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

JONJAUA RANOJAEC, MIRJANA DJURIĆ, MIROSLAVA RADEKA*, PEOJA JOVAČIC**

University of Novi Sad, Faculty of Technology, 21000 Novi Sad, Yugoslavia

*University of Novi Sad, Faculty of Technical Sciences, 21000 Novi Sad, Yugoslavia

**Institute for Technology of Nuclear and other Mineral Raw Materials, 11000 Belgrade, Yugoslavia

Submitted February 3, 1998; accepted December 17, 1999.

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 °C, and flowing oxygen, at temperatures 400 - 600 °C, 600 - 800 °C and 800 - 1000 °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...
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 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) was 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 1. Particle size ranges for spray dried ceramic powder.

<table>
<thead>
<tr>
<th>fraction</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d$ ($\mu$m)</td>
<td>&lt;63</td>
<td>63 - 90</td>
<td>90 - 200</td>
<td>200 - 315</td>
<td>315 - 400</td>
<td>400 - 500</td>
<td>&gt;500</td>
</tr>
</tbody>
</table>

### Table 2. Specific surface area of green samples.

<table>
<thead>
<tr>
<th>fraction</th>
<th>$d$ ($\mu$m)</th>
<th>pressure</th>
<th>pressure</th>
<th>surface increase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>63-90</td>
<td>6.4 MPa</td>
<td>21 MPa</td>
<td>16.4</td>
</tr>
<tr>
<td>VI</td>
<td>400-500</td>
<td>15.9</td>
<td>19.2</td>
<td>20.8</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>fraction</th>
<th>mass loss*</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>$\Sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>13.2</td>
<td>50.9</td>
<td>15.2</td>
<td>2.9</td>
<td>7.5</td>
<td>6.0</td>
<td>2.4</td>
<td>2.3</td>
<td>100.4</td>
</tr>
<tr>
<td>VI</td>
<td>12.8</td>
<td>52.9</td>
<td>16.8</td>
<td>1.9</td>
<td>8.4</td>
<td>3.8</td>
<td>2.1</td>
<td>1.4</td>
<td>100.1</td>
</tr>
</tbody>
</table>

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

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.

<table>
<thead>
<tr>
<th>temperature (°C)</th>
<th>20</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
<th>573</th>
<th>700</th>
<th>800</th>
<th>900</th>
<th>1040</th>
</tr>
</thead>
<tbody>
<tr>
<td>time period (min)</td>
<td>0</td>
<td>40</td>
<td>50</td>
<td>55</td>
<td>65</td>
<td>80</td>
<td>90</td>
<td>100</td>
<td>110</td>
<td>120</td>
<td>130</td>
</tr>
</tbody>
</table>

Table 4. Temperature regime during sintering.

<table>
<thead>
<tr>
<th>atmosphere</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>CaO</th>
<th>MgO</th>
<th>Σ R₂O*</th>
<th>Σ R₂O*/Σ RO**</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.1</td>
<td>1</td>
<td>0.8</td>
<td>0.2</td>
<td>0.055</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>0.1</td>
<td>1</td>
<td>0.4</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>4</td>
<td>0.35</td>
<td>0.2</td>
<td>1</td>
<td>0.7</td>
<td>0.55</td>
<td>0.162</td>
</tr>
<tr>
<td>5</td>
<td>0.12</td>
<td>0.34</td>
<td>1</td>
<td>0.1</td>
<td>0.46</td>
<td>0.21</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>atmosphere</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>CaO</th>
<th>MgO</th>
<th>Σ R₂O*</th>
<th>Σ R₂O*/Σ RO**</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.33</td>
<td>0.3</td>
<td>1</td>
<td>0.7</td>
<td>0.63</td>
<td>0.185</td>
</tr>
<tr>
<td>3</td>
<td>0.32</td>
<td>0.34</td>
<td>1</td>
<td>0.6</td>
<td>0.66</td>
<td>0.206</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>0.2</td>
<td>1</td>
<td>0.8</td>
<td>0.60</td>
<td>0.167</td>
</tr>
<tr>
<td>5</td>
<td>0.45</td>
<td>0.19</td>
<td>1</td>
<td>0.3</td>
<td>0.64</td>
<td>0.246</td>
</tr>
</tbody>
</table>

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

* - Na₂O + K₂O, ** - CaO + MgO

Amorphous phase quantity and composition

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

Ceramics – Silikáty 44 (2) 71-77 (2000)
Porosity and relative density

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

\[ \rho = \frac{\gamma}{\gamma_s} \times 100 \]

where \( \gamma \) denotes the density obtained by dividing sample mass by its volume:

\[ \gamma = \frac{m}{V} \]

while \( \gamma_s \) 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 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
cементный порошок. Важные факты, сжато изложенные в таблицах 6-9, были замечены.

Влияние атмосферы на спекание компактов из мелких и крупных (но измельченных) частиц также может быть проанализировано, как показано на фигурах 4-7. Такое сравнительное представление показывает, что крупные частицы, относящиеся к частице VI, приводят к образцам с

- большим содержанием аморфной фазы (фигура 4),
- меньшей пористостью (фигура 5),
- большей плотностью (фигура 6) и
- большей сжимаемостью (фигура 7)

в сравнении с частицей II. Это подтверждение для всех спекающихся атмосфер. Единственным исключением является случай в случае потока воздуха при температурах 400-600 °C. Это сильное указание на то, что размер частицы - гораздо более влиятельный фактор, чем атмосфера спекания. Оно также подчеркивает, что большее содержание аморфной фазы, меньшая пористость, т.е. большая сжимаемость.

Анализ содержания аморфной фазы приводит к следующим выводам. Содержание щелочных оксидов (шесть столбец в таблице 5), которые способствуют понижению температуры плавления, меньше в случае частицы II, чем в случае частицы VI. Это согласуется с тем, что частицы II содержат меньше аморфной фазы, чем частицы VI.

С другой стороны, жидкость с высоким содержанием щелочных оксидов имеет высокую вязкость из-за образования комплексов Al-Si-O [21]. Однако, щелочно-земельные оксиды (в частности Mg^{2+} и Ca^{2+} ионы) разрушают эти комплексы и уменьшают вязкость.
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.

References


Submitted in English by the authors.

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

JONJAU RANOGAJEC, MIRJANA DJURIC, MIROSLAVA Radeka*, PEDJA JOVANIC**

University of Novi Sad,
Faculty of Technology,
21000 Novi Sad, Yugoslavia

*University of Novi Sad,
Faculty of Technical Sciences,
21000 Novi Sad, Yugoslavia

**Institute for Technology of Nuclear and other Mineral Raw Materials,
11000 Belgrade, Yugoslavia

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 zhusněny a slinuty při odlišným experimentálních podmínkách: statický a proudící vzduch vzduch při teplotách 400 - 600 °C a proudicí 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, půrovitost, relativní hustota, smrštění a pevnost v tlaku.