The influence of granulated powder temporary organics composition on ceramic structure and properties

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Abstract. The influence of granulated powder binder/plasticizer ratio on microstructure and properties of sintered ceramic specimens is shown using submicron alumina. The fracture mode, microstructure and properties analyses of a green part and sintered samples obtained with different organic ratio contained in granulated powder are presented. It was stated that the usage of PVA (grade 16/1) and PEG 400 at an equal ratio results in a uniform distribution of granulated powder in a die and high green density. It is also shown that an addition of 2 wt. % of PVA and 2 wt. % of PEG400 into granules of ceramic press powder allows obtaining Al$_2$O$_3$ ceramic with apparent density of about 3.91 g/cm$^3$ and bending strength of up to 410 MPa.

1. Introduction

A ceramic production technological procedure that contains a dry pressing technique includes temporary organic additives (binders and plasticizers) usage. These additives act as a glue for ceramic particles in granules and can change physical-chemical properties of press powder. Organics exert main influence on the granulated powder behavior during the green part formation. Green part defects related with incorrect organics selection are partially saved in sintered ceramic and significantly affects mechanical properties. However the question related with a proper organic composition selection has not been paid enough attention in the literature and the existing information is of general nature that is applicable to a wide range of organics. The temporary additives composition is determined in relation with raw ceramic powder characteristics and almost each technological stage of ceramic production. Regarding this the revealing optimal composition of organics for widely spread advanced fine-grained alumina ceramic obtained using a dry pressing technique is a very important task for industry.

2. Materials and experimental procedure

Alumina powder brand CT 3000 SG (Almatis) was used as a raw material for ceramic production. According to the preliminary investigation [1] typical particle size characteristics of the powder are d$_{50} <$ 0.6 $\mu$m, d$_{90} <$ 2.0 $\mu$m. Ceramic specimens were produced by using a widely spread manufacturing technology including the following steps: ceramic powder water suspension dispersing, granulation with a spray drying technique, dry pressing and free sintering. Detailed technological parameters of samples preparation and their proofs were published in [2, 3].

At the granulation stage the suspension was mixed with 10 wt. % water solution of PVA brand 16/1 and PEG 400, which were used as a binder and a plasticizer correspondingly. Several series of samples with different binder (PVA16/1)/plasticizer(PEG400) ratios (0:4 for the 1$^{st}$ series, 1:3 for the 2$^{nd}$ series,
2:2 for the 3\textsuperscript{rd} series, 3:1 for the 4\textsuperscript{th} series, 4:0 for the 5\textsuperscript{th} series) were prepared and analyzed in the paper. Each press powder contained 4 wt. % of the total organic amount.

The granulation process was performed with a Mobile Minor 0.8 (GEA Niro) spray dryer which allows obtaining press powder with a particles size in the range from 10 to 150 μm. The granulated powder behavior was studied on the green cylinders with the height of 10 mm and about 40 mm diameter. The forming uniaxial pressure was 100 MPa. To find out the strength of sintered ceramics the green bars of 5×5×55 mm size were also made. Sample sintering was performed in the LHT 02/17 (Nabertherm) laboratory furnace under 1600 ºC temperature during 3 hours of soaking.

The green sample fracture surface and the sintered ceramic microstructure were analyzed with the Carl Zeiss EVO 50 scanning electron microscope. The green density was estimated with geometry and weight measurements. Apparent density measurements were performed in accordance with GOST 2409-95. To reveal mechanical properties sintered ceramic was subjected to bending strength measurements. Mechanical tests were done according to GOST 24409-80 under a 3-point loading condition on an Instron 3369 testing machine.

3. Results and discussion
A preliminary investigation of the organic additives (binder/plasticizer) ratio influence on a ceramic producing process was carried out using the data of the green samples fracture analysis. Figure 1 shows fracture surfaces of the green samples with 1 wt. % and without PVA in the granules. A distinctive feature of these samples is almost total absence of granule boundaries and junctions (Figure 1a). This effect is related with low granules strength that maintains their shape only with capillary forces. Applying any pressure to the granulated powder results in their complete destruction. At the same time low press powder strength results in the occurrence of strong pressure gradients throughout the green sample cross – section and unpressed granules in local areas. It was stated that at

![Figure 1. Fracture surface of green ceramics obtained with a small amount of binder in the press-powder: a, b, c – 0 wt. % PVA 16/1 + 4 wt. % PEG 400, d – 1 wt. % PVA + 3 wt. % PEG 400.](image-url)
the initial stage of forming the granules cannot be redistributed in the die and provide a uniform pressure application throughout the cross-section. As a confirmation of this hypothesis the presence of a small amount of initial granules in the local areas (Figure 1b, c) and macro cracks caused by local over pressing (Figure 1d) were revealed.

