

INFLUENCE OF PARTICLE SIZE AND FURNACE ATMOSPHERE ON THE SINTERING OF POWDER FOR TILES PRODUCTION

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The effect of both particle size and furnace atmosphere on the sintering of ceramic powder used in the production of tiles was studied. The investigation was performed on two powders having different grain sizes: 63 - 90 μm and 400 - 500 μm . The samples were compacted and sintered at different experimental conditions; steady air and flowing air, at temperatures 400 - 600 $^{\circ}\text{C}$, and flowing oxygen, at temperatures 400 - 600 $^{\circ}\text{C}$, 600 - 800 $^{\circ}\text{C}$ and 800 - 1000 $^{\circ}\text{C}$. In order to investigate particle size and furnace atmosphere influence, the following characteristics of samples were measured: quantity and composition of amorphous phase, porosity, relative density, shrinkage and compressive strength. The results indicate negligible influence of atmosphere, in comparison with the influence of the initial particle size.

INTRODUCTION

There are many factors which influence densification of ceramic products during sintering; one of them is the particle size distribution of the raw ceramic powder. The particle size has a complex effect on liquid phase sintering. Usually, the densification rate is increased with smaller particle size [1]. A narrow particle size distribution promotes densification [1]. Even mechanical properties of the final product are improved by small particle size [2]. In the first (rearrangement) stage of sintering, densification of small particles takes place. Likewise, in the second (solution - reprecipitation) stage, higher degree of densification occurs when using finer particle size. It is well known that small grains have a higher solubility than the large ones. This sets up the condition for grain coarsening by solution-reprecipitation. However, an unbalanced solubility can lead to Kirkendall porosity and compact swelling [3]. During microstructural coarsening in the final stage of sintering, large grains might induce exaggerated grain growth [4]. Size of particles might influence the kinetic of reactions inside the solid-liquid system [5 - 7].

However, instead of considering the particle size influence only as an isolated phenomenon, it is appropriate to find also its correlation with green density and sintered product density. Spray dried ceramic powder, e.g., has a complex response to compaction. When exposed to pressure, small particles

show plasticity, while large ones are easy to crush [8 - 11]. Actually, an increase in diameter causes a decrease in stress required for brittle fracture [12]. Consequently, small particles can give lower green densities than the large ones. On the other hand, the final density of the product mostly increases with the increase of green density [13 - 15]. This effect becomes particularly evident in the second (intermediate) stage of liquid phase sintering [1]. In the first stage of sintering, high green density locks the microstructure and inhibits the rearrangement. In the final stage, when the volume fraction of liquid increases, some other factors are likely to become more important than green density.

Another factor of interest is the atmosphere surrounding the green bodies. Industrial furnaces contain an air- like gas mixture flowing due to pressure differences. However, the atmosphere can be changed if necessary. Many investigations try to clarify the mechanisms (as well as their consequences) taking place due to the influence of an atmosphere. The contact between gas and a porous ceramic body is particularly important. In the solution - reprecipitation stage and coarsening stage of sintering, atmosphere improves melt flow by removing films from the surface. In this way the best densification can be achieved. The phenomenon (reduction of surface films) can alter dihedral or wetting angles - important factors for successful liquid phase sintering [1]. Sintering in the presence of soluble gas can cause problems related to

Table 1. Particle size ranges for spray dried ceramic powder.

fraction	I	II	III	IV	V	VI	VII
d (μm)	<63	63 - 90	90 - 200	200 - 315	315 - 400	400 - 500	>500

the physical characteristics of the product, particularly related to its porosity. Residual atmosphere will be sealed when trapped in pores during liquid flow. This inhibits full densification. Actually, two aspects are important: i) solubility of gas in the liquid and ii) diffusion of gas molecules through the liquid. On the other hand, sintering in the presence of reactive gases can improve the process. Wetting is best when there is a chemical reaction at the solid-liquid interface [1]. In accordance with the Le Chatelier principle, some chemical and phase changes of a solid-liquid system can be promoted or suppressed by oxidative or reductive atmosphere. This can happen as a consequence of combustion of organic compounds, after thermal destruction of carbonates, due to oxidation of polyvalent elements (Fe, Mn, V) etc. [16 - 20]. Apart from mass transfer, there is a heat transfer between a ceramic body and the surrounding gas [19]. As is well known, flowing intensifies the mentioned phenomena. Thus it can be expected that forced convection (coupled with heat radiation) improves sintering, particularly at high temperatures.

