Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 29 (2009) 2691–2696
www.elsevier.com/locate/jeurceramsoc

Reduction of the porcelain firing temperature by preparation of the raw materials

E. Kivitz [a,*], B. Palm [a], J.G. Heinrich [a], J. Blumm [b], G. Kolb [c]

[a] *Clausthal University of Technology, Institute of Nonmetallic Materials, 38678 Clausthal-Zellerfeld, Germany*
[b] *Netzsch Gerätebau GmbH, Selb, Germany*
[c] *Netzsch Feinmahltechnik GmbH, Selb, Germany*

Received 27 October 2008; received in revised form 19 March 2009; accepted 30 March 2009
Available online 29 April 2009

Abstract

An innovative way of reduction of firing temperature of porcelain tableware is reached by preparation of raw materials down to submicron- and nanoscaled powder for higher reactivity. In this study a common slurry was ground in an agitator ball mill from $d_{50} = 5.0$ μm to 0.9 μm, green bodies were prepared, and glost firing was simulated in a dilatometer. The sintering temperature has been decreased by approximately 180 °C. A reflection between ball mill and agitator ball mill regarding the grinding cost shows no difference which means that the ball mill could be replaced. The energy consumption during the grinding process will be discussed regarding to energy savings resulting from reduced firing temperature. Furthermore a comparison between experimental and literature data will be done. The effect of grinding of raw material is finally evaluated concerning sintering behaviour and material properties.

Keywords: Sintering; Porcelain; Milling; Energy saving

1. Introduction

For keeping up competitive capability and high quality the porcelain industry needs new innovations which also require a change in firing process, sintering time, and energy cost.[1–5] First improvements were achieved with introduction of the fast firing process in the past years.[4,6–12] Here for example time for glost firing was reduced from 20–25 h (1965) to 8–12 h (cold–cold) and in some times to approximately 5 h (2000).[10] Second improvements can be the change to the single firing technology[13] which is rarely used at the moment for the production of tableware. Another promising idea to decrease energy demand is the reduction of temperature during glost firing. A reduction of energy consumption implies a decline of energy cost and a lower environmental pollution because of less CO_2 emission. An innovative way of reduction of firing temperature can be reached by change of batch composition[5,14–18] or by preparation of raw material up to submicron- and nanoscaled powder for higher reactivity. The use of conventional ball mills for mass preparation is state of the art in porcelain tableware industries. It is expected that the use of agitator ball mills results in a submicron particle size distribution[19,20] with influence on sintering temperature, shrinkage behaviour, microstructure and related properties. The reduction of sintering temperature leads to energy savings which have to be compared to the energy consumption of the agitator ball mill. The comparison of the phase composition and pore size distribution of agitator ball milled with conventional ball milled materials is a further issue of this paper.

2. Experimental procedures

The slurry used in this work is an established porcelain slurry for pressure casting, consisting of kaolin/clay (36.85 wt.%), feldspar (12.73 wt.%), quartz (17.42 wt.%), water (33 wt.%) and an industrial commercial deflocculant (Formsil D), that was conventionally batch prepared by the industry. The chemical analysis of the starting material is given in Table 1 (XRF, X-ray fluorescence spectroscopy, X-ray spectrometer Phillips PW 1410) and Table 2 (XRD, X-ray diffraction analysis, Diffraktometer Siemens D5000 Kristalloflex).

* Corresponding author. Tel.: +49 5323722384; fax: +49 5323723119.
E-mail address: ellen.kivitz@tu-clausthal.de (E. Kivitz).

0955-2219/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2009.03.029

Table 1
Single XRF determination of raw material (LOI = loss on ignition).

