Comparative Study on Lab-Scale Granulations Techniques

N. Rosenberger, C. Compson, J. Atria

In order to find the best suitable processing route for laboratory scale experiments for alumina powder and binder evaluation a comparative study on granules produced with different techniques was performed. The results are compared to CT 3000 SDP from regular Almatis production, which achieves unique performance in terms of thermal reactivity and resulting excellent mechanical strength.

1 Dry pressing in the ceramic industry

Dry pressing is the most common forming technique for technical ceramics, as this is the most energy efficient way to produce a ceramic body [1]. Most ground ceramic powders do not flow well, pack densely or compact into a uniform microstructure [1–2]. Therefore they often get mixed with binders and pressing agents and granulated. Granules may be formed directly by the proper admixing of a liquid or a solution of the binder and other additives into a stirred powder or, indirectly, by drying the material out of a slurry [1, 3]. The most common slurry drying technique is spray drying, which is effective at producing a variety of pressable granules [4]. One common struggle encountered with the spray drying process is the development and scale up of formulations, since production-scale granule distributions are hard to replicate at the bench-scale [5].

2 Granulation techniques

In this paper, three potential techniques were evaluated for preparing granulates in order to verify the best processing route for laboratory scale experiments. One direct granulation method was used, which added binder to the powder in a high intensive Eirich mixer and the other two methods involved granule preparation from a slurry via spray drying and freeze drying.

2.1 Granulation via Eirich mixer

For the production of granulates in an Eirich mixer (hereafter referred to as "CT 3000 SG construction granulate construction granulate – CG") 2500 g of starting powder was mixed with 75 g of polyethylene glycol binder, which had been previously dissolved in 125 g deionized water. The material was mixed for 36 min with a mixing rotation speed of 300–3000 rpm and pot rotation speed on level 1.

2.2 Granulation via freeze drying

3 l of the slurry from regular production of Almatis CT 3000 SDP (Spray Dried Powder – commercially available material from Almatis) were frozen in a standard freezer at −14 °C and then dried in the freeze-dryer for 60 min in a vacuum at −20 °C. The granulate hereafter is referred to as "CT 3000 SG freeze dried granulate – FG".

2.3 Granulation via spray drying

15 l of the slurry from regular production of Almatis CT 3000 SDP was processed in the delivered state. The material was fed into a spray dryer from Co. ICF type 1C-FM/5/UDF with an air pressure of 2 bar. The droplets were sprayed using nozzle B6 nozzle sleeve S14 from Co. ICF. The inlet temperature was 300 °C and the exit temperature was 110–120 °C. The angle of the suction opening for slurry inlet was 70°. The granulate hereafter is referred to as "CT 3000 SG spray granulate – SG".

All of the granules obtained by these techniques were dried for 24 h at 110 °C and sieved to a size range between 63–500 µm, in order to reduce the oversized material and the amount of dust. The granules were initially evaluated for particle size, moisture and loss-on-ignition (LOI). Further characterization included green and fired density as well as the mechanical strength of uniaxially and isostatically pressed ceramic pieces.

3 Granule properties

As a first step, the structure of the different granules were analyzed with a microscope. Images can be found in Fig. 1–3. In Tab. 1 the properties of the prepared powders are shown. The granules produced in the spray dryer show the smallest granule sizes and

Fig. 1 Picture of CG (63–500 µm)

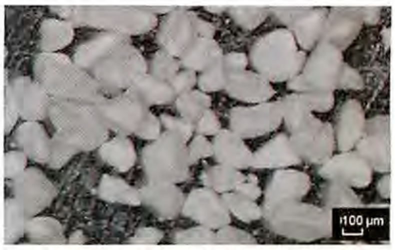

Fig. 2 Picture of FG (63–250 µm)

Fig 3 Picture of SG (63–500 µm)

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Tab. 1 Properties of granules

