this method can be shown.

2 State of the art

In literature the description of granule morphology often will be carried out by producing light- and scanning electron microscopic pictures of surfaces or fracture surfaces. The results are often subjective interpreted by means of images. Particle distribution and porosity between different samples are compared qualitatively. By mercury intrusion total porosity and determination of pore neck size distribution can be characterized. The weak point is used for differentiation between internal porosity within the granules and the porosity of the bulk material.
Another method to characterize granules is immersion liquid technique [1, 2]. Within this preparation method the cavities between the primary particles are filled with a liquid having a refractive index similar to the primary particle. That's why the beam of light goes straight through the specimen. With optical microscopy or confocal laser scanning fluorescent microscopy it is possible to detect large pores or defects which are responsible for weak granule strength. A quantification of primary particle distribution or microscopic porosity is limited by resolution. Using modern methods like computer tomography it is possible to realize resolutions in a low µm-scale [3, 4]. But for the quantitative characterization of structures and pores in submicron and nanometer scale these methods are not sufficient. Visualization of the distribution of organic agents in the samples is not possible as well.
Optimal resolution offers the scanning electron microscopy on polished areas. The main problem is the preparation of soft bonded hard ceramic particles. Stabilization of the granule structure by infiltration in epoxy resin offers only partly remedy, because some of the particles usually break out during the preparation by mechanical grinding and polishing. A falsification of the structure is the consequence. Conclusions about the distribution of the organic components are also not possible with this method, so that a new preparation method is required.

3 Experimental

3.1 Ion beam preparation

The preparation of the granules with ion beams solves the problem. The cross-sections are prepared without insertion of mechanical damages by a physical sputter process. An optimal method is the broad-ion-beam technique (BIB) [5]. With the ion beam etching system BAL-TEC RES 101 it is possible to remove and polish the ceramic particles simultaneously with the soft organic additives. In comparison to the focused-ion-beam technique (FIB) the BIB method offers the advantage to prepare areas in the size of some square mm for a significant

quantification of structures. Additionally the sample damage by milling with argon ions is gentler. By high resolution visualization of the internal granules structure with SEM (Zeiss NVision 40) a characterization down to nanometer scale is possible.

3.2 Model granules

For valuation of the preparation method and for a later correlation to the process parameters model granules were produced. Alumina powder (Nabalox 713-10, d50 = 0,41 µm) was used as raw material. By variation of the process parameters granule batches with mainly full (sample A) and with mainly hollow (sample B) macroscopic structure as well as a sample with high organic additive concentration (sample C) were prepared.

3.3 Quantitative structure analysis

Beside the quantification of the porosity by gray value detection, the direct neighbor distances (barylayer distances) of the primary particles were determined based on an algorithm of Voronoi tessellation [6] and Delaunay triangulation [7]. Quantification is carried out with the software programms analySIS® FIVE and ImageJ.

4 Results

4.1 Visualization of macroscopic and microscopic structure

Figure 1 and 2 display SEM micrographs of the inner granule structure of sample A and B. The internal porosity and pore structure as well as the position of primary particles in cross-section can be determined without infiltration of the specimens in epoxy resin. The qualitative comparison of sample A and B reveals differences in the packing density of primary particles.

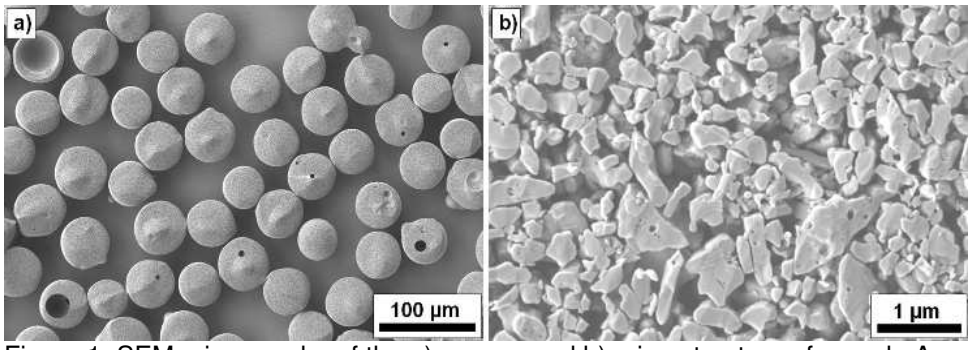

Figure 1: SEM micrographs of the a) macro- and b) microstructure of sample A

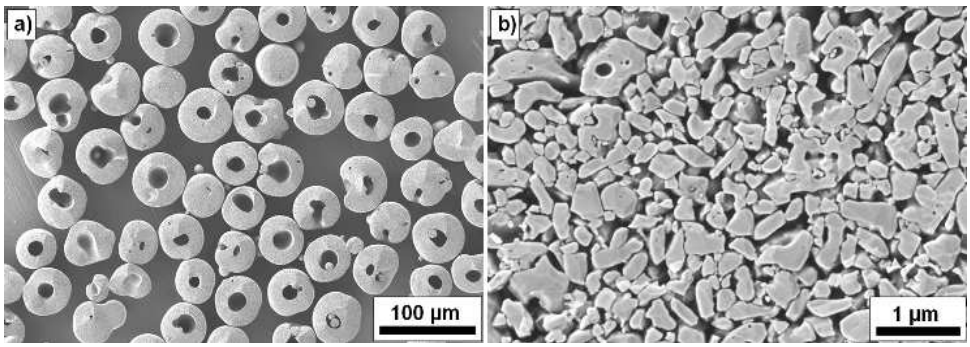

Figure 2: SEM micrographs of the a) macro- and b) microstructure of sample B

The micrographs of granule C show clearly, that it is possible to prepare edge sharp ceramic particles simultaneous with soft organic additives with the ion beam

preparation method (Figure 3). It is obvious that the additives are partly segregated.

