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Original article

Effects of granule density on strength and granule related defects in zirconia

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Abstract

A suspension of zirconia powder (TZ3YSE) with a solids loading of 50 vol% was prepared by ball milling. Binders were added and some of the suspension was diluted to 40, 30 and 20 vol% before freeze granulation was performed. A spray dried material (TZ3YSEB) was used as a reference. The pore size distribution of the different granules was evaluated and from the microstructure it was shown that inhomogeneities were present in both the freeze granulated as well as in the spray dried granules. In addition, the density, microstructure as well as the strength of sintered materials prepared from the granules were studied. The results showed that a high green density or sintered density was not sufficient in order to achieve a high strength material. It was further shown that the strength was significantly influenced by the granule density and not by the inhomogeneities found in the granules.

Keywords: Granule density; Freeze granulation; Defects; Mechanical properties; Zirconia; Microstructures; Dental ceramics

1. Introduction

New high strength ceramic materials are continuously being developed to improve the mechanical performance beyond that of the ceramics used today. However, there are few materials that have been able to show significantly improved properties compared to the conventional materials already used. A major reason for this is that the strength is not mainly controlled by the material itself, i.e. the strength is instead determined by the microscopic defects present in the material. These defects can be caused by the raw material, contaminations or by the processes used.[1,2] Once formed, the defects will be difficult to remove and the sintered material will have an accumulated defect population. With a suitable powder processed in a clean environment, the fabrication processes such as granulation, compaction and machining will most likely be responsible for the strength limiting defects present. To reduce the negative influence of the process related defects caused by granules a better understanding is required regarding suitable granule characteristics for the compaction processes used. This has however been a somewhat neglected field of the ceramic research even though it might be one of the most important areas in order to reach the full potential of the ceramics developed.

The research related to ceramic granules has mainly been focused on how various aspects such as suspensions,[3–6] binder systems,[7–10] migration of binder,[11] moisture content,[10,12] granule morphology,[3,4,13] granule sizes,[10,13,14] granule density[13,15] as well as the compaction behaviour[10,16] influence the granule characteristics, compaction behaviour and the properties of the green body. The results from studies of granules and green bodies may however not be directly transferable and valid also for sintered high strength ceramics. Especially since the sintered materials will be more sensitive to defects and stress concentrations compared to a green compact where the sensitivity to stresses can be reduced by the presence of an elastic binder. The strength limiting defects may further not be found when the green compact was evaluated by conventional methods such as density measurements or pore size distributions.

When the influences from the granules are to be investigated, it can be assumed that the performance of the sintered material would be of great importance to study. In spite of this the studies performed on sintered materials[6,11,13,17] are few compared to the studies performed on compaction and green bodies. Even though some general principles are known such as hard elastic granules tend to form larger flaws compared to softer granules,[8] there has been a limited attention to find desired characteristics of the granules to reduce the granule related defects. A sufficient knowledge to design a granulated material for compaction in order to reduce the granule related defects in sintered materials is thus still to a large part missing. The aim of the present work was

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to evaluate the influence of the granule density and homogeneity on the prepared ceramics with respect to density, process-related bulk defects and mechanical properties.