	Slurry unground	Slurry ground for 720 min
SiO_2 (%)	62.44 ± 0.3	62.17 ± 0.3
Al_2O_3 (%)	25.40 ± 0.2	24.68 ± 0.2
K_2O (%)	3.55 ± 0.04	3.37 ± 0.04
Fe_2O_3 (%)	0.45 ± 0.02	0.41 ± 0.02
Na_2O (%)	0.44 ± 0.03	0.44 ± 0.03
CaO (%)	0.24 ± 0.04	0.15 ± 0.04
SO_3 (%)	0.11	0.00
TiO_2 (%)	0.10 ± 0.03	0.10 ± 0.03
MgO (%)	0.09 ± 0.03	0.07 ± 0.03
P_2O_5 (%)	0.09	0.09
Trace elements %	0.09	0.04
LOI (%)	6.85	7.82

Table 2
Single XRD determination of raw material and sintered bodies, equipment accuracy ±2 wt.%.

Powder	Phase in wt.% ±2%				
	Feldspar	Kaolin/clay	Quartz	Mullite	Glassy phase
Raw material	19	55	26	–	–
Unground, sintered	–	–	2	43	55
Ground for 720 min, sintered	–	–	8	39	53

Half of the slurry was used as reference, which means no further grinding took place. The other half was ground for 720 min in an agitator ball mill (Netzsch RWKM LME 1) with Si_3N_4 grinding balls (diameter = 1 mm) in a Si_3N_4 cylinder. This shows hardly any abrasion (see Table 1). Measurements of particle size distribution were accomplished controlling the progress of the grinding process using laser diffraction (Coulter LS 230).

Both unground and ground slurry were spray-dried at 200 °C (Mobile Minor) and cuboid samples were prepared by cold isostatic pressing (System Uhde-Lohrengel). The following conditions were used: pressure of 200 MPa and dwell time of 2 min. Density of green bodies was measured using a solid pycnometer (GeoPyc 1360). The samples were biscuit fired in an electric laboratory kiln at 900 °C in air with a dwell time of 15 min.

After determination of density of biscuit fired bodies with solid pycnometer glost firing in air was simulated in dilatometers (Netzsch DIL 402 PC). The relative linear length change was measured up to 1300 °C for samples prepared from ground material or 1500 °C for bodies from unground material. Heating was carried out with rates of 5 K/min, dwell time was 15 min at maximum temperatures and cooling rates were also 5 K/min.

Density of sintered bodies was measured using solid pycnometer. To gain insight into microstructure as well as pore sizes and pore distributions of the differently prepared samples light microscopy (LM) and scanning electron microscopy (SEM) were applied (Zeiss Axiophot and CamScan CS4). The open porosity was measured by mercury porosimetry (Porotec Pascal 240). X-ray diffraction analysis of the sintered samples (XRD, Diffraktometer Siemens D5000 Kristalloflex) finished up the study.

3. Results and discussion

Based on the fact that there was no information about the milling behaviour of porcelain slurries in the ball mill used for these experiments, the particle size distribution was measured in regular time periods. The d_{90}-, d_{50}- and d_{10}-values in dependence of the milling time are given in Fig. 1.

As expected the change of particle size is exponential and it is obvious that the decrease of the d_{90}-value is higher than the decrease of the d_{50}-value. The change of the d_{10}-value is only minimal because of the natural fineness of the kaolin/clay particles. Therefore further grinding will not produce finer particles,

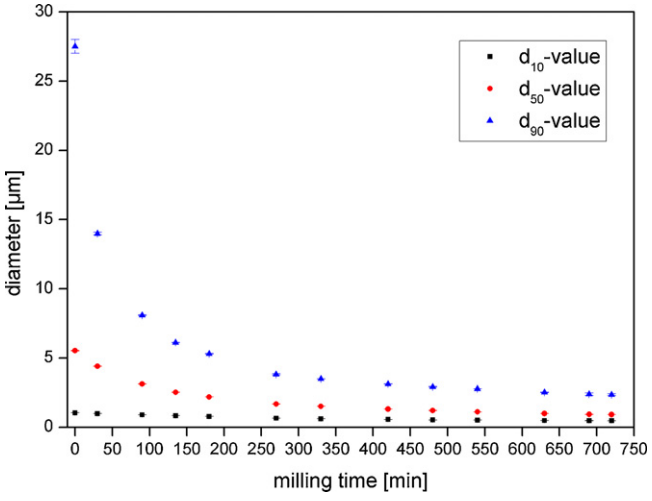

Fig. 1. Reduction of d-values in dependence of milling time.

