

Development of lightweight porcelain stoneware tiles using foaming agents

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Abstract

Recent market trends for porcelain stoneware tiles indicate that there is a growing interest for lightweight products, to be used vertically, in internal walls or ventilated facades. The decorative and structural functions have now been coupled with additional features, such as thermal insulation. The optimization of all functionalities depends on a careful control of porosity, in terms of overall amount, size and morphology. In this paper, we propose fundamental correlations between mechanical properties, water absorption, porosity and technological aspects, and particle size and the amount of foaming agent (SiC). The data indicate that the addition of SiC powder with a size < 10 μm enables the fabrication of tiles possessing a suitable strength, negligible water absorption and a weight reduced by 26%. The loss of mechanical strength of the tiles and their pyroplastic deformation controls the maximum attainable decrease in weight.

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1. Introduction

Porcelain stoneware tiles are characterised by their high density (2380–2450 kg/m³), very low water absorption (<0.5%), and limited porosity with small pore size (<50 μm).^{1,2} These characteristics provide them with high mechanical strength and frost resistance, which is why they were initially used for internal and external flooring.^{3,4} However, in recent years, porcelain tile applications have spread to other areas, such as internal walls and ventilated facades.^{5–7} One disadvantage for some of these new applications is the porcelain tile's high density, which makes handling difficult (particularly for large sizes) and raises transport and distribution costs. The reduction of porcelain tile density during firing could enhance the use of this product in these new areas and improve at the same time other properties, such as thermal and acoustic insulation.

Porcelain stoneware tile densification involves a liquid-phase sintering process.^{8,9} During firing, at temperatures of about 900–1000 °C, a significant quantity of liquid phase is formed,

producing a capillary pressure (P_C) at the particle contact points that brings the particles closer together, increasing shrinkage and lowering porosity, while at the same time altering pore size and shape. At an intermediate stage, pores start closing as inter-pore connections are eliminated. The occluded pores contain gas that exerts a pressure (P_g) on the pore walls, acting against densification. At temperatures around 1200 °C, occluded pore gas pressure is high and counteracts capillary pressure, causing the product to expand. The sintering rate of this type of material can be obtained from the equation shown below¹⁰:

$$-\frac{d\varepsilon}{\varepsilon dt} = \frac{3}{4\eta_S}(P_C - P_g) \quad (1)$$

with

$$P_C = \frac{-2\gamma}{r} \quad (2)$$

where ε is the porosity, η_S is the effective viscosity, P_g is the gas pressure in the closed pores, and P_C is the capillary pressure of the liquid phase, which depends on surface tension (γ) and pore radius (r).

The addition of foaming agents that release gases at high temperature raises P_g , which lowers the tile bloating temperature

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Table 1
Chemical composition of the spray dried powder (STD) used.

Oxide	Content (wt%)
SiO ₂	68.7
Al ₂ O ₃	18.9
Fe ₂ O ₃	0.45
CaO	0.50
MgO	0.57
Na ₂ O	3.80
K ₂ O	2.50
TiO ₂	0.75
MnO	<0.01
P ₂ O ₅	0.26
l.o.i	3.50

and accelerates the expansion process. This approach has been investigated in a previous paper, using CeO₂ as foaming agent,¹¹ in which the difficulty of producing high porosity tiles with very low open porosity was shown. In other papers^{12–14} the research is focus on the recycling of residues from the polishing stage of porcelain tiles that contains SiC particles from the abrasive tools. Results showed that the SiC particles oxidizes at temperatures higher than 1000 °C, reducing the sintered density and increasing the pore size of porcelain tiles.¹² This effect limits the amount of residues that can be recycled in porcelain tiles to 15%.¹³ Other alternative to recycle this residue is the manufacturing cellular ceramic materials for the building industry.¹⁴

In this study, SiC was used as foaming agent with the aim to determine the feasibility of obtaining lightweight porcelain tiles with appropriate mechanical strength and water absorption below 0.5%. In addition, the effect of foaming agent particle size on the expansion process and on the properties of fired tiles has been studied considering the following two target requirements: processing conducted at 1200 °C and production of tiles with a bulk density of 1700 kg/m³.

2. Experimental procedure

The study was conducted with an industrial spray-dried powder customarily used to manufacture porcelain tiles (STD), obtained from kaolinitic–illitic clays, quartz, and sodium feldspar. The chemical composition is given in Table 1. Silicon carbide (Navarro SiC, S.A.; purity > 99.7%) of different particle sizes, ranging from $d_{50} = 0.5 \mu\text{m}$ to $d_{50} = 55 \mu\text{m}$, was used as the foaming agent.

Batches were prepared by adding 0.2 wt% for each of the different SiC powders to an aqueous suspension of the spray-dried powder (solids content = 65 wt%). After mixing, the suspensions were dried in an oven at 110 °C and deagglomerated.