2. Materials and methods

An aqueous suspension with a solids loading of 50 vol% of ZrO_2 stabilized with 3 mol% Y_2O_3 (TZ3YSE, Tosoh, Japan) and 0.3 wt.% of dispersant (Dolapix PC 75, Zschimmer-Schwarz, Germany) was prepared. The suspension was milled in a planetary ball mill, with a zirconia milling media using a rotary speed of 200 rpm. Equal amounts of PEG (Polyglykol 4000S, Clariant, Germany) and latex emulsion (LDM 7651S, Celanese, Sweden) was added to reach a total amount of 3 wt.% of binder. The suspension was divided and diluted with water in order to obtain suspensions with a solids loading of 20, 30, 40, and 50 vol% of zirconia. The suspensions were sprayed into liquid Nitrogen and freeze dried. Granules with a size above 500 μm were removed by sieving. A spray dried powder (TZ3YSEB, Tosoh, Japan) with 3 wt.% of binder was included in the study as a reference material. The freeze granulated and spray dried granules were used to prepare discs by compaction at a low pressure in a steel die followed by cold isostatically pressing (CIP) at 100, 200 or 300 MPa. For evaluation of granule morphology, pore size and density measurements the granules and CIPed materials were sintered for 2 h at 900 °C. For evaluation of the biaxial bending strength and microstructure CIPed materials were sintered for 2 h at 1500 °C. Density measurements were performed by Archimedes' method and the pore size distribution was studied by mercury intrusion (Micromeretics, USA). The density data obtained from these measurements were used to calculate the linear shrinkage needed for the granules and the mould filled with granules to reach the green density. The morphology of the granules and the microstructure of the sintered materials was studied with a scanning electron microscopy (JSM 840A, JEOL, Japan). Sintered discs were machined to a thickness of around 1.4 mm. The final material removal to reach a sample thickness of 1.2 mm was performed by grinding and polishing where the final polishing step was made with a 1 μm diamond suspension. The biaxial bending strength of at least 10 polished samples for each material was measured with a pin on three balls using an electromechanical test frame (Zwick Z50, Germany).

3. Results

3.1. Pore structure of the granules and fill density

Mercury intrusion–porosimetry characterisation of presintered granules showed two distinct pore size distributions (Fig. 1). Pores with a size between 10 and 100 μm represent the inter granular porosity while the pores with a size between 0.1 and 1 μm represent the porosity within the granules. When the pore volume of the granules was recalculated to granule density, a close resemblance between the granule density and solids loading of the suspension was obtained as shown in Fig. 2. The relative density of the spray dried TZ3YSEB granules used as a reference was around 35%. These density values were obtained from the presintered granules where the binder was removed before the measurements were performed. The total pore volume obtained from the mercury intrusion measurements was assumed to represent the initial fill density obtained before compaction, which increased from around 13% for granules with a low density to around 29% for the granules with a high density (Fig. 2).

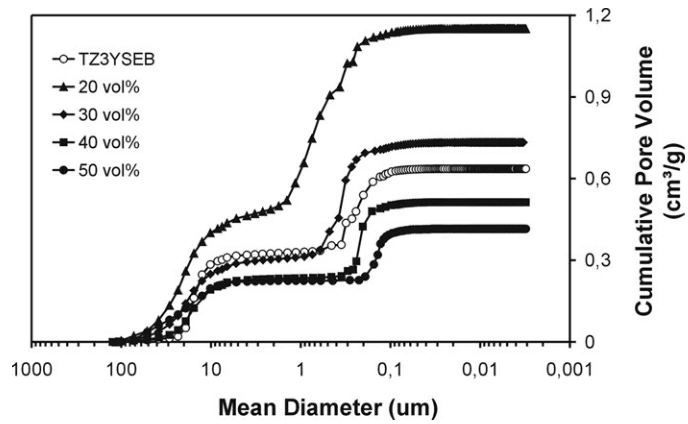

Fig. 1. Cumulative pore size distribution of presintered granules prepared from suspensions of TZ3YSE with different solids loading and TZ3YSEB.

3.2. The density of green compacts versus the granule density

The samples prepared from spray dried TZ3YSEB granules obtained a relative green density after presintering at 900 °C of ∼47% when compacted at 100 MPa and ∼51% when the compaction pressure was increased to 300 MPa (Fig. 3). A similar increase of the relative density with 3–4% was also obtained for the green compacts derived from the freeze granulated granules as the compaction pressure increased from 100 MPa to 300 MPa. However, the density of the green compacts derived from the freeze granulated granules were higher than that from the spray dried TZ3YSEB granules and it was further found that the green density increased with the increase of the granule density. This

