VISCOUS FLOW SINTERING OF PORCELAIN STONEWARE REVISITED

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1. ABSTRACT

Porcelain stoneware tiles, as porcelain items, are sintered by vitrification through viscous flow of an abundant liquid phase formed at high temperatures. Such a process must be kept under strict control to achieve the desired properties of final products and prevent defects induced by pyroplasticity. This is particularly true for large tiles, where production emphasises on requirements of uniform densification and minimal deformations at high temperatures. This contribution will critically overview the state-of-the-art of porcelain stoneware sintering and the challenges for the development of large slabs. The level of acquaintance with different phenomena involved in viscous flow sintering will be discussed, discerning what is already known, what is recognised, but still needs to be fully understood, and what could arise from in-depth comprehension. The KNOWNS: the evolution of microstructure and phase composition during firing is well known and phenomenological models have been developed for viscous flow densification of porcelain stoneware. Combined effects on pyroplasticity by liquid phase viscosity and solid load have been disclosed. The way by which Na/K ratio and other chemical keys of porcelain stoneware composition affect sintering kinetics is known. The role of mullite crystallisation/dissolution and beta-alpha quartz transition on technological properties has been recognised. The KNOWN UNKNOWNS: dynamic changes in composition and physical properties of the liquid phase during firing are envisaged, but vitrification and reactive sintering have not been modelled yet. In particular, there are uncertainties regarding the actual effect on sintering kinetics and

pyroplasticity due to crystals suspended in the melt according to their variable shape and size distribution. The effect of starting porosity on densification degree and kinetics; the homogeneity and miscibility of liquid phases; gas solubility in the liquid phase at the highest firing temperatures (and its role on closed porosity and bloating); the Fe^{2+}/Fe^{3+} ratio dependence on temperature and its consequence on the melt viscosity remain unclear. The UNKNOWN UNKNOWNS: modelling of densification curves and prediction of physical properties of porcelain stoneware tiles, through computational calculations, may prefigure the role of further variables not considered yet. The extension of such modelling efforts from laboratory to industrial scale may disclose the occurrence of scale effects, particularly in the case of large slabs and different shaping techniques. A better comprehension of kinetic aspects, resulting by the convolution of various factors, may unveil unexpected results, such as memory effects from raw materials or microstructural features.

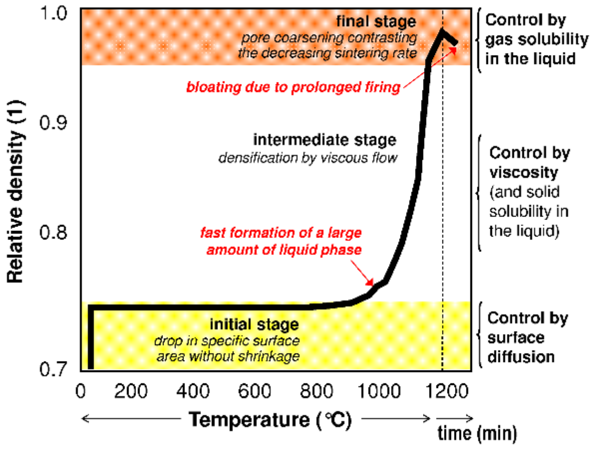
2. INTRODUCTION

Porcelain stoneware tiles are manufactured by fast firing (typically, 1200-1230°C of maximum temperature and 50-70 min cold-to-cold).As in porcelain bodies, sintering proceeds by vitrification with consequent viscous flow of the abundant liquid phase formed at high temperatures [1, 2].This process entails a fast densification rate (5-8% linear shrinkage in 8-10 min) that must be kept under strict control to achieve the desired properties of final products [3, 4].In particular, water absorption must be kept well below 0.5%, and defects connected with pyroplasticity have to be prevented [5-7].

The concern on firing control is even more pronounced in the case of large slabs, e.g. 360x120 cm, whose production requires uniform densification and minimal deformations at high temperature [8, 9].From this standpoint, the present contribution aims at critically overviewing the state-of-the-art of porcelain stoneware sintering, emphasising the challenges for the development of large ceramic slabs. This review follows the level of acquaintance achieved in the literature with the different phenomena involved in viscous flow sintering, first approaching the present background (*the Knowns*).Then the discussion will discern what is already recognised, but still needs to be fully understood (*the Known Unknowns*) and what might arise by sharpening the comprehension of what occurs in viscous flow sintering (*the Unknown Unknowns*).