The resulting powder was used to form test pieces by uniaxial pressing. Pressing moisture content was 5.5 kg water/kg solid, and the applied pressure was 40 MPa. The samples were dried in an oven at 110 °C before testing. Their bulk density was then determined by the mercury displacement method. The test pieces were subsequently fired in an electric laboratory kiln at different peak temperatures (ranging from 1140 to 1260 °C), with a

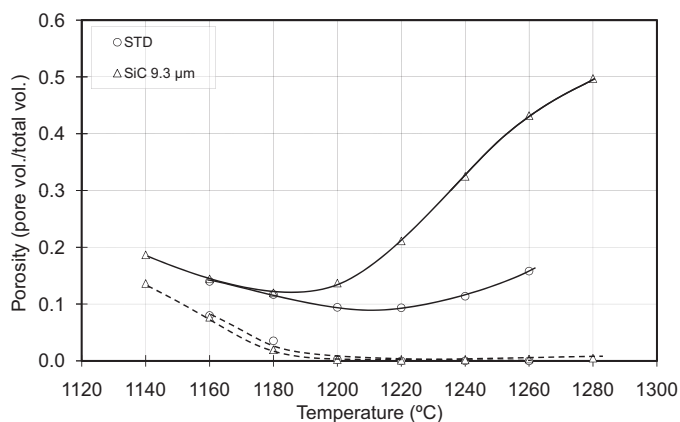


Fig. 1. Evolution with firing temperature of the total (solid lines) and open porosity (dashed lines) of samples produced from the STD composition and from the composition with 0.2 wt% SiC ($d_{50} = 9.3 \mu\text{m}$).

heating rate of 25 °C/min and a 6 min hold at peak temperature. Cooling was performed by forced convection.

The bulk density (ρ_{ap}), linear shrinkage and water absorption (EN 14411)¹⁵ were determined using cylindrical test pieces, 6 mm thick and 40 mm in diameter. The total porosity (ε_{T}), open porosity, and closed porosity were calculated from the bulk density, true density (Quantachrome, Helium Pycnometer UPY-10T), and water absorption data. Polished cross-sections of the samples were observed by SEM (Philips, XL-30 CP).

The mechanical strength (σ_{cr}) and pyroplasticity index (IP) were determined from prism-shaped test pieces, 6 mm thick, 20 mm wide, and 80 mm long. The bending strength was determined by the three-point bending method (Instron, Universal testing machine 6027) and the pyroplasticity index by measuring the test piece deflection (s), when the samples were fired while supported by their centre area, according to the following equation¹⁶:

$$\text{IP} = 2 \cdot \frac{e^2 \cdot s}{L^4} \cdot \frac{1}{\rho_{\text{ap}}} \quad (3)$$

where e is the bar thickness, L is the bar length and ρ_{ap} is the apparent density.

A procedure based on the international standards (ISO 8301:1991 and 8302:1991)^{17,18} was fine-tuned to determine thermal conductivity (λ). Thermal conductivity was determined with square test pieces (10 mm thick, with a 100-mm side length) from the Fourier law: the method consists of determining the temperature of both sample surfaces when a constant heat flow is established through the sample.

3. Results and discussion

3.1. Influence of SiC and of the processing temperature on the foaming process

Fig. 1 shows the evolution of total porosity (solid lines) and open porosity (dashed lines) of test pieces made from the STD composition and from the composition containing 0.2 wt% SiC (average diameter 9.3 μm). Porosity varied with temperature for