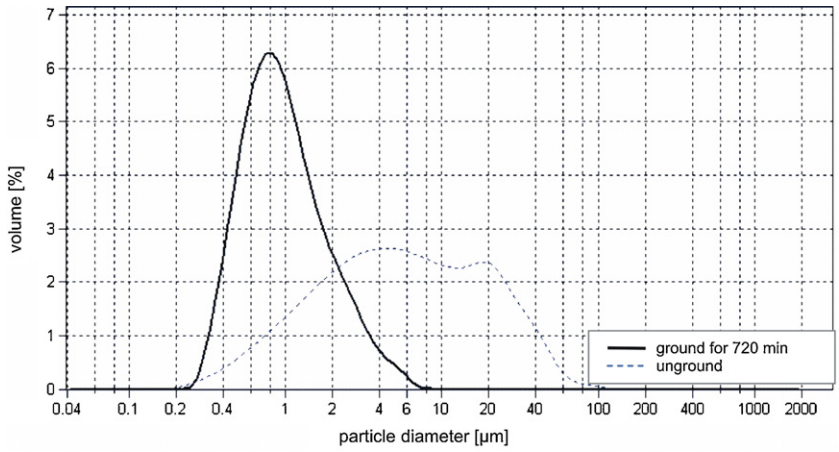

Fig. 2. Comparison of particle size distribution before and after grinding.

but will increase the energy consumption.[21] For these reasons grinding was terminated after 720 min.

A difference in particle size distribution between unground and ground material (Fig. 2) was clearly verified. The d_{50} value of solids in the unground raw material is 5.0 ± 0.51 μm whereas the d_{50} value of ground solids is 0.90 ± 0.01 μm. As the particle size decreases the distribution of particle sizes changes from bimodal to monomodal and narrows. From the sintering point of view a bimodal distribution is better than a monomodal distribution at the same d_{50} value.[22] In this paper the effect of the different d_{50} values on sintering performance and material properties (density, porosity, microstructure and phase composition) has to be determined.

Because of smaller particles the ground material has a larger surface area and consequently an improved sintering behaviour,[23] which counterbalances the disadvantage of a monomodal distribution. The consequences can be seen in the results later discussed in this paper.

In industrial production porcelain tableware is mainly fired twice – biscuit fired at about 900 °C and glost fired at about 1450 °C. Sintering temperatures set for these experiments were chosen after discussion with porcelain industry (see acknowledgement). Both firing steps were done with samples from unground and ground material. Due to the fact that shrinkage takes place in glost firing, this firing step was made in a dilatometer and relative linear length change was detected (Fig. 3). In this context one has to pay attention that sintering behaviour in dilatometers cannot be compared exactly to sintering in industrial equipment because of different sintering conditions (rates and atmospheres) and different sample geometries.

A clear difference between unground and ground material can be seen. The unground porcelain material (dotted line in Fig. 3) shows three sintering steps and has its maximal shrinkage at 1422 °C with 6.6%, whereas the ground material (solid line in Fig. 3) shows two sintering steps and already reaches the maximal shrinkage at 1244 °C with 11.4%. That means sintering temperature can be decreased by about 180 °C after grinding of raw material and the result will still be a dense sintered article. Due to the fact that small particles enhance the quantity of contact points between the single particles in the cold isostatic pressed green bodies, sintering is accelerated.[23] By closer examination of the second sintering step it is evident that the start of sintering is shifted to lower temperatures about 33 °C after grinding. A similar behaviour concerning the onset sintering temperature was already reported for alumina by Roosen and Bowen.[24]

The difference in relative linear length change (6.6% compared to 11.4%) suggests differences in number, size and distribution of pores and therefore in density. To confirm these presumptions, measurements of density and light microscopy were done (Figs. 4 and 5).