This paper considers the influence of particle size and furnace atmosphere on some characteristics of ceramic products obtained by sintering in the presence of liquid phase.

EXPERIMENTAL PART

Ceramic powder

The investigation was performed on two fractions extracted from spray dried ceramic powder. The powder was taken from an industrial raw material batch (for ceramic tile production). It was separated by sieving into seven fractions, whose particle size ranges are presented in table 1.

The experiments were performed by using the particle sizes 63 – 90 μm and 400 – 500 μm . Small particles (< 63 μm) were rejected as well as the largest particles (> 500 μm). Compacting characteristics of particular fractions are presented in figure 1, where their compaction curves are shown. The fractions at the

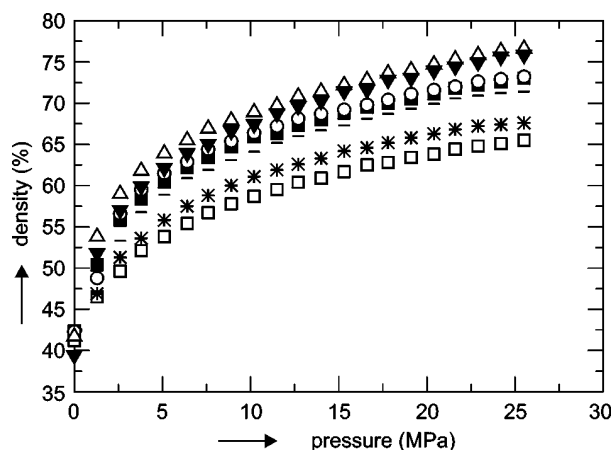


Figure 1. Compaction curves for all the fractions.

□ - fraction I, * - fraction II, - - - fraction III, ■ - fraction IV, ○ - fraction V, △ - fraction VI, ▼ - fraction VII.

Table 2. Specific surface area of green samples.

fraction	d (μm)	specific surface ($\text{m}^2 \text{g}^{-1}$)		
		pressure $p = 6.4 \text{ MPa}$	pressure $p = 21 \text{ MPa}$	surface increase (%)
II	63-90	14.8	17.2	16.4
VI	400-500	15.9	19.2	20.8

opposite sides of a family of green density curves (figure 1) were investigated.

The specific surface area of green samples (made of the investigated fractions) is presented in table 2. It was measured by static low temperature nitrogen adsorption (ASAP 2000, Micromeritics).

Table 3 presents chemical composition of raw components determined by standard chemical analysis. Phase composition was investigated by X-ray powder diffraction.

Table 3. Chemical composition of raw components (wt.%).

fraction	mass loss*	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Σ
II	13.2	50.9	15.2	2.9	7.5	6.0	2.4	2.3	100.4
VI	12.8	52.9	16.8	1.9	8.4	3.8	2.1	1.4	100.1

* - at $t = 1000 \text{ }^\circ\text{C}$ and $\tau = 2 \text{ h}$

Table 4. Temperature regime during sintering.

temperature (°C)	20	100	200	300	400	500	573	700	800	900	1040
time period (min)	0	40	50	55	65	80	90	100	110	120	130

Table 5. Composition of amorphous phase (in terms of the CaO content).