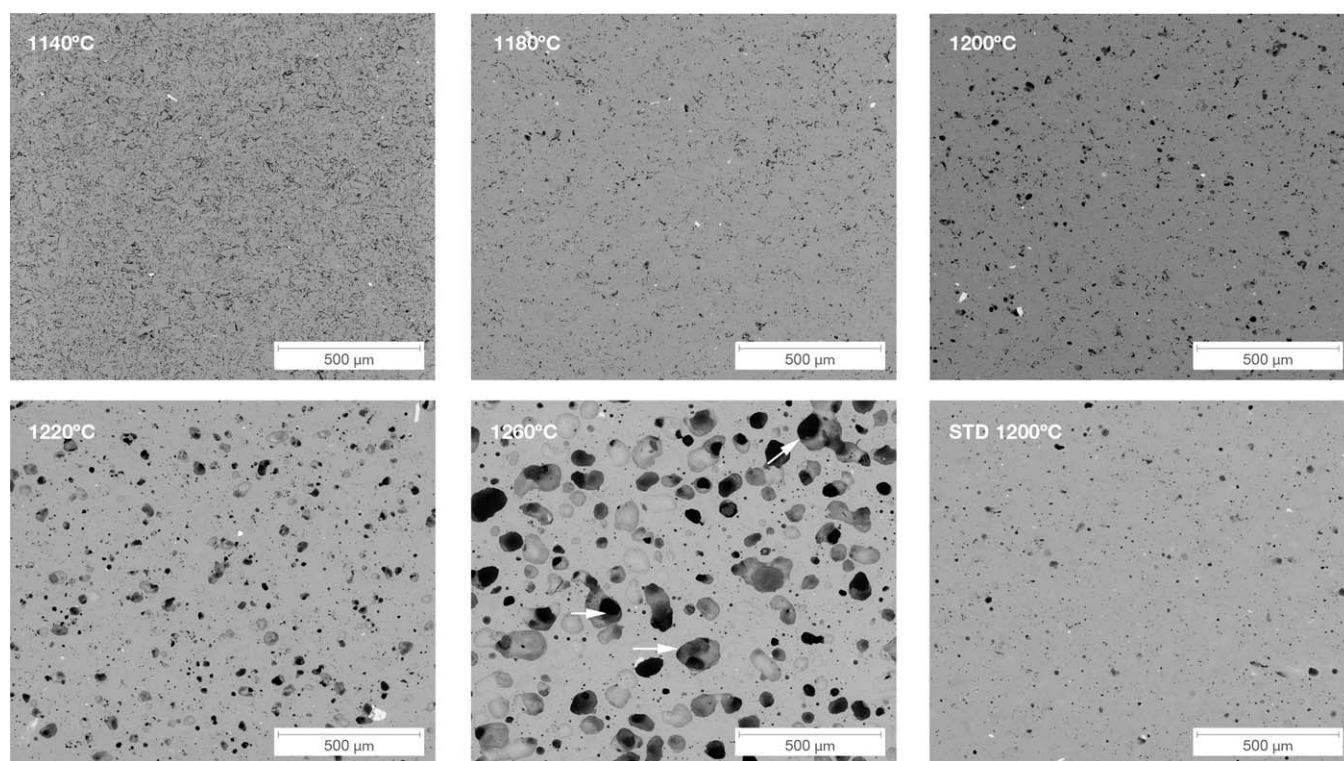
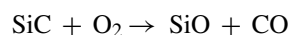
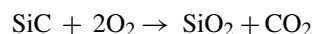


Fig. 2. Variation of the microstructure with firing temperature for samples produced from the composition with 0.2 wt% of SiC ($d_{50} = 9.3 \mu\text{m}$), and microstructure of a tile with STD composition fired at 1200 °C.

the STD composition according to the microstructural evolution described in the introduction. The STD composition reached a minimum open porosity value at 1200 °C, and began to expand at temperatures above 1210 °C, when all retained porosity was closed.

The presence of SiC in the composition lowered the expansion temperature of the pieces to 1190 °C, and notably accelerated the expansion process, as evidenced by the greater slope of the porosity–temperature curves above the minimum porosity point. This is due to the increased gas pressure in the pores (P_g) from the release of CO_2 and CO during SiC oxidation at temperatures over 1000 °C^{12,14} according to the equations¹⁹:



Once the temperature of 1200 °C was reached, the open (i.e. apparent) porosity remained virtually negligible, unlike what has been observed for other materials, such as glass cullet, when using foaming agents, in which the apparent porosity increases with processing temperature.^{20,21} This difference could be however related the much lower amount of total porosity present in the porcelain tiles, in comparison to glass foams. A higher processing temperature might still lead to pieces with open porosity, because of the lower viscosity in the pyroplastic mass leading to pore coalescence and expansion.

Fig. 2 shows how the microstructure of the samples containing SiC ($d_{50} = 9.3 \mu\text{m}$) changes with increasing firing temperature. The microstructure for the STD composition at

1200 °C, which is its industrial firing temperature, is included for comparison purposes. The evolution of the microstructure of the SiC-containing composition is very similar to that of the STD composition until 1180 °C (figures of the STD composition not reported here for the sake of brevity), and is characterised by a porous texture made up of a network of highly interconnected, small pores at low temperature (1140 °C). When the temperature rises (1180 °C), the liquid-phase content increases and the liquid-phase viscosity decreases. This allows the smallest pores to be removed, thus reducing the total and open porosity, while the remaining pores increase slightly in size due to coalescence and expansion. The initially interconnected pore system progressively loses its connectivity, and the pores begin to close (see the reduction in open porosity, Fig. 1).

The STD composition reaches its minimum porosity at 1200 °C, while the samples containing SiC have already begun to swell, as highlighted by the greater number of pores visible in the sample. The fact that the size of the pores at this temperature is no larger than that of the STD composition pores is because the gas pressure (P_g) is not very high yet. This means that the SiC oxidation is just beginning, or that part of the evolved gas has escaped from the piece through the remaining pore interconnections as other authors pointed out.¹²

When the temperature rises (1220 °C), the pore system begins to display a wider pore size distribution. The diameter of the largest pores, related to SiC particle oxidation, increases rapidly as a result of the released gas. In the smallest pores, typical of porcelain tile compositions, the gas present (air and water vapour) exerts a greater pressure than the capillary pressure,

P_C , which also contributes, though to a lesser degree, to the expansion of the piece.