3. THE KNOWNS

The mechanisms governing the viscous flow sintering are known (Fig. 1): after the initial stage, where sintering is essentially driven by surface diffusion with progressive reduction of specific surface area, the formation of a large amount of melt occurs in a narrow temperature range (1000-1100°C).This gives rise to a viscous flow, controlled by viscosity and surface tension of the liquid phase, which are in-turn influenced by the solubility of crystals into the melt. Such a process brings about the fast densification characterising the intermediate stage. The sintering rate gradually decreases while approaching the maximum density achievable in the final stage, where viscosity and gas solubility in the liquid control the pore coarsening, and where bloating phenomena may occur [10-12].



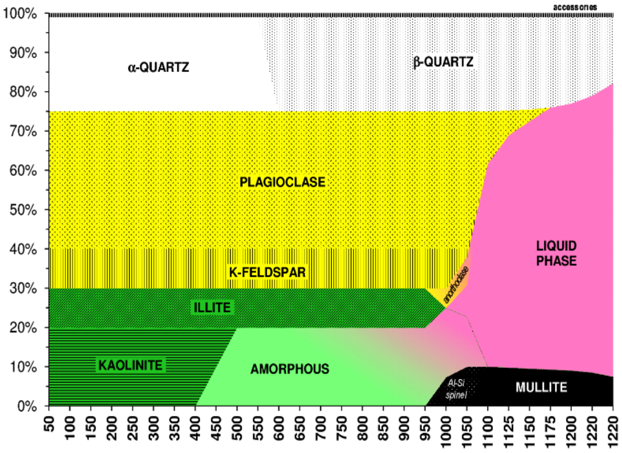


Figure 1*.Sintering stages and mechanisms active during firing of porcelain stoneware.*

Figure 2. *Phase evolution with firing temperature of a typical porcelain stoneware body.*

Densification curves of porcelain stoneware are known in detail, at both industrial and laboratory conditions, and phenomenological models have been proposed [13-16].This knowledge paved the way to the first attempt to get a computational prediction of firing shrinkage in porcelain stoneware tiles [17] by analogy with sanitary-wares [18, 19].

The combined evolution of microstructure and phase composition during firing has been thoroughly investigated in porcelain stoneware tiles [2, 20-31] as well as in vitreous China [7, 30-31]. This allows to draw a generalised picture of phase transformations occurring to mineral components in porcelain-like bodies (Fig. 2):

- clay minerals breakdown and transformation into amorphous phases [25, 27];
- melting of feldspars, involving amorphous clay remnants and successively silica phases [2, 27, 30];
- formation of new compounds, particularly mullite, and transient phases [20, 25, 31] which was sometimes observed in porcelain stoneware (Al-Si spinel, anorthoclase, sanidine);
- persistence of refractory phases [25, 30, 31] although partially dissolved in the melt (quartz, mullite, zircon, rutile).
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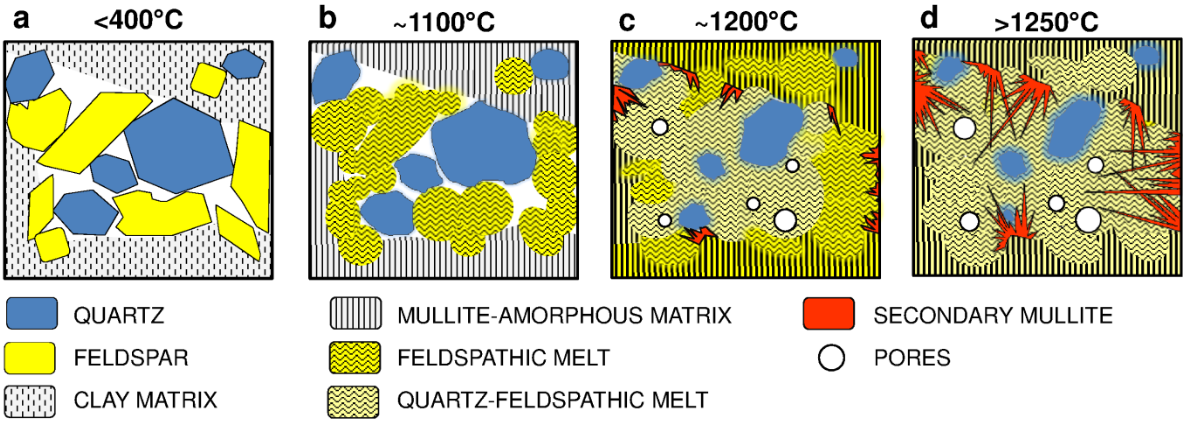