number of moles of oxides of alkali and alkali-earth metals for the fraction II						
atmosphere	Na ₂ O	K ₂ O	CaO	MgO	Σ R ₂ O*	Σ R ₂ O*/Σ RO**
1	0.1	0.1	1	0.8	0.2	0.055
3	0.2	0.1	1	0.4	0.3	0.1
4	0.35	0.2	1	0.7	0.55	0.162
5	0.12	0.34	1	0.1	0.46	0.21
number of moles of oxides of alkali and alkali-earth metals for the fraction VI						
atmosphere	Na ₂ O	K ₂ O	CaO	MgO	Σ R ₂ O*	Σ R ₂ O*/Σ RO**
1	0.33	0.3	1	0.7	0.63	0.185
3	0.32	0.34	1	0.6	0.66	0.206
4	0.40	0.2	1	0.8	0.60	0.167
5	0.45	0.19	1	0.3	0.64	0.246

* - Na₂O + K₂O, ** - CaO + MgO

The X-ray diffraction patterns show the presence of quartz, calcite and dolomite, orthoclase, albite, anorthite, chlorite, illite and mica minerals in both fractions. Negligible differences in the phase compositions between two fractions were found.

Sintering regimes

During sintering of green samples in a laboratory furnace (diameter 5 cm, length 75 cm), two conditions (temperature and atmosphere) were controlled. The temperature changed in a way to simulate the process in a real furnace (see table 4). This is the reason why maximal temperature did not exceed 1040 °C.

In addition, the atmosphere inside the furnace was adjusted while the temperature regime was kept constant. Steady air in the furnace was disturbed by introducing a stream of air (or oxygen), at particular stages of heating. Five sintering regimes were used:

1. Steady air from the beginning to the end of the sintering process.
2. Flowing air at temperatures: 400 - 600 °C.
3. Flowing oxygen at temperatures: 400 - 600 °C.
4. Flowing oxygen at temperatures: 600 - 800 °C.
5. Flowing oxygen at temperatures: 800 - 1000 °C.

The gas velocity was approximately 0.1 m s⁻¹. At the end of sintering process, the electric heater was turned off. The furnace and the samples were cooled by surrounding air to room temperature.

RESULTS

Quantity and composition of the amorphous phase as well as porosity, density, shrinkage and compressive strength of the sintered samples were chosen as their representative characteristics.

Amorphous phase quantity and composition

The phase composition of samples sintered under different conditions did not significantly differ one from another. Diopside (CaO×MgO×2SiO₂) and akermanite (2CaO×MgO×2SiO₂) were found by X-ray diffraction method in all the samples. This fact is contributed to an elevated content of MgO favoring the appearance of magnesium compounds, even at low temperatures.

However, the amount of amorphous phase is affected by the particle size and the sintering atmosphere. The amorphous phase content was determined by employing IPAS (Image Processing Analyzing System). The photographs were taken by a Philips microscope equipped with a system for picture acquisition. Forty cross-sections (magnification 500×) were recorded for every sample and used for the estimation of the volume fraction of amorphous phase.

AUGER Spectro- photometry with XPS- Fluorescent Spectroscopy was applied to determine the content of alkali- and alkali-earth- metals (such as Na, K and Mg), in terms of the Ca- content. Using these data, a ratio of particular groups of oxides was determined, as presented in table 5.

Porosity and relative density

The porosity of all samples was determined by IPAS. Relative density is defined as following dimensionless ratio:

$$\rho = \frac{\gamma}{\gamma_s} \cdot 100$$

where γ denotes the density obtained by dividing sample mass by its volume:

$$\gamma = \frac{m}{V}$$

while γ_s represents density determined by pycnometric method.

Shrinkage

During sintering, the samples show tendency to swell and/or shrink. This was quantified by dilatometry. Linseis dilatometer experiments were carried out with green samples (5 × 5 × 30 mm) and shrinkage curves, presented in figures 2 - 3, were obtained.