At higher temperatures (1260 °C) the small pores grow slowly, while the large ones grow markedly owing to the continuous generation of gas. In addition, pore coarsening is observed to begin, which is mainly due to the coalescence of the larger pores, as may be deduced from the presence of cell windows (marked with arrows) in some of these pores. The same trend has been observed by other studies,¹² in which the pore size increases exponentially with temperature, reaching an average pore size of 300 μm at 1240 °C.

In order to determine whether the pore coalescence process leads to a system of interconnected pores, the water absorption of rectified test pieces was determined (a 0.5 mm thick layer was removed from the top and bottom surfaces). The water absorption findings were similar to those obtained with the original pieces (<0.5%), thus indicating that the pore system remains very poorly interconnected, even at the highest firing temperature. This is of course a very positive feature, as it allows the pieces to be rectified and porcelain tile frost resistance to be preserved.

To determine whether the entire SiC addition (0.2 wt%) to the composition oxidized during the foaming process, XRD tests were conducted on unfired pieces and on pieces fired at various temperatures. To enhance the signal, the data were acquired for 90 min; SiC content in the pieces were calculated using an internal standard.²² The XRD data (figures omitted) show that the unfired pieces contained 0.22 wt% SiC, which matches the quantity initially added to the composition. At 1140 °C, the SiC amount was 0.16 wt%, and then further decreased very slowly, beyond this temperature, reaching a minimum value of 0.11 wt% at 1260 °C. The results qualitatively match the existing ones in the bibliography¹² in which a clear reduction of the SiC particle size is observed between 1000 and 1180 °C due to the SiC oxidation. These findings suggest that SiC oxidation is encouraged at low temperatures because the porous texture of the piece is very permeable, allowing O_2 to enter the piece and CO_2 to exit it (in addition, the silica protective layer formed on the SiC particle surface reacts with the surrounding glassy phase causing its corrosion¹² and allowing the oxidation of the SiC particles). At temperatures beyond 1180 °C, the increasingly unconnected pore network and the high CO_2 partial pressure inside the pore system make it difficult for the SiC to oxidize. As a result, at those temperatures, SiC oxidation needs to take place at the expense of reducing some elements present in the liquid phase.²³ A way to improve the SiC reaction would be the addition of oxidizing compounds, such as MnO_2 , CeO_2 and Fe_2O_3 ,²⁴ even though potential colouring effects to the tiles should be considered.

3.2. Influence of SiC particle size on the expansion process

Fig. 3 shows the evolution of total porosity (solid lines) and open porosity (dashed lines) of the compositions containing SiC of different particle sizes (d_{50}). The reduction in SiC particle size lowers the bloating temperature and enhances the foaming process of the pieces, as a result of the larger specific surface area of the SiC in the sample. This is because the SiC

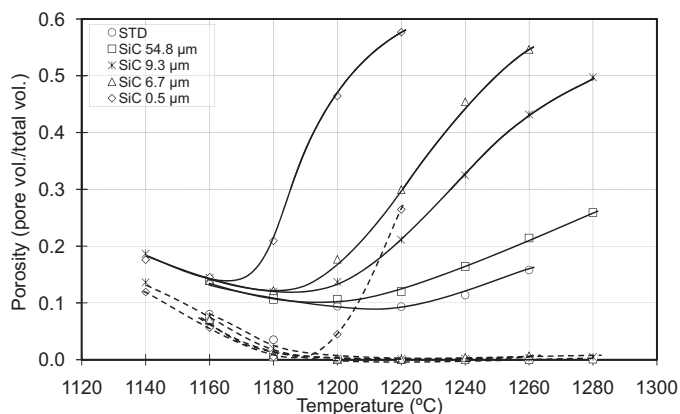


Fig. 3. Evolution with firing temperature of total (solid lines) and open porosity (dashed lines) for samples in which the SiC particle size was modified.

oxidation reaction takes place from the external surface inwards into the particle, and therefore the rate at which the process occurs depends, among other factors, on the total specific surface area of the SiC particles contained in the sample. Additionally, we can observe that the total porosity values increase significantly with decreasing SiC powder size, going from ~0.12 (at 1220 °C) for the coarse grained foaming agent powder to ~0.58 vol.% for the finer size (see later).

The reduction in the foaming rate, when total porosities above 0.4 are reached, could indicate that there is a shortage of free O_2 inside the pores of the pieces, since there is no residual open porosity and the SiC has not been entirely consumed, as was discussed in the previous section.