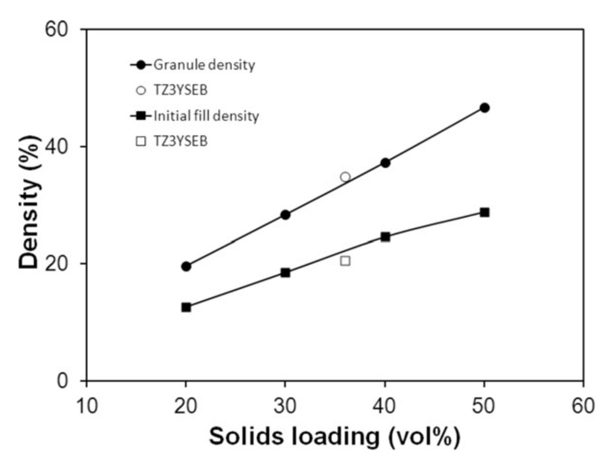

Fig. 2. Granule density and initial fill density of the prepared granules calculated from the cumulative pore volumes. The solids loading of the reference material was not known.

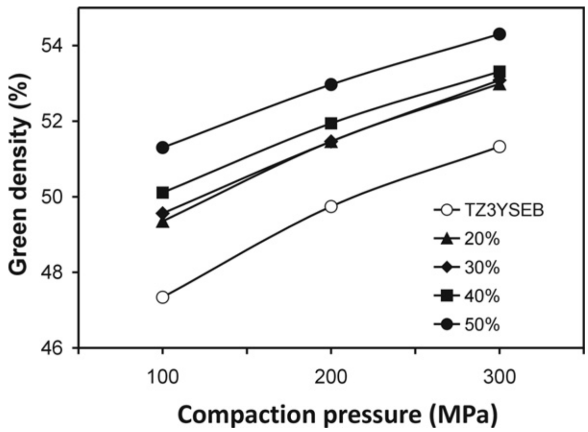

Fig. 3. Green density of CIPed and presintered materials.

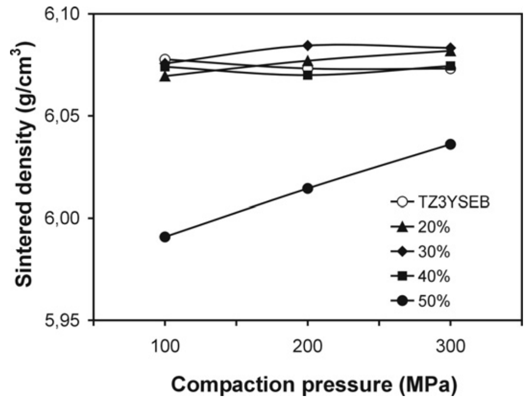

Fig. 4. Sintered density of CIPed materials.

was assumed to be related to an increased particle density within the granules where a smaller and narrower pore size distribution was obtained as the density of the granules was increased. The compacts derived from freeze granulated granules with a density of 50% reached a green density of around 2–3% above the corresponding density of the spray dried TZ3YSEB material.

The total shrinkage during compaction was determined by the initial fill density and the final green density while the shrinkage and deformation of the granules were determined by the granule density. A change of the granule density would further influence the compaction behaviour with a different contribution to the shrinkage from an increased particle density within the granules and deformation of the granules. With a granule density close to the green density, only a small increase of the particle density within the granule would be necessary for the final green density to be reached. The main contribution to the total shrinkage during compaction would then be due to deformation of the granules. This would further cause a large ratio between the shrinkage needed for the initial filled mould compared to the granules in order to reach the green density (Table 1). As the granule density was decreased the difference in shrinkage between the granules and the initial filled mould was reduced. This allowed the granules to both deform and increase the particle density within the granule to a larger extent during compaction.

3.3. The density of the sintered material versus the granule density

When the compacted materials were sintered, all materials except one reached a sintered density that can be considered as a fully dense material (Fig. 4). In spite of the high green density obtained in the material prepared from granules with a density of 50%, the sintered density was significantly lower compared to all the other materials and shows that a high green density is not sufficient in order to also reach a high sintered density.

3.4. The micro structure of granules

From the cross section of the spray dried granules, the microstructure showed inhomogeneities consisting of porosity as well as dense fragments of zirconia (Fig. 5). Also the granules prepared by freeze granulation had pores and an inhomogeneous particle distribution within the granules as well as the same type of dense zirconia fragments as was found in the spray dried granules. The inhomogeneities in the freeze granulated materials were caused by the formation of ice crystals during freezing. As the size of the granules and the water content in the granules were increased, the formation of ice crystals was facilitated and the degree of segregation within the granules was enhanced.