The green density of pressed samples from unground material is higher than the green density of ground material (2.09 g/cm^3 compared to 1.8 g/cm^3). This is based on densification behaviour during isostatic pressing,[25] because monomodal particle distribution results in lower packing density compared to bimodal particle distribution. Another problem is worse venting of finer material during isostatic pressing[26] which results in inferior green densities of ground material compared to unground material. After sintering densities are comparable (2.52 g/cm^3

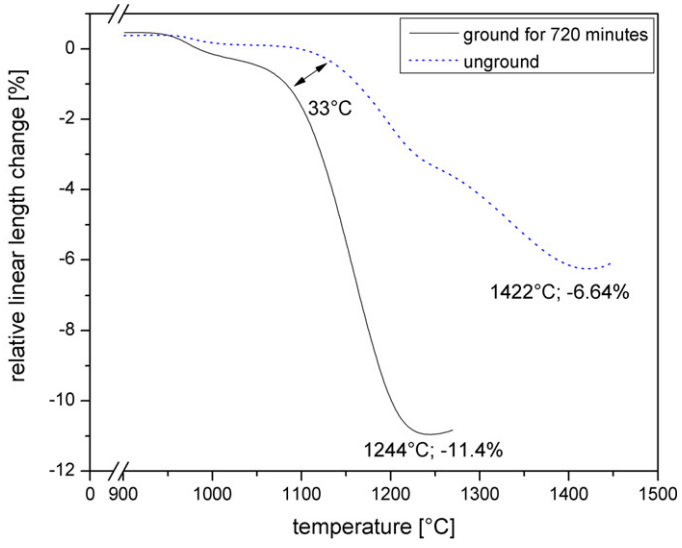

Fig. 3. Effect of grinding on sintering behaviour of porcelain samples.

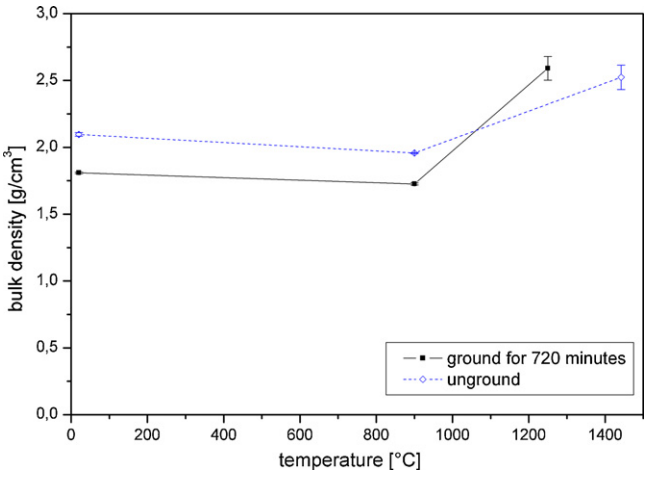

Fig. 4. Effect of grinding on density of raw (0 °C), biscuit fired (900 °C) and sintered bodies (1250/1450 °C).

unground compared to 2.59 g/cm^3 ground). Density of bodies from ground material increases stronger because the green body has a higher porosity. The adjustment to a lower d_{50} value compensates for the slower sintering behaviour of the monomodal particle size distribution. Measured densities of