Concerning the open porosity, SiC particle size does not seem to influence this property significantly, as open pores are eliminated for all compositions at 1190 °C, except for the composition with the smallest SiC particle size ($d_{50} = 0.5 \mu\text{m}$), which shows a pronounced increase in open porosity at temperatures above 1190 °C. This behaviour, typically found in glass foams,^{20,21} indicates that under these conditions the porous texture of these pieces is made up of a connected pore network that is open to the outside, as a result of the high pore coalescence and of the more effective oxidation of SiC, generating higher gas pressure inside the bubbles facilitating the formation of cell windows.

Two different requirements, related to the industrial processing procedure, were chosen to determine the influence of SiC particle size on the characteristics of the samples. The first one was to keep a constant firing temperature of 1200 °C (firing time was 6 min for all samples). The second one was to fabricate samples possessing a 30% reduction in weight, which is equivalent to a bulk density 1700 kg/m^3 ; to achieve this, the firing temperature for each sample was appropriately modified (firing time was 6 min for all samples).

3.3. Influence of SiC particle size on the properties of tiles fired at 1200 °C

The influence of SiC particle size on tile porosity and shrinkage is reported in Fig. 4. It shows that the use of SiC, with particle sizes above 10 μm , has no significant influence on total porosity

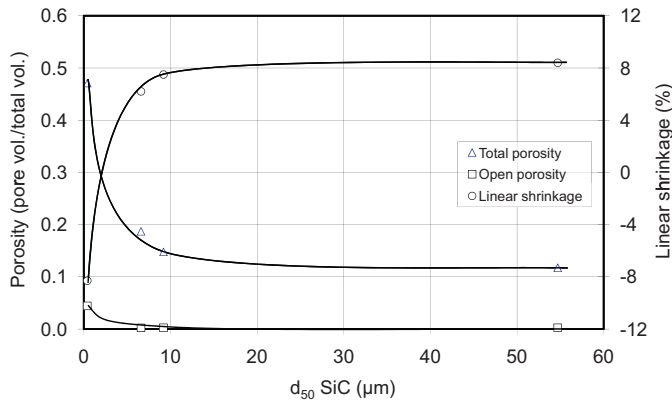


Fig. 4. Influence of the SiC particle size on sample porosity and shrinkage. Firing temperature = 1200 °C.

or shrinkage values, when the firing temperature is 1200 °C. However, when using SiC particle sizes smaller than 10 μm , the samples possessed a rapidly increasing amount of porosity and displayed a (much) smaller shrinkage with decreasing SiC particle size. This behaviour can be attributed to the greater expansion provided by SiC, as its specific surface area increases enabling a more effective oxidation and gas generation.

Although the use of SiC with a very small particle size yields pieces with high total porosity, it also leads to the presence of some open porosity, which could adversely affect the frost resistance of tiles.

Fig. 5 shows how the mechanical strength and the pyroplasticity index evolve with total porosity for samples fired at 1200 °C. The use of SiC with a smaller particle size, suitable for obtaining lightweight tiles, leads to a reduction in mechanical strength: in the tested range of porosities, the mechanical strength decreases exponentially with porosity, in accordance with the equations cited in the literature (Knudsen²⁵). The porcelain tile mechanical strength required by the applicable standards (EN 14111) is 35 MPa. Under the tested processing conditions, this limits the increase in tile porosity to ~ 35 vol.%, which means a 26% decrease in weight.

In contrast, when the tile porosity increases, due to the use of a finer SiC, the pyroplastic deformation increases. This increase

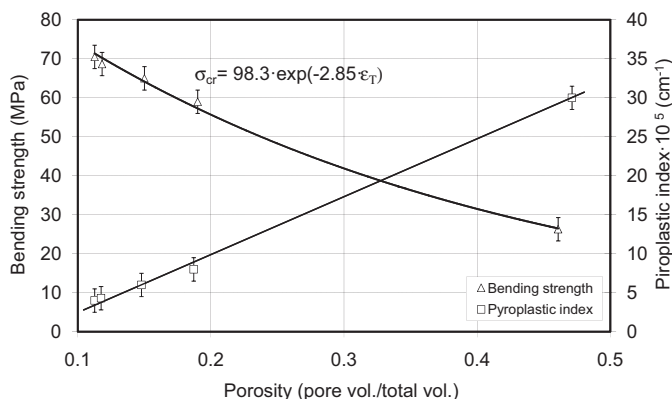


Fig. 5. Variation of the bending strength and pyroplasticity index with total porosity. Firing temperature = 1200 °C.