3.5. Microstructure and strength of sintered materials

The microstructure of the sintered material prepared from granules with a density of 50% showed the presence of defects formed in between adjacent granules which were not merged completely during the compaction (Fig. 6). The size of these defects can be large from a mechanical point of view and still represent a very small volume. The same type of defects with a reduced size was found in the material prepared from granules with a density of 40% even though the density measurements gave no indication of any significant porosity. In the other materials prepared from granules with a density of 30% and 20% as well as the spray dried powder, no obvious granule related defects were found.

As revealed in Fig. 7, the strength of the sintered materials was significantly influenced by the granule density. Strength of only around 400 MPa was reached when the granules had a density of 50%, around 800 MPa when the granules had a density of 40% and around 1200 MPa when the granules had a density of 30%. When the density of the granules was further reduced to 20%, the strength seemed to be slightly reduced. It was further found that the strength of the sintered materials derived from freeze granulated granules with a granule density of 30% was not influenced by the compaction pressure used. This can be compared with the materials prepared from the spray dried powder where the strength was reduced for lower compaction pressures, which may indicate that the spray dried granules were harder and a higher compaction pressure was required in order to reduce the size of the granule related defects compared to the freeze granulated materials. The difference in strength observed between the spray dried and the freeze granulated materials could be due to hard agglomerates present in the TZ3YSE powder, which could be formed during the powder

Table 1
Densities and the calculated linear shrinkage needed for the granules and the mould filled with granules to reach the green density obtained when compacted at 300 MPa.

Sample	Granule density (%)	Initial fill density (%)	Green density (%)	Linear shrinkage of the granule (%)	Linear shrinkage of the compact (%)	Shrinkage ratio (compact/granule)
20%	20	13	53	28	38	1.3
30%	28	19	53	19	30	1.6
40%	37	25	53	11	23	2.0
50%	47	29	54	5	19	3.8
TZ3YSEB	35	21	51	12	26	2.2

fabrication process when the powder was spray dried without binder. Other reasons could be due to the smaller granules in the spray dried powder compared to the freeze granulated material, which would reduce the size of the granule related defects.

4. Discussion

For a high strength ceramic component produced by compaction of granules, the type of defects may be divided into three different categories, powder related defects, granule related defects and surface related defects. The powder and the fabrication processes used will thus determine how each of these defect populations will influence the strength.

4.1. Powder related defects

Powder related defects such as large grains, hard agglomerates, impurity inclusions, etc. should be possible to be reduced by a careful control of the powder production in combination with a clean environment in the following production processes. However, even in well known and frequently used powders, dense fragments were found, which will cause inhomogeneities in the green body with respect to particle packing and density. As long as these fragments are small in size they may not influence the mechanical performance or the overall sintering shrinkage of a component. While on the microscopic level, the density variation caused by these fragments may result in the formation of micro pores that might influence the optical behaviour such as the translucency of zirconia ceramics used in dentistry.

4.2. Granule related defects

Even tough the freeze granulation process has been claimed to produce granules with a high degree of homogeneity[18] it was found that the formation of ice crystals during freezing could cause segregation and thereby induce the formation of porosity in the granules. Both the size of the granules and the solids loading of the suspension used were shown to influence the amount and distribution of ice crystals formed and thus the homogeneity of the granules. Spherical pores were found in both the spray dried and freeze granulated material. The presence of these pores were more frequent in the larger granules and was assumed to be due to air, introduced and entrapped in the droplets during spraying in the granulation process. Even if the porosity caused inhomogeneities in the granules, the porosity within the granules can be assumed to be smaller and less crucial for the strength compared to the larger inter granular defects formed during the mould filling. Since 1 g of powder corresponds to approximately