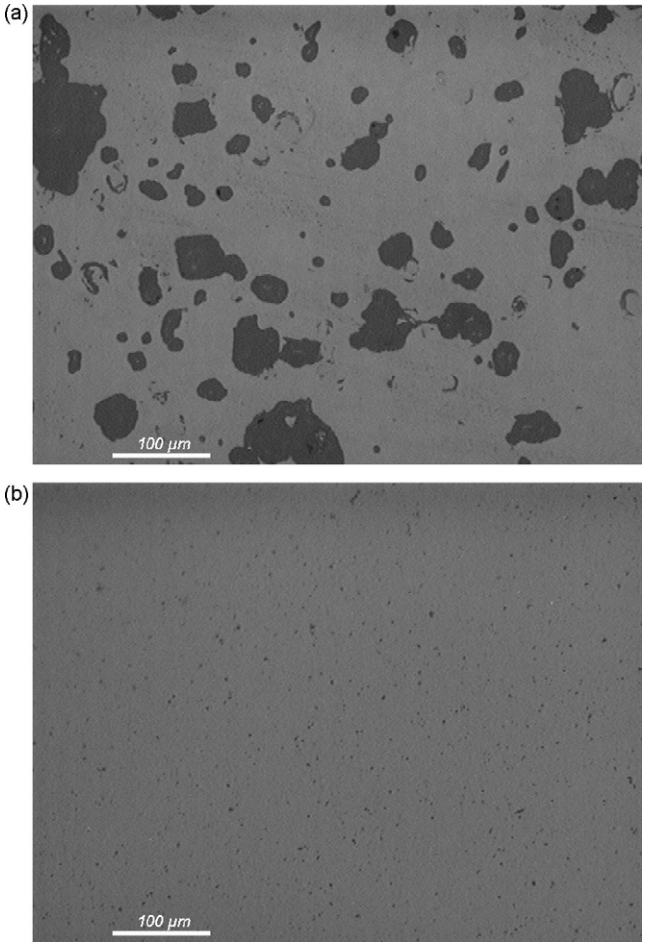

Fig. 5. Effect of grinding on porosity of sintered bodies (a) unground, (b) ground for 720 min.

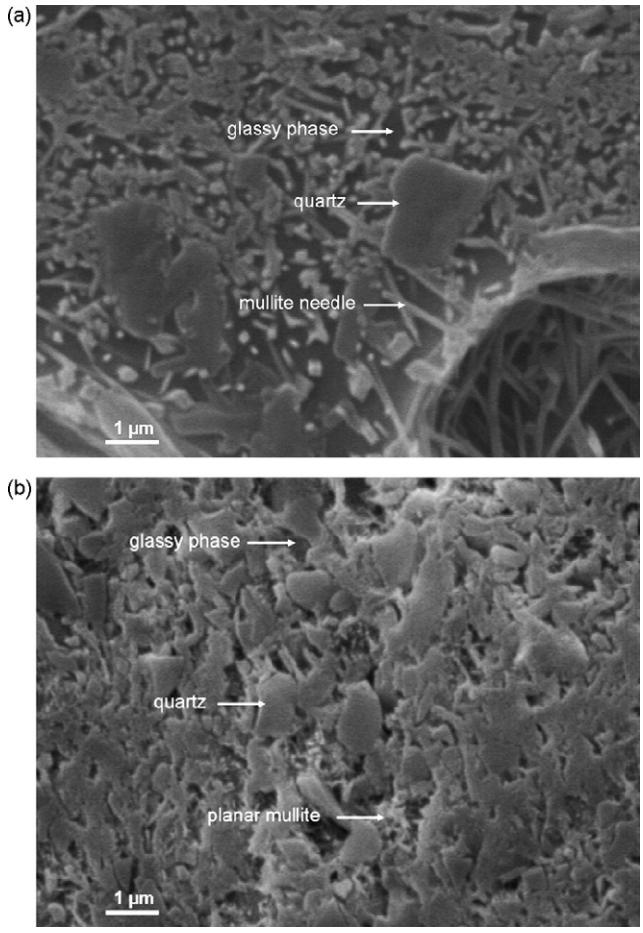

Fig. 6. Scanning electron micrographs of polished and chemically etched (HF 10 vol.% 1 min) surfaces. Effect of grinding on microstructure of sintered bodies (a) unground, (b) ground for 720 min.

sintered specimen are similar to densities of sintered tableware. The micrographs show much smaller pores for the ground material at constant total porosity compared to the unground material (Fig. 5). This reduction of pore size probably leads to an increased strength which has not been investigated in this paper.

The micrograph of sintered unground sample (Fig. 5a) shows an irregular texture with wide range of pores sizes. In comparison the picture of sintered ground sample (Fig. 5b) shows mainly pores smaller than 5 μm. Measurements of pore size distribution by mercury porosimetry confirm that the unground sample primarily exhibits pores around 10 μm, whereas the ground sample primarily exhibits pores around 3 μm. The unground sample has a higher total open pore volume (7.5%) than the ground sample (0.3%).