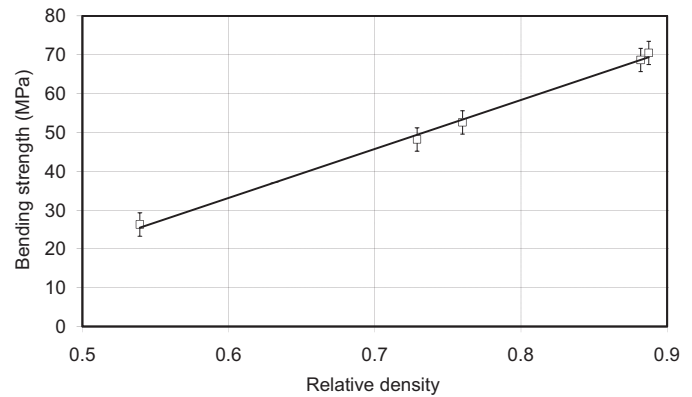


Fig. 6. Variation of bending strength with relative density. Firing temperature = 1200 °C.

is due, firstly, to the lower apparent viscosity of the sample as a result of its greater porosity. Secondly, the reducing effect of SiC on some components of the composition should be considered. The fluxing effect of the reducing atmosphere during the firing stage is in fact described in the literature.^{26,27} Thus, the reduction of the Fe^{3+} present in the raw materials to Fe^{2+} by SiC led to a decrease of the glassy phase viscosity,²⁶ and this might also justify the observed increase in pyroplasticity.

Classical models for the compressive strength of cellular solids, provided by Gibson and Ashby,²⁸ predict the dependence of strength (σ_{cr}) on the flexural strength of the solid phase (σ_{fs}), a constant (C) characteristic of the cell geometry and, above all, on the relative density (ρ_r) as a combination of exponential and linear terms, as follows:

$$\frac{\sigma_{\text{cr}}}{\sigma_{\text{fs}}} = C(\phi \cdot \rho_r)^{3/2} + (1 - \phi) \cdot \rho_r \quad (4)$$

In this equation, the mechanical strength depends on the relative density and on a correction factor ($1 - \phi$), which indicates the solid fraction present in the cell walls, and therefore the degree of open cells present in the material. For foams with fully open cells (like those obtained by replication methods), pores are completely interconnected and it may be assumed, therefore, that there is no solid in the cell walls ($1 - \phi = 0$). For closed-cell foams, which resemble more closely the pieces obtained in this study, this factor has a value of 1. Therefore, a linear relationship ($R^2 = 0.997$) might be expected between the mechanical strength and the relative density of the samples, as confirmed by Fig. 6.

The very limited interconnectivity of the pores present in the samples is in agreement with the SEM micrographs in Fig. 7: all samples display a densified glassy matrix with a wide pore size distribution made up of small pores (about 15 μm in size), which are characteristic of porcelain tile compositions, and larger pores (between 50 and 100 μm) deriving from the oxidation of SiC.

When the SiC particle size changes, the number, size, and interconnectivity of the pores formed by the foaming agent vary, while the characteristic porcelain stoneware tile pores do not change appreciably. The reduction in SiC particle size leads to a greater number of pores and a decrease in pore size. This is due to the presence of a higher number of SiC particles, which have a smaller geometric surface area, as the particle size decreases.

