Energy Efficiency during Production of Ceramics

Introduction

About 1000 PJ (1 PJ = 10^{15} J) per year are consumed for heat treatment processes with a maximum temperature above 1000 °C in Germany [1]. This corresponds to 7 % of the total primary energy demand of Germany. It is assumed that other developed countries spend a similarly high contribution of primary energy for heating processes.

The ceramic industry is one of the most energy intensive branches and consumes more than one percent of primary energy in Germany. Energy cost amounts 7,3 % of gross value added in the glass, ceramics and industrial minerals branch [2]. The improvement of energy efficiency is currently driven by cost reduction. But other reasons for a careful minimization of energy consumption gain more importance: the CO_2 footprint of products influences the decision of end consumers to purchase. Moreover, the sustainability of companies affects their image.

Recently the joint project ENITEC was finished after three years. Results were presented in a workshop in Bayreuth [3] and a final report [4]. It was demonstrated that energy can be saved during ceramic production by improving composition and forming processes of green compacts, drying parameters, heat treatment and finishing processes.

A very important contribution comes from the optimization of the debinding and sintering process. It was shown, that significant energy savings can be achieved without loss of product quality. In situ measurement methods and computer simulation, based on the in situ data, play an important role in well aimed process optimization. These methods were already presented in a previous article in the current journal [5].

Since the ceramic production chain is rather long, many process parameters have to be carefully optimized in order to achieve the best product quality with lowest energy consumption. A significant reduction of complexity can be achieved when the quality of the green compacts is evaluated before firing

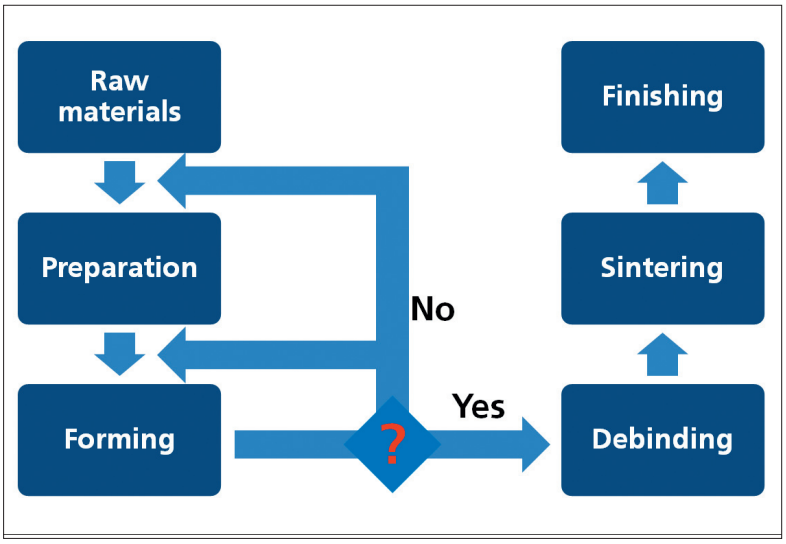

Fig. 1 Reduction of complexity in ceramic process development by green compact evaluation

(Fig. 1). If this quality is insufficient the previous process steps of raw material selection, preparation and forming have to be improved.

Green compacts need excellent homogeneity on the micro-, meso- and macro scale. Reasons are:

- Micro scale: the ceramic particles have to be arranged homogenously on a scale smaller than 20 µm. Otherwise preferential sintering of particles in a locally denser configuration will occur. Agglomerates are formed, reaching final density much earlier than the residual structure. Grain growth sets in within the agglomerates, which often deteriorates the mechanical properties of the ceramics. In addition the large pores which form between the agglomerates need very high thermal energy to be eliminated by further sintering.
- Meso scale: microstructure variations on a scale of 20–100 µm have to be eliminated as well. Frequently, this is the size range of defects which control the strength of the ceramic parts. Already few defects in the size of 20–100 µm per cubic centimeter can significantly deteriorate strength and reliability of ceramics. Elimination of these defects enables material-saving designs and reduces waste. In either case energy savings are obtained with ceramic production.
- Macro scale: the green density has to be in a very small range within the entire component. Otherwise an uneven shrinkage occurs during sintering causing deformation and loss of near net shape performance. This leads to the exceedance of dimensional tolerances or increasing finishing cost. Since the final density is nearly constant after sintering, the deviation is roughly proportional to the variation of green density. E.g., a 1 % increase of green density leads to an increase of shrinkage of 100 µm in a component of 10 mm diameter. So green density variations within a component or between different components have to be carefully avoided.

In this article methods are discussed which enable a careful evaluation of green compacts on the micro-, meso- and macro scale.