The analysis of microstructure with scanning electron microscope (see Fig. 6) presents grains of quartz and mullite in needle form for sintered unground material and mullite in planar form for sintered ground material. This difference can be explained by the different sintering temperatures for the samples: primary planar mullite is developed from metakaolin at temperatures between 950 °C and 1000 °C and secondary needle mullite by crystallization from liquid phase above 1200 °C.[27,28]

Table 3
Specific energy consumption at different sintering temperatures [private communication, Friedherz Becker, Riedhammer GmbH].

Parameter	Material					
	Sanitary ware				Porcelain	
	Shuttle kiln		Shuttle kiln with car conveyance		Rapid firing kiln	
Sintering temperature (°C)	1260	1160	1260	1160	1364	1264
Specific energy consumption (kWh/t)	1826	1550 (15%)	1466	1263 (14%)	3253	2963 (9%)

To complete the evaluation of samples from unground and ground material the results of X-ray diffraction (Riedfeld analysis) are shown in Table 2 and the X-ray patterns in Fig. 7.

The porcelain raw material used consists of kaolin/clay, feldspar, quartz, dispersed in water with deflocculant. Sintered samples consist of quartz (Q in Fig. 7), mullite (M in Fig. 7) and glassy phase. The XRD diagrams (Fig. 7) show almost no difference between sintered samples from ground and unground material except for the differing characteristic of the peak at about 31°. Chemical composition is almost the same for both samples because variance of measurement method is ±2 wt.%. The mullite content can be expected to increase due to the increased reactivity of smaller particles after grinding. This would lead to a higher mullite content in the samples from ground material, which could not be observed. Besides the influence of particle size on mullite formation time and temperature must also be considered. Because of a decrease in sintering temperature (from 1500 °C to 1300 °C) and sintering time (from 311 min to 271 min) less mullite is generated. This illustrates that the influence of sintering temperature on mullite formation is higher than the effect of grinding.

The analysis of the results shows that it would be possible to reduce the sintering temperature and therefore the energy consumption during sintering by grinding the raw material. To transfer these results to industrial application it is necessary to compare energy input by milling and energy saving with reduced sintering temperature.

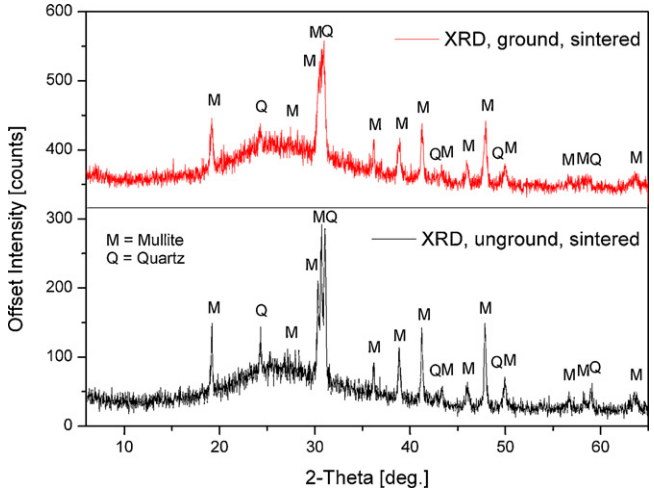

Fig. 7. Single XRD determination of sintered bodies from ground (top) and unground (bottom) material, equipment accuracy ±2 wt.%.

Becker (see acknowledgement) investigated specific energy consumptions of three different kiln types when firing temperatures are reduced by 100 °C (Table 3). The percentage reduction of energy consumption for reducing the sintering temperature about 100 °C depends on the kiln and ranges between 9% and 15%. This implies an energy saving of approximately 270 kWh/t for a temperature reduction of 100 °C. Basically energy saving is higher in shuttle kilns than in tunnel kilns.