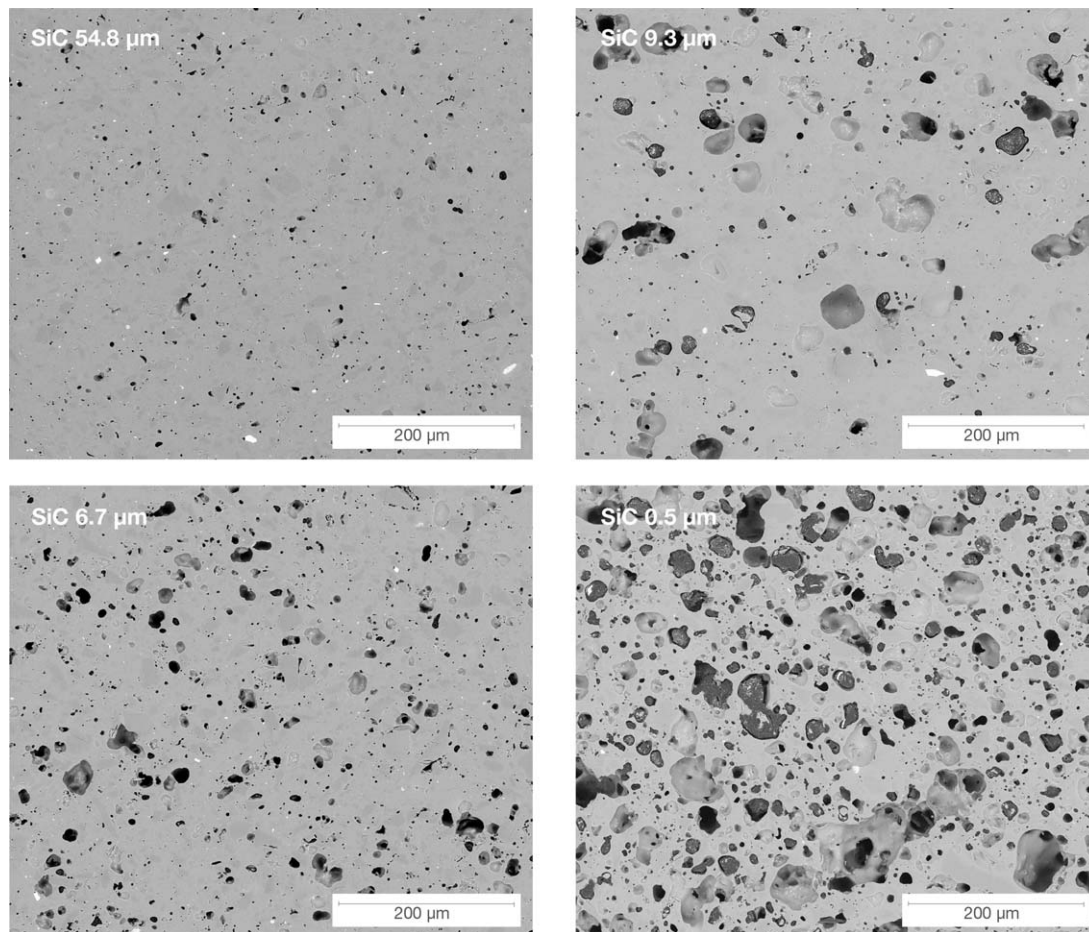


Fig. 7. Influence of SiC particle size on the microstructure. Firing temperature = 1200 °C.

An exception is represented by the sample produced with the finest SiC particles, which developed larger pores than expected (Fig. 7, bottom right), that may be due to a poor homogenisation with the other raw materials. The excessive growth of these pores reduced cell wall thickness, which leads to the opening of some of the pores within the sample and, as a result, to an increase in open porosity. The fact that rectified samples had the same water absorption values of non-rectified samples indicates that the interconnected pores are homogeneously distributed throughout the samples, and not concentrated at the surface.

3.4. Influence of SiC particle size on the properties of tiles with a bulk density of 1700 kg/m³

In this section, fired samples with a bulk density of 1700 kg/m³, involving a 30% decrease in weight, were obtained from compositions containing SiC with different particle sizes, for which the firing temperature was modified. The data for samples produced using the largest SiC particle size are not shown, because of the very high firing temperature that would be needed to reach the targeted density in this system.

Fig. 8 reports the evolution of the temperature at which the required density was reached (T_{1700}) as a function of SiC particle size. The use of smaller SiC particles reduces the firing temperature because the larger specific surface area of the foaming agent

particles boosts the expansion process. The relationship between both variables is linear in the studied range of SiC particle sizes.

The values of the open porosity of the pieces are also plotted in the figure. The compositions with SiC particles of 9.3 and 6.7 μm yielded pieces with very low open porosity values, while for the composition with the finest SiC particles (0.5 μm), the water absorption values exceeded 1.0 wt%. These results again confirm that, though the use of SiC with a very small particle size enables low bulk densities to be reached at low temperature, the

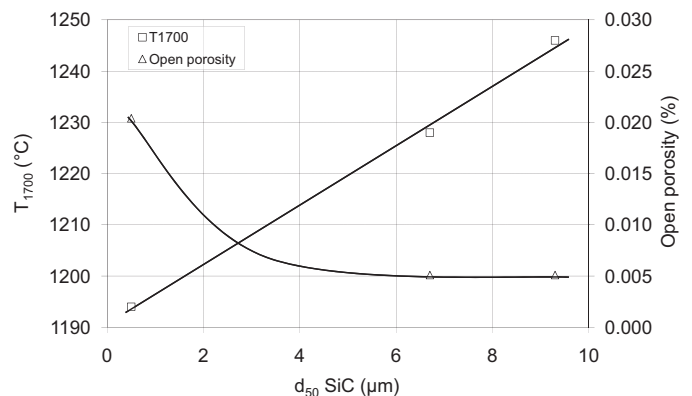


Fig. 8. Influence of SiC particle size on the firing temperature and open porosity. Tile bulk density = 1700 kg/m³.

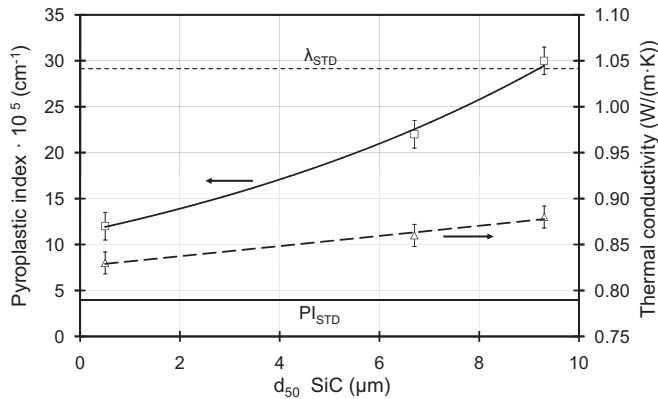


Fig. 9. Influence of SiC particle size on the pyroplastic index and thermal conductivity. Tile bulk density = 1700 kg/m³.

resulting water absorption values border on regulatory requirement limits. The mechanical strength values do not change with SiC particle size (values ranged from 33 to 36 MPa), because the samples contained the same amount of total porosity, and are of the same order as those required by the standards for porcelain tiles (35 MPa).