Compressive strength

One of the most important characteristics of sintered product is its resistance to stresses. Here, compressive strength was taken into consideration. The compressive strength values were obtained by using Instron-press 1122 (with a cross-head speed of 50 mm min⁻¹), for all investigated samples having diameter 12 mm and height 10 mm.

DISCUSSION

This paper studies the effect of surrounding atmosphere on sintered sample density and related changes. At temperatures below 600 °C, flowing gases can remove gases (such as H₂O, CO₂, etc.) appearing in the system after dehydroxylation of clay minerals and decarbonization of carbonates. This fact increases the quantity of amorphous phase, relative density and compressive strength. At temperatures above 800 °C a considerable quantity of liquid phase appears. Flowing oxygen improves the sintering process by accelerating the heat and mass transfer and by taking part in chemical reactions (for example, oxidation of polyvalent elements, formation of high-temperature oxide compounds, etc.). It is also expected that the surrounding atmosphere affect sintering of small and (crushed) large particles in different ways.

The plan of experiments, applied during this investigation, allows three kinds of comparisons among the obtained results. First of all, it is possible to compare the characteristics of samples sintered in

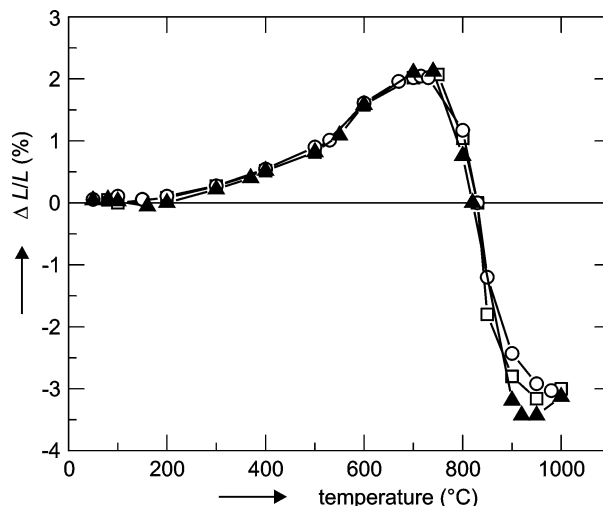


Figure 2. One-dimensional size change during heating of samples prepared from fraction II.

□ - fraction II, steady air; ○ - fraction II, O₂ at 400 - 600 °C; ▲ - fraction II, O₂ at 600 - 800 °C.

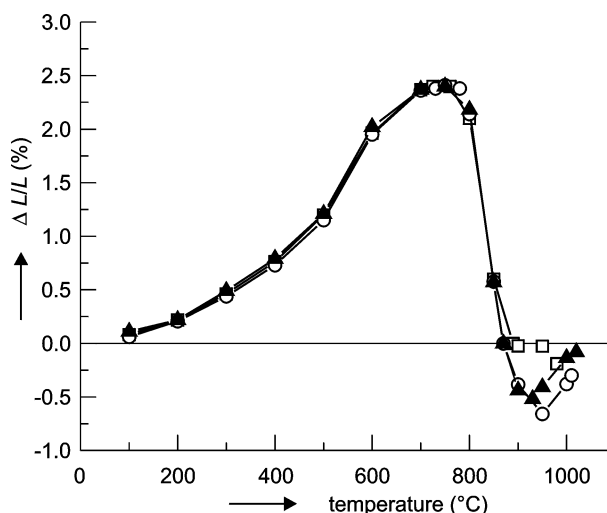


Figure 3. One-dimensional size change during heating of samples prepared from fraction VI.

□ - fraction VI, steady air; ○ - fraction VI, O₂ at 400 - 600 °C; ▲ - fraction VI, O₂ at 600 - 800 °C.

steady air with the properties of the samples sintered in flowing air. This analysis will shed light upon the influence of the flowing regime on sintering. Secondly, it is possible to compare products obtained in air with the products obtained in an oxidative atmosphere, under equal flowing regimes and temperature conditions. Finally, an analysis of oxidative atmosphere influence onto the sintering processes at different stages of heating is possible.