Figure 3*. Microstructural evolution of porcelain-like materials during firing.*

These phase transformations imply a parallel microstructural evolution with increasing temperature from the starting assemblage of feldspars and quartz grains dispersed into a fine-grained matrix that accommodates clay minerals and porosity (Fig. 3a). Vitrification causes the main microstructural changes by formation, from 1000 to 1100°C, of glassy ponds (Fig. 3b). Such a melt wets the crystalline grains and its permeation through the mush accounts for densification in the 1100-1200°C range (Fig. 3c). Along with vitrification and viscous flow, solid-liquid reactions occur, particularly quartz partial melting and dissolution/crystallisation of mullite, with eventual growth of elongated crystals of secondary mullite (Fig. 3d). The final microstructure consists of a vitreous phase with crystals embedded [21-23, 28, 29].Such features can be compared with those observed in porcelain and vitreous china [7, 30-33].

Thermal transformations may translate into deformations at high temperature, usually referred to as *pyroplasticity* [5, 6]. It is generally acknowledged that both liquid phase viscosity and solid load (amount, size and shape of crystals) govern the pyroplastic behaviour [34-40]. On the other hand, it is well known that the Na_2O/K_2O ratio and other chemical keys of porcelain stoneware composition do affect sintering kinetics [34, 37, 38, 41-46] as well as in porcelain-like materials [47-51]. This control is exerted through the amount and physical properties of the vitreous phase, which vary according to the chemical composition of the melt [2, 52].

Mullite and its role in technical performance of porcelain stoneware tiles have been extensively investigated [25, 47, 53-58]. Both the kinetics of mullite formation from metakaolinite [47, 53, 56-58] and the development of secondary mullite [20, 27, 54, 59] were of particular concern.

The role of the $\beta \leftrightarrow \alpha$ quartz transition is amply recognised, not only for possible ruptures during cooling [60-64] but also for its effect on elastic properties and residual stresses [61, 64-66].

4. THE KNOWN UNKNOWNS

The microstructural and phase transformations, as pictured in Figures 2 and 3, imply dynamic changes in phase assemblage and chemical composition of melt. Consequently, the physical properties of the liquid phase, which depend on its chemical characteristics, are continuously changing during firing. This evolution is known just approximately [1, 2], despite its key-role in vitrification and sintering, and it has not been modelled yet.

There is uncertainty regarding the actual effect of crystals suspended in the melt on sintering kinetics and pyroplasticity. Despite having evidences of the determinant role of a variable solid load arose, contrasting views still exist on the effect of crystal shape and size on firing deformations [5, 7, 21, 35, 39, 40]. The case of mullite is emblematic; its effect on mechanical properties of porcelain stoneware is still debated. A direct correlation of modulus of rupture and fracture toughness with the mullite amount has been reported [67-69], claiming for strengthening mechanisms analogous to those known in porcelain [70]. However, the mullite percentage present in porcelain stoneware is much lower than in porcelain wares [2, 70] and in several cases an adverse relationship with mechanical properties stood out [24, 71, 72].This varying behaviour likely depends on the complex microstructural features of mullite, including the possible occurrence of elongated secondary crystals, as its crystallisation/dissolution fate during the vitrification path [73].

In the attempt of lowering the firing temperature of porcelain stoneware tiles, the interest for unconventional and strong fluxes has grown, e.g. those containing large amounts of alkaline-earth oxides or boron compounds [34, 42, 43, 46]. In these bodies, a peculiar firing behaviour was disclosed [44] that is not completely clarified yet. Instead of the usual firing curves, converging towards a minimum water absorption matching the maximum shrinkage and bulk density (Fig. 4a), it may happen that the minimum water absorption is reached only after the shrinkage and bulk density turnaround (Fig. 4b).