	Unit	CG	FG	SG
d_{50} (Malvern)	µm	169	204	122
d_{90} (Malvern)	µm	398	433	276
Apparent density	g/cm³	1,18	1,14	1,23
Moisture	%	0,32	0,29	0,59
LOI @1050 °C	%	0,81	1,75	2,20

Tab. 4 Data of 4-point-bending strength test

4-point bending strength	Unit	CG	FG	SG
Characteristic strength	MPa	304	364	328

Tab. 5 Grain and pore sizes of uniaxial pressed specimen

Grain Size	Unit	CG	FG	SG
Average grain size (150 MPa)	µm	2,13	2,27	2,28
Max. grain size (150 MPa)	µm	7,50	7,45	9,41
Average pore size (150 MPa)	µm	0,63	0,52	0,61
Max. pore size	µm	8,82	4,31	4,12

Tab. 2 Green densities of pressed bodies (*no defect-free specimens could be pressed)

Green Density	Unit	CG	FG	SG
Axial 100 MPa	g/cm³	2,23	2,34	2,28
Axial 150 MPa	g/cm³	2,27	2,38	2,36
Iso 100 MPa	g/cm³	*	2,31	2,23
Iso 150 MPa	g/cm³	*	2,29	2,26

Tab. 3 Fired densities of pressed bodies (*no defect-free specimens could be pressed)

Fired Density	Unit	CG	FG	SG
Axial 100 MPa	g/cm³	3,94	3,94	3,92
Axial 150 MPa	g/cm³	3,94	3,95	3,93
Iso 100 MPa	g/cm³	*	3,89	3,86
Iso 150 MPa	g/cm³	*	3,91	3,86

are close to granules from regular production; however the particle shape is not as uniform as would be achieved with a production spray dryer. The freeze dried material is splintered and the coarsest with a d_{50} >200 µm. The construction granules are in between and show similar to the freeze dried granules a broader granule size distribution compared to the spray dried granules. The apparent density follows the same pattern, while LOI at 1050 °C shows some variation. The significant lower value for the CG material can be explained with uneven binder distribution during the processing in the Eirich mixer. The higher LOI for the SG-material might be related to residual OH^- groups, as the moisture value also shows residual humidity in the material. To check the behaviour of the granules during pressing, pellets were uniaxially and isostatically pressed at 100 and 150 MPa respectively. The green densities of the resulting pieces can be found in Tab. 2.

The highest green densities were achieved with uniaxial pressed freeze dried granules. The values achieved at 100 MPa are comparable to the standard CT 3000 SDP Almatis production material, which has an average value of 2,35 g/cm³ (uniaxial pressed at 100 MPa). Granules produced via spray drying are also close to CT 3000 SDP standard production; however a higher pressing pressure of 150 MPa is necessary to achieve a similar green density. Construction granules had the lowest green density values for uniaxial pressing. Increasing the pressing pressure from 100–150 MPa did improve the green density result, however it was still below the values achieved by freeze drying and spray drying. Defect-free specimens could not be obtained from construction granules when isostatic pressing was used, and therefore no green density result could be reported.

4 Sintering and strength results

Test specimens sintered at 1580 °C were used to determine the density by means of helium pycnometry from Micromeretics (Accupyc 1330). The results are shown in Tab. 3.

The specimen using FG-material and uniaxial pressed at 150 MPa achieved the highest fired density. The other FG-samples, as well as both uniaxial pressed CG-samples, have fired densities on a similar high level. For the isostatic pressed parts the fired density is generally lower. For the CG-material no defect free specimen could be obtained by isostatic pressing. Again the density of the FG-samples is higher compared to SG-samples. Users of CT 3000 SDP report fired densities of up to 3,95 g/cm³, which matches the results from freeze dried material.

The four-point bending method was performed on 10 samples from each granule type in accordance with DIN EN 623-3. The specimens were uniaxially pressed at 150 MPa and fired at 1580 °C, and bending rates of 0,5 mm/min ensured 5–15 s before sample failure.