These methods have been developed and tested within the project ENITEC. Experimental effort, accura-

Friedrich Raether
Fraunhofer-Institut für Silicatforschung
95448 Bayreuth, Germany

E-mail:
friedrich.raether@isc.fraunhofer.de
www.htl.fraunhofer.de

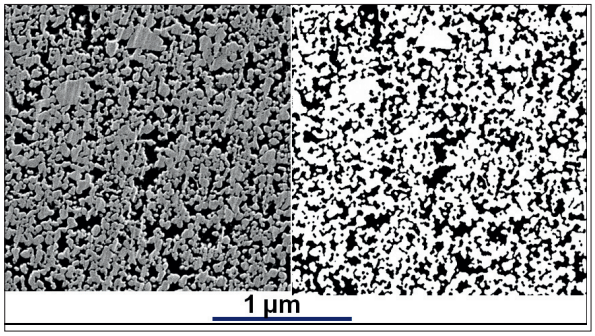

Fig. 2 SEM image of a green sample after CSP preparation (l.) and corresponding binary image (r.)

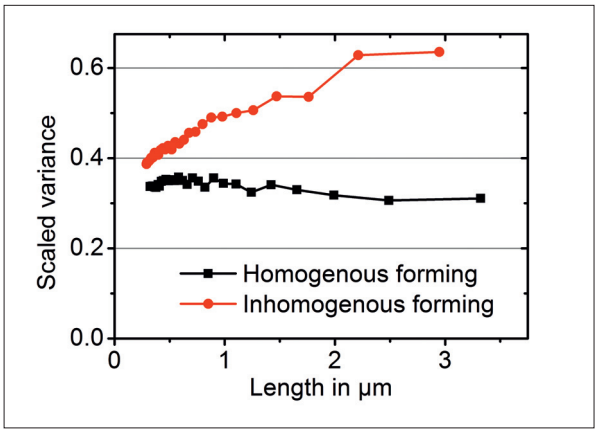

Fig. 3 Variance in binary SEM images using different forming parameters

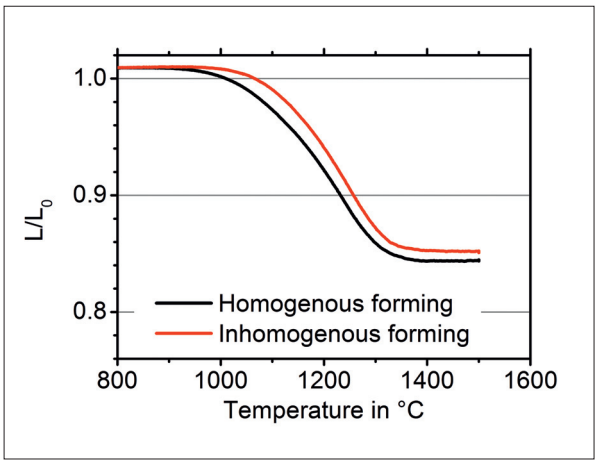

Fig. 4 Sintering shrinkage L/L0 of the green samples shown in Fig. 3

cy and field of application of the methods will be presented.

Evaluation methods for green compact quality

Micro scale

Particle size of most technical ceramics is in the range of 0,1–10 µm. In this size range, Scanning Electron Microscopy (SEM) is the most appropriate method for imaging of microstructure. Planar cuts through the structure are required for a quantitative evaluation of homogeneity. With green compacts, the preparation of planar surfaces by traditional grinding and polishing is not applicable because they are too weak. After a careful thermal treatment at temperatures below the onset of sintering, strength is improved by surface diffusion without affecting particle arrangement.

Then grinding and polishing can be successful but particle break off during machining can cause preparation artifacts. In contrast, ion beam techniques are universally applicable to prepare planar cuts.

Especially suitable is the so called Cross Section Polishing (CSP). An argon ion beam hits the sample surface parallel to the planar cut and produces a planar area of about 100 x 100 µm². Since the sample is not subjected to any forces, particle break out is completely avoided. Yet, the preparation of a planar cut by CSP technique requires about 5 h. Afterwards a SEM imaging technique, which provides a very high contrast between pores and particles, has been used (Fig. 2).

In-house software for processing and analysis of these SEM images has been developed. In a first step brightness gradients are removed on a scale much larger than the particle size and then the images are binarised (Fig. 2).

The binary images are divided in subsections and the pore fraction in each subsection is automatically determined. The variance of this pore fraction is used as measure for micro scale homogeneity. The variance depends on the size of the subsections. Therefore, it is scaled by the variance obtained from a random distribution of pores.