The comparative analysis was applied to sintered samples made from the two respective fractions of the

Table 6. Comparative analysis of amorphous phase content.

comparison of amorphous phase content	fraction II range \cong 2 - 8 vol.%	fraction VI range \cong 4 - 12 vol.%
flowing air at 400 - 600 °C with steady air	increase \cong 140 %	increase \cong 90 %
flowing O ₂ with flowing air, both at 400 - 600 °C	decrease \cong 40 %	decrease \cong 50 %
flowing O ₂ at raising temperatures	increase \cong 300 %	increase \cong 250 %

Table 7. Comparative analysis of porosity.

comparison of porosity	fraction II range \cong 49 - 56 %	fraction VI range \cong 41 - 46 %
flowing air at 400 - 600 °C with steady air	decrease \cong 15 %	negligible change
flowing O ₂ with flowing air, both at 400 - 600 °C	increase \cong 5 %	increase \cong 10 %
flowing O ₂ at raising temperatures	negligible change	decrease \cong 10 %

Table 8. Comparative analysis of relative density.

comparison of relative density	fraction II range \cong 59.75 - 62 %	fraction VI range \cong 62.3 - 63.5 %
flowing air at 400 - 600 °C with steady air	increase \cong 3 %	negligible change
flowing O ₂ with flowing air, both at 400 - 600 °C	decrease \cong 2 %	decrease \cong 1 %
flowing O ₂ at raising temperatures	increase \cong 3 %	negligible change

Table 9. Comparative analysis of compressive strength.

comparison of compressive strength	fraction II range \cong 15 - 24 MPa	fraction VI range \cong 22 - 28 MPa
flowing air at 400 - 600 °C with steady air	increase \cong 20 %	negligible change
flowing O ₂ with flowing air, both at 400 - 600 °C	decrease \cong 5 %	negligible change
flowing O ₂ at raising temperatures	increase \cong 40 %	increase \cong 20 %

ceramic powder. Important facts, concisely presented in tables 6-9, were noticed.

The influence of the atmosphere onto the sintering of compacts made from small and large (but crushed) particles can also be analyzed as in figures 4-7. Such a comparative presentation shows that large particles, from the fraction VI, result in samples having

- higher amorphous phase content (figure 4),
- lower porosity (figure 5),
- higher density (figure 6) and
- higher compressive strength (figure 7)

in comparison with the fraction II. The conclusion is valid for almost all sintering atmospheres. An exception can be noticed only in the case of flowing air at temperatures 400 - 600 °C. The conclusion strongly

suggests that the particle size distribution is a much more influencing factor than the sintering atmosphere. It also suggests that the higher the content of amorphous phase, the lower porosity, i.e. the greater compressive strength.

An analysis of the amorphous phase composition leads to the following conclusions. The content of alkali oxides (the sixth column in table 5), which contribute to the lowering of the melting temperature, is smaller in the case of fraction II than in the case of fraction VI. This is in agreement with the fact that the fraction II samples contain a smaller quantity of amorphous phase than the fraction VI samples.

On the other hand, liquid phase with high content of alkali oxides has a high viscosity due to occurrence of Al-Si-O complexes [21]. However, alkali-earth oxides (particularly Mg²⁺ and Ca²⁺ ions) destroy these complexes and reduce the viscosity of the