The ceramic specimens pressed from freeze dried granules achieved the highest strength values, followed by the spray dried and constructed granules. The specimen strength's therefore follows the same trend as green density. Scanning electron microscopy was used to characterize the microstructure of each uniaxially pressed sample. Grain and pore size distributions were determined using an aggregate value achieved by the line intercept method on five images according to DIN EN ISO 643. The results of the intercept grain size and pore size distributions can be seen in Tab. 5. The average crystal size is smallest for the construction granules. The freeze and spray dried materials are similar in value, and slightly coarser than the construction granules. The max grain size of the construction and freeze dried granules are on a similar level and ~20 % smaller than the spray dried granules.

Considering the trends in green density and strength, in combination with the aforementioned granule results, a reasonable initial hypothesis is that freeze dried granules provide a more homogeneous microstructure.

The pore size distribution explains the differences in 4-point bend strength between the samples. Specimens produced from freeze dried granules show the lowest aver-

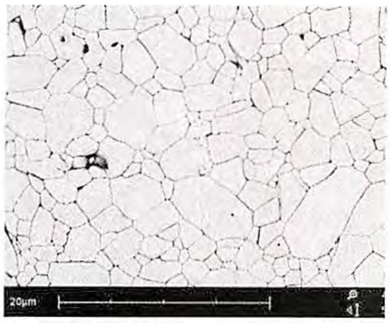

Fig. 4 Microstructure of tablet out of CG uniaxial pressed at 150 MPa

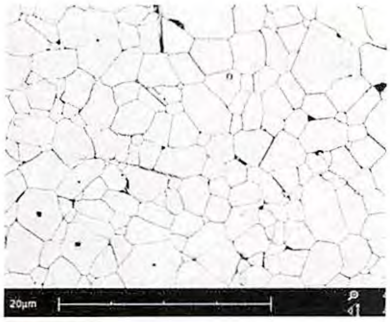

Fig. 5 Microstructure of tablet out of FG uniaxial pressed at 150 MPa

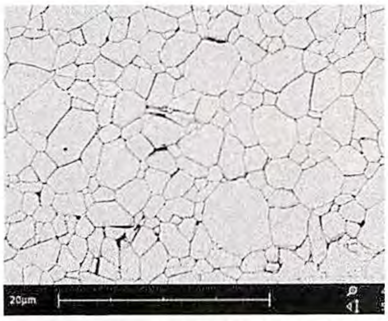

Fig. 6 Microstructure of tablet out of SG uniaxial pressed at 150 MPa

age pore size as well as a low maximum pore size. These granules concurrently had the highest bend strength. The specimens from spray dried and construction granules have similar average pore sizes, both higher than that achieved with freeze dried granules. The max pore size of the microstructure produced from the spray dried granule is the lowest of any specimen. The intermediate bend strength value achieved from spray dried granules is reasonable, given the combination of a higher average pore size and the lowest max pore size. The constructed granules, with the highest average pore size and by far the highest max pore size, recorded the lowest bend strength, which is also quite reasonable. Microstructure images of specimen using the different granules are shown in Fig. 4–6.

5 Summary

The target of the study was to find the most suitable method to generate lab-scale granules for powder and binder evaluation studies. Three granulation techniques were evaluated: direct forming in an Eirich mixer, freeze drying and spray drying.

The spray dried granules had the most favourable size distribution for production-scale processing, however the green and fired density, as well as strength results were all lower than freeze dried granules. The constructed granules in the Eirich mixer achieved good results for fired density, but the green densities were low and specimens were difficult to form with isostatic pressing. The granules failed in the end, as the strength is the lowest, resulting from a microstructure that contained large pores and was most inhomogeneous. Although the granules of the freeze dried material were large in size, which is not beneficial, the resulting green and fired densities as well as 4-point bending strength were highest for the specimens pressed out of these powders. Combined with the most homogeneous microstructure and closest results to production scale granules, the freeze dried granules are the best overall solution. Additionally, the equipment is easier to use than the second best option, which is the spray dried powder approach.

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