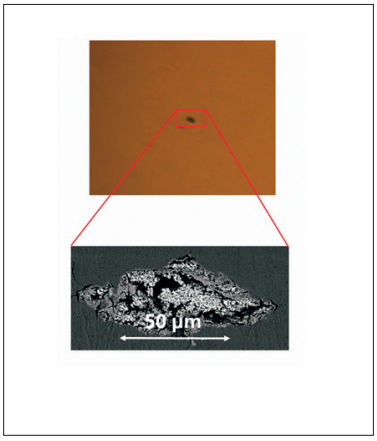

Fig. 5 Defect in a green compact which was infiltrated with immersion liquid (top) and SEM image of the defect prepared by CSP technique (bottom)

Fig. 3 shows a variance analysis of an alumina green compact. Although the green density was similar, a clear difference between different forming parameters can be seen.

Fig. 4 demonstrates the higher sintering activity of the more homogenous green sample emphasizing the benefits of evenly distributed particles on the micro scale.

The experimental effort for CSP preparation, SEM imaging and variance analysis is comparatively high in spite of automatic image analysis. Alternatively, micro-scale homogeneity can be evaluated indirectly by in situ measuring sintering shrinkage. The experimental effort of the in situ measurement is smaller but a unique interpretation of the measurements requires a narrow process window (identical raw materials, compositions etc.).

Meso scale

Computed tomography (CT) is a versatile tool to detect microstructure defects in a size range of 20–100 µm. It provides a 3D image of the green compact with a resolution of some microns. The time required for measuring a CT image is between 30 min and some hours. Usually the manufactures of ceramics cannot dispose of CT devices due to their high cost.

Therefore an alternative method was tested to detect defects on the meso scale which needs small investment. It is based on an immersion liquid which has the same index of refraction as the ceramics. The immersion method can only be used if the ceramics consists of a single inorganic phase and if this phase is optically isotropic. The index of refraction of the immersion liquid has to be matched accurately to the index of refraction of the ceramics. For that, organic liquids with different indices of refraction are mixed in the appropriate ratio to obtain the target index.

After infiltration of the immersion liquid the compacts become optically transparent because light in the visible wave length range is only weakly absorbed in most ceramics and the immersion liquid eliminates scattering effects.

Defects which are located within the infiltrated volume can be detected by their different optical density.

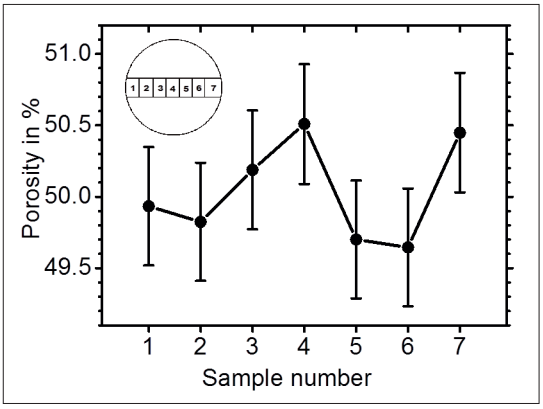

Fig. 6 Porosity derived by Archimedes method in small samples extracted from a cylindrical green compact (sample position is indicated in the insert)

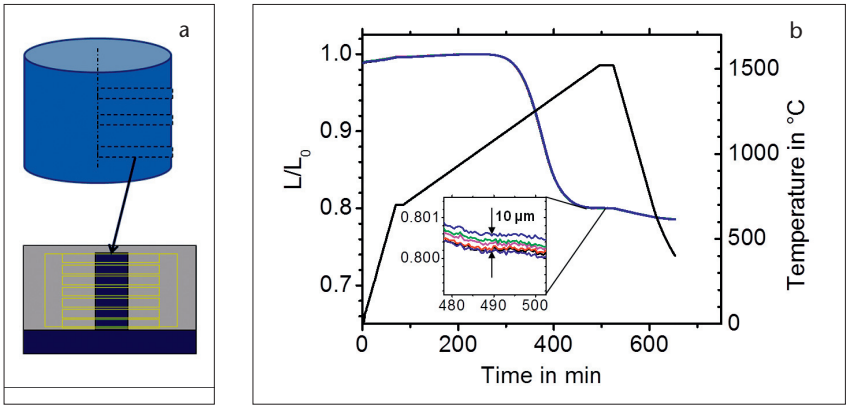

Fig. 7 a–b Extraction of small samples from a larger cylindrical green part and measuring windows used during sintering(a), change of sample width L/L0 within measuring windows (b) (the magnification shows the spread between individual windows)

Small defects are identified using a light microscope (Fig. 5). Defect density can be evaluated statistically. Moreover, the area of a defect can be selected for target preparation, e.g. by CSP technique (compare previous section) and SEM analysis (Fig. 5). This allows conclusions about possible sources of impurities. The immersion method can be modified to detect large pores or cracks in the compacts.

For that, a small part of the immersion liquid is removed after infiltration. This causes a redistribution of immersion liquid within the compact depleting the larger pores and cracks whereas small pores are still filled completely with the liquid. So light is scattered at the depleted structures and they become visible in the light microscope [4].