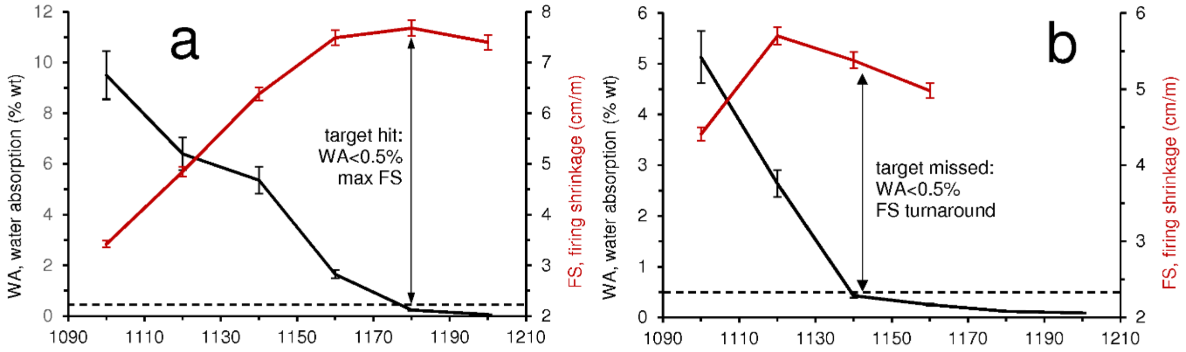

Figure 4. *Sintering curves of (a) a typical porcelain stoneware body and (b) a modified batch containing 2.5% of a strong flux (ulexite); data after Melchiades et al.[44].*

The effect of the initial porosity on the densification degree is still undefined. It was observed that the larger the pore volume of unfired tiles, the faster the sintering kinetics [12, 59]. Although a lower bulk density value of the green tile leads to a lesser dense porcelain stoneware, after the same firing schedule, the initial porosity difference is largely recovered during sintering and the final values of bulk density exhibit a limited difference. The influence of the starting porosity is recognised in glass sintering [74] but its relevance in porcelain stoneware is still to be proven.

Another matter that raises questions is the homogeneity and miscibility of liquid phases formed in porcelain stoneware bodies. The time available with fast firing schedules is generally thought to be insufficient to allow a homogenous melt to form, in as much microstructural investigations highlighted compositional gradients in the glassy phase of slow-fired porcelain [32, 33, 73]. Nevertheless, alkali diffusion in silicate melts is very rapid and experimental evidences demonstrate it can take place over a time span of minutes [75].

Another pending question concerns the role of gas solubility in the liquid phase at the highest temperatures, when the sintering pressure is decreasing and the closed porosity may increase, giving rise to bloating for prolonged firing. Water vapour is able to increase the sintering kinetics in porcelain [76]. In addition, it was envisaged that the flue gas solubility could change along with variations in viscosity and composition of the melt [77], but no experimental demonstration is available for porcelain stoneware.

On the other hand, it is thought that the oxygen release due to iron reduction (e.g., hematite breakdown: $Fe_2O_3 \rightarrow 2FeO + ½O_2$) could contribute to the pore coarsening in the final sintering stage [78]. In addition, the occurrence of Fe^{2+} could significantly drop the melt viscosity [79]. However, no data about the Fe^{2+}/Fe^{3+} ratio dependence on firing temperature are available for porcelain stoneware.

5. THE UNKNOWN UNKNOWNS

The prediction of firing behaviour of ceramic tiles is challenging, particularly for porcelain stoneware, because of several phenomena occurring at a multiple scale: from atomic mobility (e.g., ionic diffusion through the melt) to microstructural rearrangement (consequent to phase transformations and vitrification) to shrinkage and deformations regarding the product as a whole.

The need of computational calculations for modelling the firing behaviour will require further efforts to improve the comprehension of phenomena entailed in porcelain stoneware sintering. This process might disclose the role of further variables, not considered yet, or the interdependence of factors.

The extension of such modelling efforts from laboratory to industrial production will likely reveal the occurrence of scale effects, particularly in the case of large slabs, and a possible dependence on technological processing (e.g., different shaping techniques).

A better comprehension of kinetic aspects, resulting by the convolution of various factors, may unveil unexpected results, such as memory effects from raw materials or microstructural features.

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