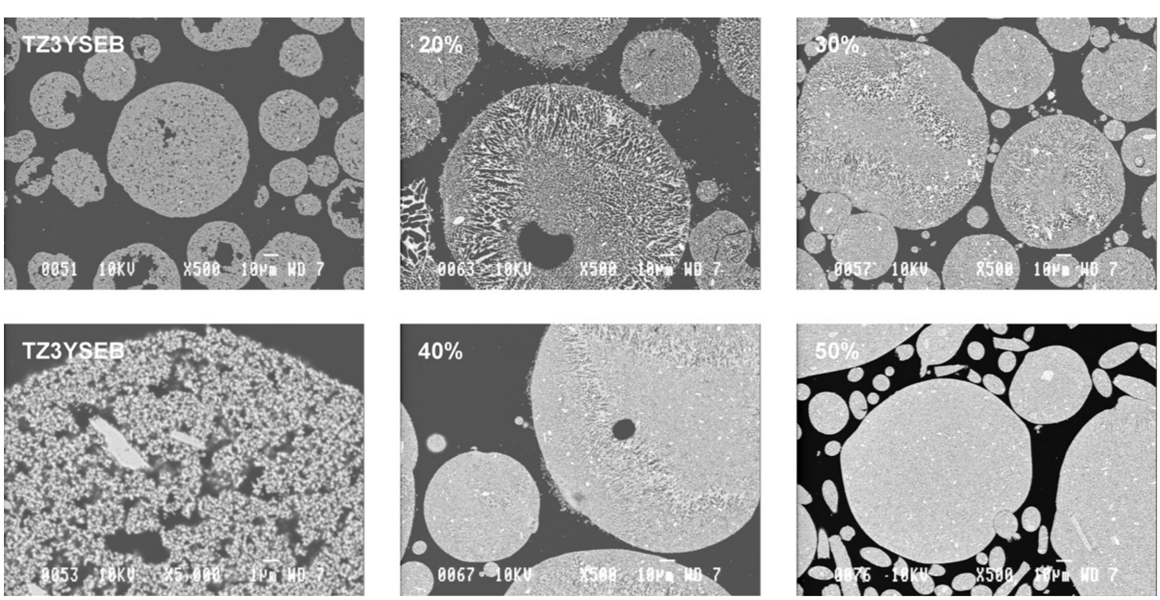

Fig. 5. Cross section of presintered granules, showing the internal microstructure of spray dried (TZ3YSEB) and freeze granulated materials with densities of 20, 30, 40 and 50%. The image with higher magnification shows an example of the dense fragments of zirconia found in both the TZ3YSEB and the TZ3YSE powders.

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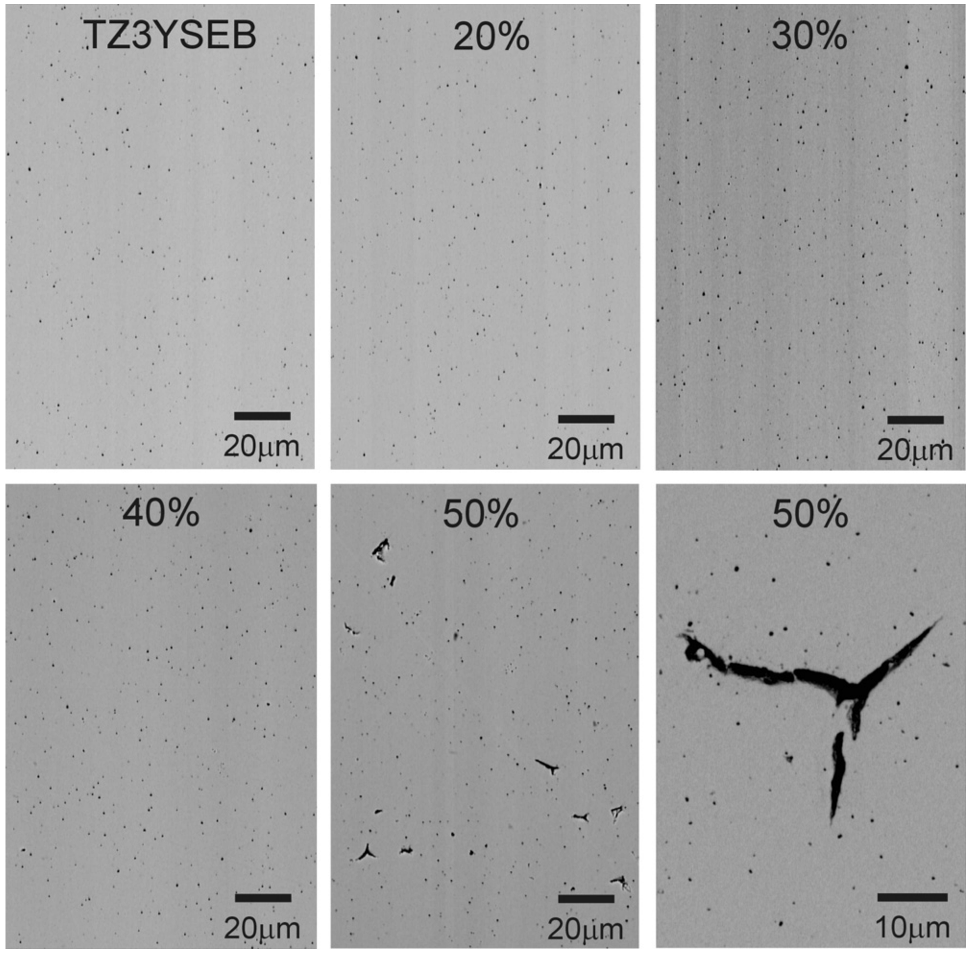