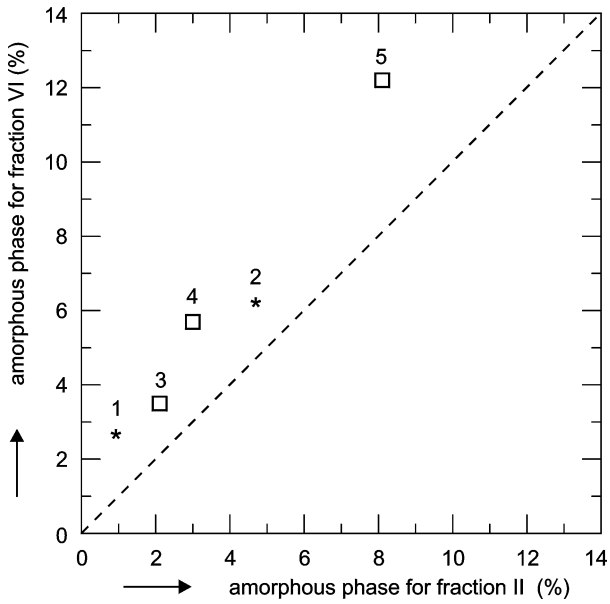


Figure 4. Atmosphere influence on amorphous phase content.
□ - oxygen, * - air.

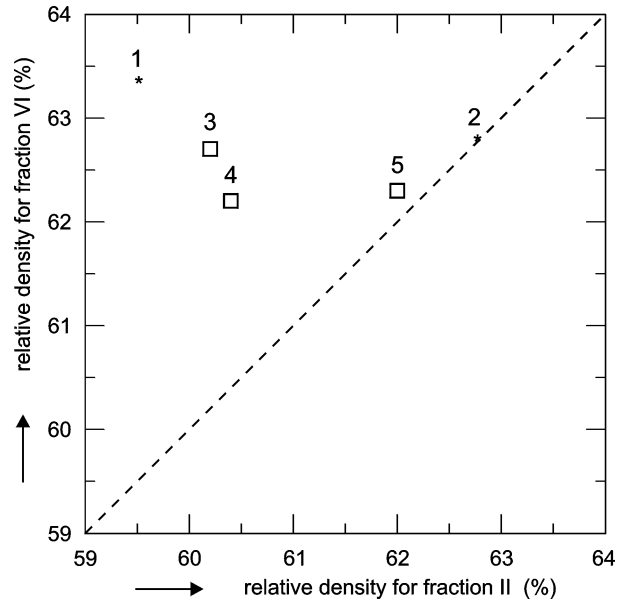


Figure 6. Atmosphere influence on relative density.
□ - oxygen, * - air.

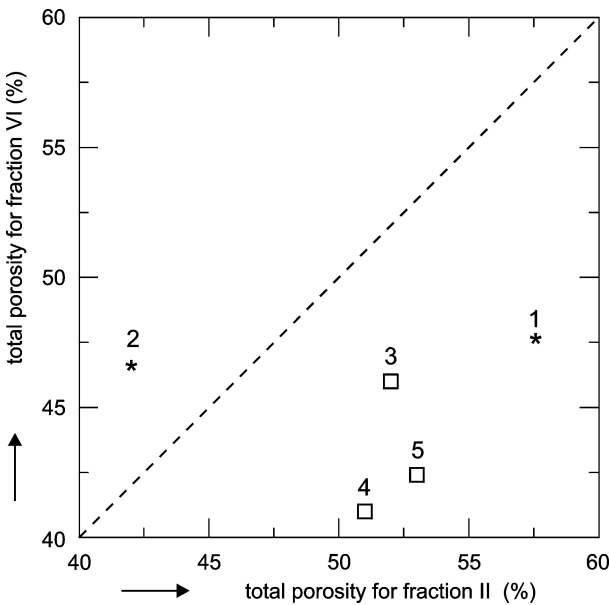


Figure 5. Atmosphere influence on total porosity.
□ - oxygen, * - air.