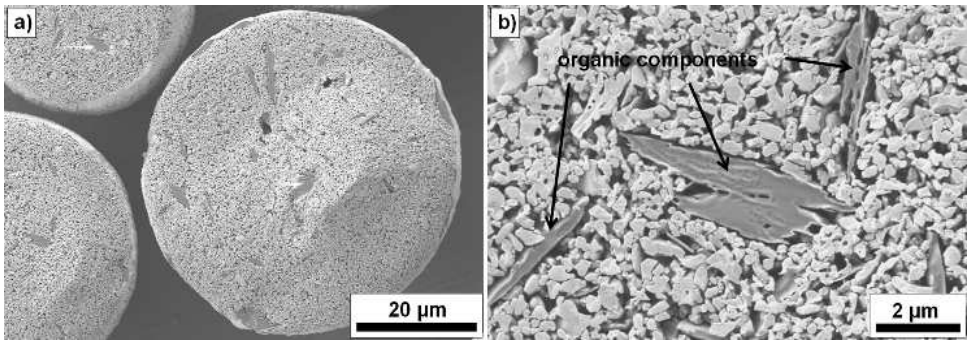

Figure 3: SEM micrographs of the a) macro- and b) microstructure of sample C

4.2 Quantification of the structure

Table 1 compares the results of the micro porosity between the primary particles (not macroscopic hollow part) of sample A and B. Sample A has a lower packing density than sample B. This result correlates with the drying mechanisms of spray granules described in literature [8]. Sample B shows a lower porosity near the shell (R) compared to the porosity at half distance between centered surface (½ R) (compare Figure 4).

Table 1: Results of the micro porosity between primary particles at different sample positions (0 – granule center, R – radius of the granules)

position	sample A porosity / %	sample B porosity / %
0 (center)	44,0 ± 0,5	-
½ R	45,2 ± 0,5	37,6 ± 0,5
¾ R	-	34,6 ± 0,5
R	44,7 ± 0,5	34,8 ± 0,5

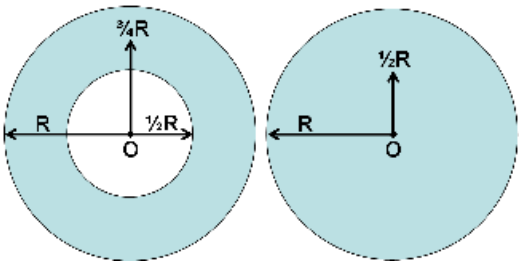

Figure 4: Positions of measurements in cross-sections of hollow and full granules

Description of the neighbor relations between primary particles is possible by determination of the barycenter distances to the next adjoining particles. Mean distance distribution of samples A and B is presented in figure 5.

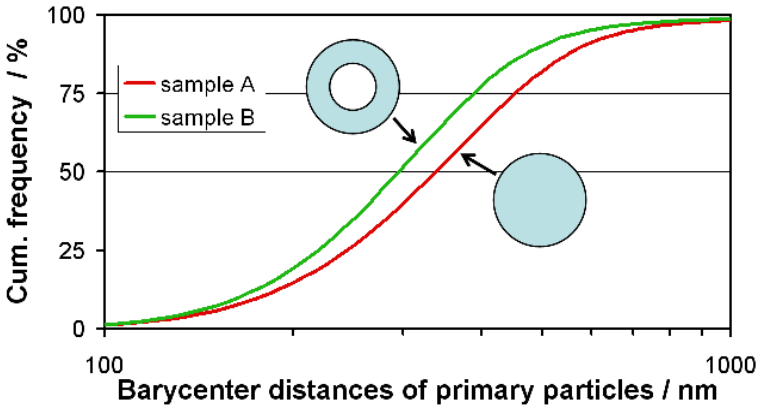

Figure 5: Distribution of the barycenter distances of the primary particles of sample A and B

5 Conclusions

In this paper was shown that the broad ion beam technique in combination with SEM visualization is an appropriate tool for the characterization of the internal structure of spray granules. The characterization of prepared model granule structures demonstrates clearly possibilities of quantification of macroscopic and microscopic structure and distribution of organic additives. Based on these results it will be possible to correlate process parameters with the granule structure in future.

6 Acknowledgments

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7 References

[1] K. Uematsu, J.-Y. Kim, M. Miyashita, N. Uchida, K. Saito, K., J. Am. Ceram. Soc. 73 (1990) 2555
[2] Y. Sato, S. Tanaka, N. Uchida, K. Uematsu, Am. Ceram. Soc. Bull. 81 (2002) 35
[3] L. Farber, G. Tardos, J.N. Michaels, Powder Techn. 132 (2003) 57
[4] P. Rajniak, C. Mancinelli, R.T. Chern, F. Stepanek, L. Farber, B.T. Hill, Int. J. Pharma. 334 (2007) 92
[5] I. Gräf, Pract. Met. 35 (1998) 235
[6] G. Voronoi, G., J. Reine u. Angew. Math., 134 (1908), 198
[7] B.N. Delaunay, Bull. Acad. Sc. USSR VII: Class. Sci Meth. (1934), 793
[8] W.J. Walker Jr., J.S. Reed, J. Am. Ceram. Soc. 82 (1999) 1711