Fig. 6. Microstructure of the sintered materials studied.

1 million granules, the formations of granule stacking faults are likely to occur during the mould filling. The sizes of such inter granular defects caused by granular stacking faults could be more than hundred microns before compaction. Even if the size of these will be significantly reduced during compaction, narrow inter granular defects may still be present if the granules were not able to deform sufficiently to merge with the adjacent granules during compaction.

The size of the granule related defects can to some extent be reduced by the use of smaller granules. A certain granule size is however still needed in order to obtain a sufficient fluidity of the granules in order to facilitate the mould filling.[1] To further reduce the influence on strength from the granule induced defects requires granules with suitable characteristics for compaction. There is unfortunately very limited information available regarding desirable granule characteristics in order to reduce the granule related defects. A reason for this may be found in the complexity of the granule system during compaction. The granules do not only deform during compaction, their characteristics changes continuously as their density is increased and may thus vary both between different granules in the compact as well as within a single granule. Some studies of the compaction behaviour of granulated ceramic materials have been performed[10,13] and will mainly give information regarding the yield pressure and the overall green density as a function of pressure. Any direct information regarding the strength of the sintered material will not necessarily be obtained, since the strength limiting defects may not be found by density measurements.

Spray drying is the most common method to produce granules for compaction and has also been used in most of the

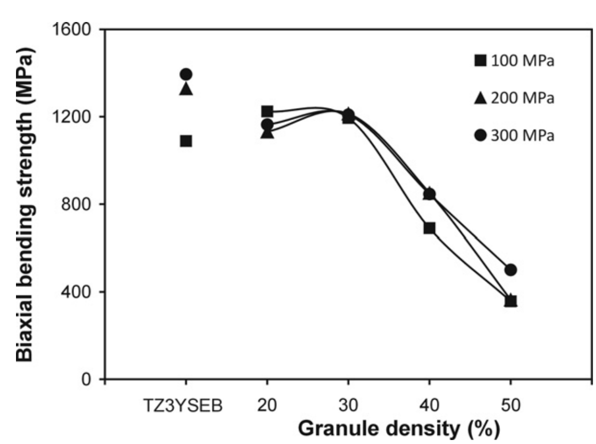

Fig. 7. Biaxial bending strength of the sintered materials studied.