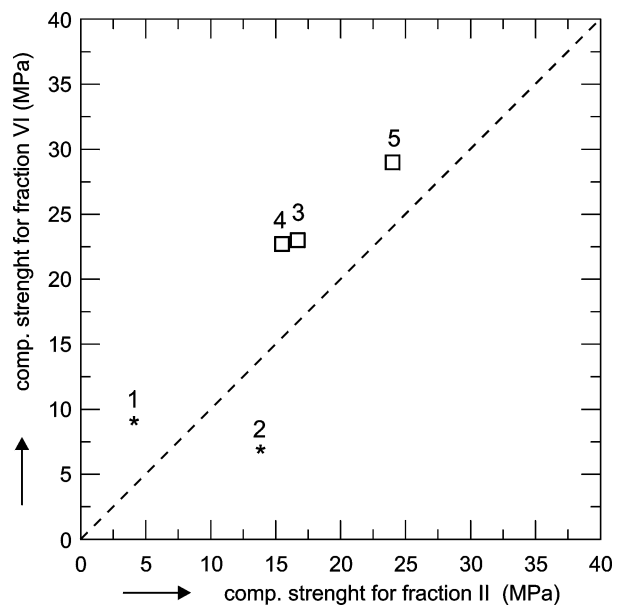


Figure 7. Atmosphere influence on the compressive strength.
□ - oxygen, * - air.

melt. The last column in table 5 contains a ratio that can be used as quantifier of melt viscosity. It is obtained by dividing the measured quantities of alkali and alkali- earth oxides. This ratio indicates that the melt viscosity is probably lower in the case of fraction II.

As for the dilatometric results, samples prepared from fraction II powder exhibit a linear shrinkage of approx. 40 % at firing temperatures of 900 - 950 °C,

while samples prepared from fraction VI show a considerably lower shrinkage at these temperatures. Compared to the particle size, the influence of atmosphere on these results is negligible.

CONCLUSIONS

When considering the results obtained, the following conclusions can be made:

Flowing air intensifies heat and mass transfer, thus being a better working fluid than steady air at temperatures below 600 °C. The influence is slightly greater in the case of fraction II than in the case of fraction VI. This is associated with the higher permeability of fraction II samples as well as higher amount of interparticle friction of fraction VI samples.

Flowing oxygen, at low temperatures (400 - 600 °C), will probably not improve sintering, neither in the case of small nor in the case of large particles. The situation can be different if the raw material contains a significant quantity of organic compounds.

A stream of oxygen at temperatures above 800 °C improves the sintering process, partly by improving heat and mass transfer, partly by taking part in the actual chemical reactions. The positive effect is more evident in the case of fraction II than in the case of fraction VI although not enough to overcome the initial advantage of fraction VI. During sintering at temperatures above 800 °C, a high solubility of small particles brings the condition for grain coarsening by solution-reprecipitation. As a consequence of all the mentioned phenomena, compressive strength increases by 20 - 40 %.

The results of this investigation suggest that an adjustment of the sintering atmosphere slightly improves the sintering process. It seems, however, that the initial particle size distribution has the dominant role, for the system investigated in the present paper. Large ceramic particles gave products with high compressive strength, mostly due to the fact that (crushed) large particles gave green samples with high density. This became an advantage, which determined the quality of the final product, regardless to all other influencing factors including the sintering atmosphere.

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VLIV VELIKOSTI ČÁSTIC A PECNÍ ATMOSFÉRY NA SLINOVÁNÍ PRÁŠKU PRO VÝROBU DLAŽDIC

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Byl studován účinek velikosti částic a pecní atmosféry na slinování keramických prášků používaných pro výrobu dlaždic. Sledování bylo provedeno v prášcích s dvěma odlišnými velikostmi částic 63 - 90 μm a 400 - 500 μm. Vzorky byly zhutněny a slinuty při odlišných experimentálních podmínkách: statický a proudící vzduch při teplotách 400 - 600 °C a proudící kyslík při teplotách 400 - 600 °C, 600 - 800 °C a 800 - 1000 °C. Vliv velikosti částic a pecní atmosféry byl hodnocen na základě měření následujících vlastností: množství a složení amorfní fáze, pórovitost, relativní hustota, smrštění a pevnost v tlaku.