SiC particle size notably influences the pyroplastic deformation, as can be seen in Fig. 9 (the horizontal solid line represents the pyroplastic index of the STD composition, PI_{STD}). Thus, as the average SiC particle diameter becomes smaller, the pyroplastic deformation decreases as a result of the lower temperature needed to reach the required density. The values of the pyroplasticity index are higher than those of the STD composition in every case, which could lead to deformation problems in the pieces at high temperature.

The thermal conductivity of the pieces with decreased weight is 20% lower than that of the STD pieces (shown in Fig. 9 as a horizontal dashed line, λ_{STD}), so that the new products should enhance thermal insulation. The reduction in SiC particle size leads to a slight reduction in thermal conductivity, which must be related to the porous texture of the pieces (see Fig. 10).

In fact, we can observe that in these tiles, in which the total porosity remains constant, the number of pores increases but their average size decreases with decreasing the particle size of the foaming agent. This change in the porous architecture most

probably decreases the heat flux by radiation inside the pores, and increases the tortuosity of the solid phase, slightly reducing heat transfer by conduction.

4. Conclusions

In this paper, the possibility to fabricate lightweight porcelain stoneware tiles with appropriate mechanical strength and water absorption below 0.5 wt% was investigated, by adding SiC with different particle sizes as foaming agent to a conventional porcelain mixture. The following conclusions can be drawn:

- SiC is a very effective foaming agent for reducing porcelain tile density, because it lowers the expansion temperature and boosts the expansion process. This effect becomes more pronounced as the SiC particle size decreases.
- The SiC addition, under the test conditions used in this study, provides a poorly connected pore system comprised of small pores (15 μm), characteristic of porcelain tiles, and large pores (between 50 and 100 μm) generated from the SiC particle oxidation. The reduction in SiC particle size leads to microstructures with a greater number of pores, but a smaller average pore size.
- In order to obtain lighter porcelain tiles at 1200 °C, it is necessary to use SiC with an average particle size below 10 μm. The maximum attainable porosity, without reducing the mechanical strength of the porcelain tiles below the values required by the standards, is 35 vol.%, which is equivalent to a product which is 26% lighter.
- To achieve a given decrease in weight of a tile, it is advisable to use SiC with a small particle size (below 10 μm). This reduces the porcelain tile firing temperature, pyroplastic deformation, and thermal conductivity, although it slightly increases the open porosity, if the SiC particle distribution in the tile is not uniform.
- Using this approach, it is possible to obtain porcelain tiles with lower density and zero water absorption at the customary porcelain tile firing temperatures. The maximum attainable decrease in weight is limited by the loss of mechanical strength of the tiles and their pyroplastic deformation.

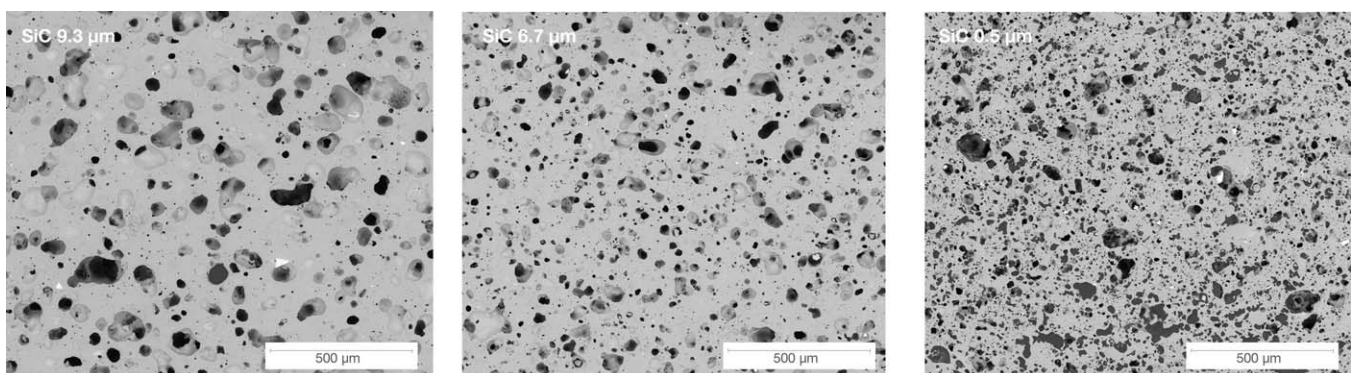


Fig. 10. Influence of SiC particle size on the microstructure. Tile bulk density = 1700 kg/m³.

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