Literature[29,30] gives information about the energy input when grinding with agitator ball mills. Stehr determined the specific energy consumption between 3 kWh/t and 600 kWh/t for grinding Al_2O_3 slurries (from 40 μm to 0.6 μm) in agitator ball mills. A comparison between Stehr/Stadler and Becker points out a similar energy input for grinding and energy saving for reducing sintering temperature. To make profit with milling an optimization is needed and possible with[31]:

- reduction of grinding time,
- only grinding of hard materials (feldspar, quartz),
- optimization of grinding body size and
- optimization of milling type.

Actually ball mills are used for mass preparation in porcelain industry. For tableware masses they can be replaced by agitator ball mills that have a better efficiency than ball mills.

4. Conclusion

The experiments conducted show that it is possible to reduce sintering temperature by grinding raw materials, that the energy input for grinding can be compensated by the energy saving during firing, and that agitator ball mills can replace conventional ball mills in porcelain tableware industries.

Further experiments in industrial kilns are necessary to control shrinkage. Due to the fact that total shrinkage increases, replacement of the moulds in use would be necessary. This would lead to high costs for the industry which is not realizable. For further use of the present moulds the total shrinkage must be adapted to actual shrinkage values by optimizing the temperature-time-program with a kinetic program based on thermal conductivity measurements. In addition the change of morphology from needle to planar mullite and its influence on the properties of industrial products needs to be analyzed.

Practical implementation can only be reached after optimizing the milling which includes the mill type and choosing a more efficient milling process. After all optimizations a new

comparison of energy input and energy output under serial conditions has to be done.

Acknowledgements

The authors thank IMERYS Tableware for providing slurries for the grinding experiment. They also thank Friedherz Becker for the calculation of energy savings.