The effort for using the immersion method is small – once an appropriate immersion liquid has been identified. It has to be applied in a fume cupboard because harmful vapors from the organic solvents occur.

Macro scale

In principle various methods are available to measure the distribution of porosity on the component size scale:

- Small samples can be extracted from the green parts and the bulk density of these samples can be measured either by the Archimedes method or by volume and weight measurement. From the bulk density, porosity can be easily calculated if the true density of the ceramics is known. Otherwise it can be measured using Archimedes method or He pycnometry.
- From X-ray absorption local density can be measured and porosity can be calculated. Either radiography or CT is available to obtain planar or 3d distribution of porosity.
- The shape distortion after sintering is related to the porosity distribution within the green parts. So indirectly sintering distortion can be used to detect uneven porosity.

In the ENITEC project these methods have been compared with regard to effort and accuracy. Cylindrical zirconia compacts with a diameter of 20 mm or 70 mm formed by cold isostatic pressing were selected for the tests. The density measurement of small samples extracted from the compacts by *Archimedes* or volume measurement required no expensive equipment.

Yet, the accuracy of the measurements was limited to ±0,5 % even if they were repeated several times (Fig. 6). X-ray methods are significantly more expensive. Moreover, it turned out, that the accuracy of the X-ray methods was rather low – especially close to the surface of the green parts.

This was attributed to scattering effects. It limits the use of X-ray methods because large density gradients are expected in the surface zone of green compacts. For measuring sintering distortion, test samples, either disks or cylindrical rods, were extracted from the green parts. Disks were cut with their symmetry axis parallel to the symmetry axis of the cylindrical compact.

Rods, with 20 mm diameter, were extracted using hollow drills with their symmetry axis perpendicular to the green part (Fig. 7a). With the sintered disks sintering distortion was measured at its faces using confocal microscopy whereas sintering shrinkage of the rods was measured at the lateral surface using thermo optical methods [6]. For the later 5 to 10 measuring windows were defined – evenly distributed over the length of the sample (compare Fig. 7a).

The change of the sample width was recorded in situ within the measuring windows during sintering (Fig. 7b).

Window position was adjusted to follow exactly the shrinkage of the sample. Total shrinkage was extracted from the width of the individual windows at 900 °C during heating and cooling of the samples before and after sintering. The resolution of the thermo-optical method was about 10 µm leading to an accuracy of ±0,3 % in porosity measurement. The resolution of the confocal microscopy was even better, within few microns, but interpretation was more difficult because deformation at the opposing faces was not well defined.

It was considered that measuring sintering distortion is the most accurate method to determine porosity distribution in green compacts. The samples used have to be extracted from the green compact in a simple geometry which reflects possible density gradients in the part.

Conclusions and outlook

The careful evaluation of green compact homogeneity contributes to the identification of process parameters which lead to lower firing cost, less waste and better near net shape performance of ceramics.

Finishing could be completely eliminated for small zirconia parts after the macro scale homogeneity of the green compacts had been ensured (Fig. 8). The energy saving was 24 % for a dental implant and 42 % for an

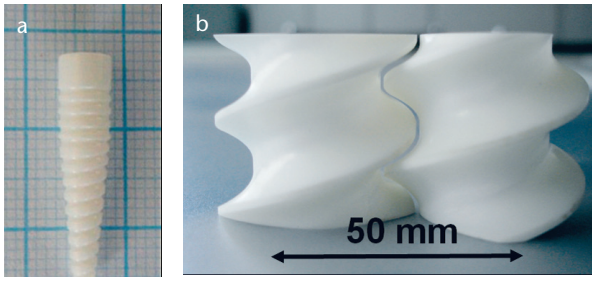

Fig. 8 a–b Dental implant (a) and extruder screw made of zirconia ceramics (b) (Source: BCE Special ceramics GmbH)

extruder screw, respectively [4]. Other important energy savings are obtained by a careful optimization of firing conditions including the design of furnaces and firing stacks [4].

Recently a large project called ENERTHERM was started at Fraunhofer HTL [7]. In ENERTHERM the energy efficiency of industrial high temperature processes shall be improved in a holistic approach considering product quality, heat treatment parameters, high temperature materials and furnace equipment. HTL will closely cooperate with material manufacturers and furnace companies in this project and present results in a further workshop in 2015.

Acknowledgement

The project ENITEC was funded by the *German Federal Ministry of Education and Research (BMBF)* with the assistance of the *Project Management Agency Karlsruhe (PTKA)*. The author gratefully acknowledges the help of *R. Herborn, J. Baber, M. Römer, H.J. Seel* and *N. Henning* with the measurements and the fruitful cooperation with the project partners *CeramTec, BCE, Lapp, Eisenmann, FCT* and *Fraunhofer IWM*.

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