The additional confirmation of this effect was obtained with a compaction curve analysis that was made for the first and the second series of samples (Figure 2). According to the theory [4] at the initial forming stage, it is important to provide press powder redistribution in the die, which is accomplished with a horizontal area at the compaction curve. If the quantity of the organic binder in the press powder is not enough its granules start to collapse immediately under any load, and this effect is accomplished with a gradual density increase on the plot.

![Compaction Curve](image)

**Figure 2.** Die-fill density and compaction response for granulated powder with different organic ratios.

The green sample gradient density and macro cracks exert influence on the microstructure and properties of sintered ceramic. Figure 3 shows the structure of local areas for the samples of the 1...2 series. According to the obtained results, the sintered samples contain such defects as boundaries and whole granules in the structure.

![Microstructure](image)

**Figure 3.** Local areas microstructure of sintered ceramic that does not contain PVA in the press.

The absence of the granule rearrangement process also influence the ceramic properties distribution. If the powder occasionally filled the die uniformly the ceramic bending strength can reach
330 MPa with the density of about 3.93 g/cm$^3$ (Table 1, series 2). However, the probability of such a state is very low and most of the time samples strength will be no more than 220 MPa with apparent density of about 3.84 g/cm$^3$ (Table 1, series 1).

### Table 1. Green and sintered ceramic properties.

| Series | PVA, wt.% | PEG 400, wt. | Total amount of organic, wt.% | Green density, g/cm$^3$ | Apparent density, g/cm$^3$ | Bending strength, MPa |
|--------|------------|-------------|-----------------------------|------------------------|--------------------------|-----------------------|
| 1      | 0          | 4           |                             | 2.18                    | 3.84                     | 220                   |
| 2      | 1          | 3           | 4                           | 2.17                    | 3.93                     | 330                   |
| 3      | 2          | 2           |                             | 2.18                    | 3.91                     | 410                   |
| 4      | 3          | 1           |                             | 2.12                    | 3.81                     | 280                   |
| 5      | 4          | 0           |                             | 1.96                    | 3.61                     | 260                   |

The analysis of compaction curves for samples with more than 2 wt. % PVA in the powder indicates the occurrence of the granules rearrangement process at the initial forming stage. The greater the fracture of the binder in the granulated powders, the more evidently the horizontal area is seen on the compaction curves (Figure 2, serial 3...5). If the powder contains 4 wt. % of PVA than rearrangement lasts up to 2 MPa formation pressure. When applying a higher load to the samples of the fifth series, a linear growth of green density is shown. According to the literature [4] this region characterizes granule deformation in the green body.

However, the fracture surface analysis of the 3...5 series samples shows that the more fraction of the binder in the press powder, the greater is the volume of undestroyed granules in the green part (Figure 4a, b). The presence of initial granules negatively influences green and sintered sample properties. It was stated that at an unloading stage of the forming procedure the springback effect in green samples appears due to elastic deformation. The measured density of green samples is lower.

![Figure 4. Green part fracture surface and sintered ceramic microstructure of the 3rd (a, b), 4th (c, d) samples series.](image-url)
than the calculated one according to the compaction curve (5 series, Table 1, Figure 2). Moreover, a microstructure analysis shows that the more PVA in the initial powder, the greater the volume fraction of defects in sintered ceramic (Figure 4 c, d).

The microstructure analysis results concerning 3 – 5 series of samples were confirmed by apparent density and bending strength examination. It was stated that the more PVA in granulated powder, the less density of green and sintered ceramic (Table 1). An increase of the micro cracks volume fraction in sintered ceramic related with granule boundaries results in strength decreasing. The best bending strength obtained in ceramic of series 3 was about 410 MPa.

4. Conclusion

Thus the development of the binder/plasticizer temporary organic additives ratio should be done in connection with providing the complex behaviour of granulated powder at the shaping stage of ceramic producing. On the one hand, granules should possess enough strength to provide their rearrangement at the initial pressing stage. On the other hand, the quantity of the binder should be less than the defined limit that determines granules destruction at the maximum applied formation pressure.

If one uses polyvinyl alcohol 16/1 as a binder and polyethylene glycol 400 as a plasticizer with 4 wt. % of the total amount of organic in granulated powder, the optimal ratio is 2 wt. % PVA + 2 wt. % PEG 400. At this ratio of organic additives in the press powder, the microstructure of sintered ceramic is characterized as one having a minimum quantity of saved granule boundary defects. Moreover, the flexural strength of this ceramic is about 410 MPa, which is the highest magnitude for the analyzed series.

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