References

1. Küsel, O. C., The position of fine and engineering ceramic industries (Die Situation der Industrie der Feinkeramik und der Technischen Keramik), cfi/Ber. *DKG*, 2001, **78**(4), 23–26.
2. Reh, H., The position of the European ceramic industry in the proceeding globalization process (Die Position der europäischen Keramikindustrie im fortschreitenden Globalisierungsprozeß), cfi/Ber. *DKG*, 2005, **82**(1/2), 24–26 [(3), 27–29].
3. Reh, H., Turning point in the ceramic industry (Zäsur in der Keramikindustrie), cfi/Ber. *DKG*, 2004, **81**(6/7), 17–21.
4. Bittner, H. G. and Bartusch, R., Adjustment of binding materials of isostatic pressed articles for fast firing (Abstimmung der Bindertypen isostatisch gepresster Artikel für den Schnellbrand), cfi/Ber. *DKG*, 1993, **70**(9), 455–462.
5. Bartusch, R., Energy saving potentials in the ceramic industry. *Interceram*, 2004, **53**(5), 312–316.
6. Sladek, R., The fast firing process, a pioneer technique for whiteware, cfi/Ber. *DKG*, 1989, **66**(5/6), 220–226.
7. Sladek, R., Actual state of the art of sintering of sanitary ware (Gegenwärtiger Stand der Technik im Brennverfahren für sanitärkeramische Produkte). *Keramische Zeitschrift*, 1995, **47**(5), 267–270.
8. Ferber, C., Possibilities and limits of fast firing of ceramic materials (Möglichkeiten und Grenzen beim Schnellbrand keramischer Massen), cfi/Ber. *DKG*, 1996, **73**(9), 489–491.
9. Schulle, W., Developments and problems of fast-firing ceramic products. *Keramische Zeitschrift*, 2000, **52**(12), 1184–1187.
10. Schulle, W., Trends and problems in the development of the porcelain firing process. *Interceram*, 2003, **52**(4), 192–196.
11. Rasch, H., Customizing of microstructure for the fast firing process (Maßschneidern von Gefügen für den Schnellbrand), cfi/Ber. *DKG*, 1997, **74**(10), 639–647.
12. Clauß, U., New technologies of tableware production and their effect on the environment (Neue Technologien bei der Geschirrporzellanfertigung mit ihren Wirkungen auf die Umwelt). *Keramische Zeitschrift*, 1991, **43**(9), 670–674.
13. Schulle, W. and Schmidt, G., The single firing of porcelain: prospects and problems, cfi/Ber. *DKG*, 2000, **77**(1/2), 31–35.
14. Olhero, S. M., Tarì, G. and Ferriera, J. M. F., Feedstock formulations for direct consolidation of porcelains with polysaccharides. *J. Am. Ceram. Soc.*, 2001, **84**(4), 719–725.
15. Liebermann, J. and Schulle, W., Basic properties of clay mineral raw materials and their influence on the microstructural formation during sintering, cfi/Ber. *DKG*, 1999, **76**(10), 31–34.
16. Schulle, W., Cost optimization with selective raw material combination for high tension isolator porcelain with special attention of firing condition (Kostenoptimierung durch gezielten Rohstoffeinsatz bei Hochspannungsisolationsporzellan unter besonderer Beachtung der Brennbedingungen). *Keramische Zeitschrift*, 2001, **53**(12), 12–16.
17. Kartal, A. and Schulle, W., Investigations of production of hard porcelain with reduced firing temperature (Untersuchungen zur Herstellung von Hartporzellan bei verringerten Brenntemperaturen), cfi/Ber. *DKG*, 2004, **81**(5), 20–23.
18. Thiede, D., Form stability of porcelain raw material during fast firing (Formstabilität von Porzellanmassen im Schnellbrand). *Keramische Zeitschrift*, 1998, **50**(4), 249–255.
19. Kolb, G., Preparation of ceramics in agitator mills – homogenization, comminution. *Interceram*, 1994, **43**(2), 94–96.
20. Szegvari, A., The fine grinding of ceramics with attritors. *Interceram*, 1994, **43**(2), 97–98.
21. Mende, S., Milling and dispersion in the field of nano technology (Zerkleinerung und Dispergierung im Bereich der Nanotechnologie), cfi/Ber. *DKG*, 2005, **82**(13), 283–286.
22. Milne, S. J., Patel, M. and Dickinson, E., Experimental studies of particle packing and sintering behaviour of monosize and bimodal spherical silica powders. *J. Eur. Ceram. Soc.*, 1993, **11**, 1–7.
23. German, R. M., Suri, P. and Park, S. J., Review "liquid phase sintering". *J. Mater. Sci.*, 2009, **44**, 1–39.
24. Roosen, A. and Bowen, H. K., Influence of various consolidation techniques on the green microstructure and sintering behavior of alumina powders. *J. Am. Ceram. Soc.*, 1988, **71**(11), 970–977.
25. Schulle, W., The cold isostatic pressing in the field of ceramics (Die kaltisostatische Preßformgebung in der Keramik). Handbuch der Keramik, Verlag Schmid GmbH, Freiburg i.Br., Germany (1991). *Beilage zu: Keramische Zeitschrift*, 1991, **43**(7).
26. Bartusch, R., "Custom-made" press granules via spray drying (Pressgranulate "nach Maß" durch Sprühtrocknung). *Keramische Zeitschrift*, 2000, **52**(9), 758–765.
27. Binkert, B., *Shrinkage Controlled Sintering of Alumina and Porcelain with a Laser Absolute Dilatometer* (*Schwindungsgeregeltes Sintern von Al_2O_3- und Porzellanmassen mit einem Absolutdilatometer*). Dissertation. Oberharzer Druckerei GmbH, Clausthal-Zellerfeld, 1982.
28. Heuschkel, H. and Muche, K., *ABC Ceramics (ABC Keramik)*. Deutscher Verlag für Grundstoffindustrie, Leipzig, 1974.
29. Stehr, N., *Milling and Material Transport in Agitator Ball Mills* (*Zerkleinerung und Materialtransport in Rührwerksmühlen*). Dissertation. TU-Braunschweig, 1982.
30. Stadler, R., Polke, R., Schwedes, J. and Vock, F., Wet grinding in agitator ball mills (Nassmahlung in Rührwerkskugelmühlen). *Chem.-Ing-Tech.*, 1990, **62**(11), 907–915.
31. Agrafiotis, C. and Tsoutsos, T., Energy saving technologies in the European ceramic sector: a systematic review. *Appl. Therm. Eng.*, 2001, **21**, 1231–1249.