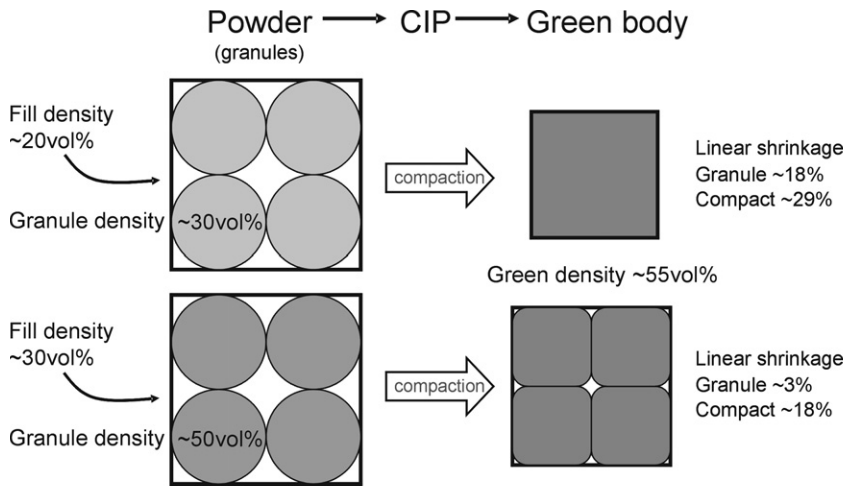

Fig. 8. Illustration of how the granule density and the fill density influence the linear shrinkage and compaction behaviour.

previous studies. A limitation with the technique is the ability to prepare a series of granules with designed characteristics. For research purposes, the use of freeze granulation becomes a suitable choice, especially when a series of granules with different densities are to be prepared. The freeze granulated material from the suspensions with high solids loadings gave granules with a high homogeneity and green density, which is normally desired to improve the densification performance during sintering. Even though the green density showed no indication of the presence of defects in the material prepared from granules with a density of 50%. The density and the strength of the sintered material were significantly reduced due to the large number of granule related defects. Density measurements of sintered material prepared from granules with a density of 40% showed no indication of an increased porosity caused by an additional defect population. The strength was however still reduced due to the same type of granule related defects, which indicates that granules with suitable characteristics for compaction are required in order to ensure a material with high strength and reliability.

The reduced strength and the presence of granule related defects may be explained by an inability of the granules to merge with the surrounding granules during compaction. A contribution to this behaviour could be due to the soft granules normally obtained by freeze granulation in combination with the soft binders used, thus the granule density may begin to increase at a lower compaction pressure. A granule with a high initial density may then approach the final green density at an earlier stage of the compaction where some inter granular cavities are still present (Table 1 and Fig. 8). As the density of the granule approaches the green density, the granules will become stiffer and more difficult to deform and may result in that the last inter granular cavities were not possible to be removed by deformation of the granules. The compaction of a granule can be compared to the compaction of the entire powder compact, which is the sum of the deformation and compaction of the granules. By a reduction of the granule density, the final green density will not be reached in the granules during the initial compaction and allow a larger granule deformation. The final stage of the compaction can then occur when the granules have been allowed to deformed sufficiently in order to remove the inter granular defects and merge completely with the surrounding granules. This was found to occur when the density of the granules were reduced to 20 or 30%. Sintered materials with high strength could then be obtained even though the granules used had a lot of internal porosity.

The results from the work presented give some additional information regarding the desired granule characteristics that has to be considered in order to reduce the granule related defects. It should however be remembered that the optimised granule density will be influenced by several other properties such as the fill density, deformability of the granule, compaction behaviour of the granule and the compact as well as the green density. These granule characteristics depend further on the powder, binder, suspension and granulation technique used.

5. Conclusion

In addition to the pores and powder related inhomogeneities found in all granules, the freeze granulated material had also inhomogeneities caused by the formation of ice crystals. The presence of these inhomogeneities increased with the granule size and the water content and the freeze granulated materials was thus found not to be as homogeneous as often claimed.

The density of the prepared granules influenced the compaction behaviour, formation of inter granular defects as well as the strength of the sintered materials. A high green density or sintered density was further shown not to be sufficient in order to achieve a high strength ceramic since the density was not necessarily influenced by the granule related defects. It was further shown that the inhomogeneities related to the porosity in the granules were not the main reason for the reduction of the strength.

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