STUDY OF THE SINTERING AND CRYSTALLISATION OF SATIN GLAZES. EFFECT OF THE NATURE OF THE GLAZE

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ABSTRACT

The sintering, crystallisation, and fusion phenomena in two glazes of the satin type for floor tiles were studied, and the aesthetic characteristics and technical properties of the resulting fired glaze coatings were determined. In one glaze formulation, boron was introduced as a calcined compound and the frit content in this glaze composition was low (30%). In contrast, the other glaze was practically made up of a frit (70%) that, among other constituents, also contained boron. Despite the different behaviour of these glazes with relation to sintering, crystallisation, and fusion, and their also very different chemical, mineralogical, and microstructural characteristics, their chemical and mechanical properties, as well as their aesthetic characteristics, were appropriate.

1. THEORETICAL ASPECTS

In accordance with the model of Exner *et al*. [1], the sintering rate of glass particles may be expressed as:

$$\frac{dX}{dt} = (1 - X) \cdot \frac{\pi}{d_0} \cdot \frac{1}{(1 - \rho_0^{1/3})} \cdot \frac{\gamma}{\eta} \qquad (1)$$

where:

X = linear shrinkage/maximum linear shrinkage or sintering degree of advance.

d_0 = average particle size (m).

ρ_0 = initial compactness of the particle bed.

γ = glass surface tension ($N \cdot m^{-1}$).

η = glass viscosity (Pa·s).

In experiments at constant-rate heating (a = dT/dt):

$$\frac{dX}{dT} = (1 - X) \cdot \frac{\pi}{a \cdot d_0} \cdot \frac{1}{(1 - \rho_0^{1/3})} \cdot \frac{\gamma}{\eta(T)} \qquad (2)$$

According to this equation, the new sintering rate (dX/dT) is the result of two antagonistic effects that develop simultaneously with the increase in temperature: a notable reduction in viscosity ($\eta(T)$) and an increase in the sintering degree (X).

Clearing $\eta(T)$ in Eq. (2) yields:

$$\eta(T) = \left[\frac{dX}{(1 - X) \cdot dT}\right]^{-1} \cdot \left[\frac{\pi \cdot \gamma}{a \cdot d_0 \cdot (1 - \rho_0^{1/3})}\right] \qquad (3)$$

This expression allows $\eta(T)$ to be estimated from the values of the variation of X and dX/dT with temperature, obtained in sintering experiments at constant-rate heating. Note that the second factor of the second member does not depend on temperature.

Glaze sintering and subsequent fusion processes are far more complex than those of glass particles, because the rate at which both processes unfold largely depends on the development of other transformations that take place simultaneously, such as the crystallisation and melting of unfritted components. Indeed, these last transformations substantially modify the natural decrease in glassy phase viscosity with an increase in temperature, and hence the sintering rate.

In order successfully to address glaze behaviour during firing, it is useful to apply the concept of glaze effective viscosity. This is defined, in the temperature range in which sintering develops, as $\eta(T)$, which is obtained on applying the pre-

vious model (equation 3) to the glaze sintering results. In the melting temperature range, the approximation of fixed viscosity points is used, which consists of assigning a viscosity value to a certain degree of circular test piece deformation.

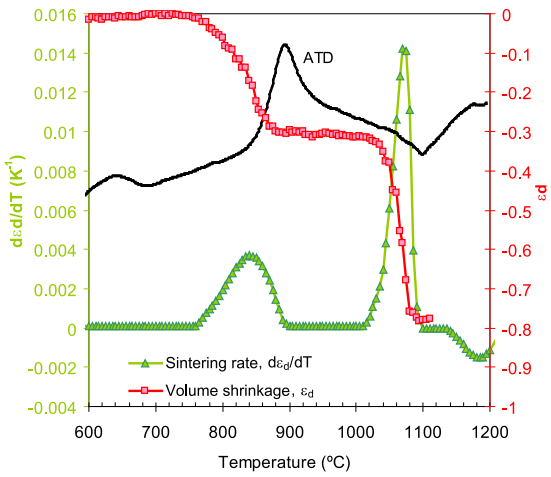
3. EXPERIMENTAL

The sintering and fusion curves were determined of glaze composition A, 70% of which consisted of a frit with a high content in alkaline earths, and of glaze composition B, which contained a low percentage of frit (30%) and a calcined boron compound, by hot stage microscopy (HSM) at a heating rate of 25ºC/min, calculating the volume shrinkage and fixed viscosity points from the projected test piece silhouettes. The crystallisation range of the glaze was determined by DTA at a rate of 25ºC/min. In order to determine the crystalline phase content of the glaze as a function of temperature, cylindrical test pieces of these glazes were prepared and fired, also at 25ºC/min, to different maximum temperatures. The phases present in the fired test pieces were determined by XRD using the Rietveld method [2]. Tiles coated with these glazes were also fired, according to an industrial cycle, at 1140ºC and the most important surface and aesthetic properties in the fired products were determined.

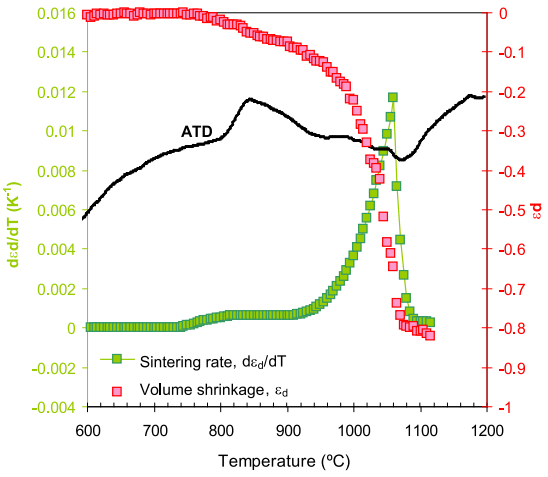
4. RESULTS

It was verified that the two fired glaze coatings, which had a matt appearance, displayed very similar technical and aesthetic characteristics because the firing temperature, coating microstructure and percentage of crystalline phases, of micrometric size, were also very similar (Figures A2 and B2).

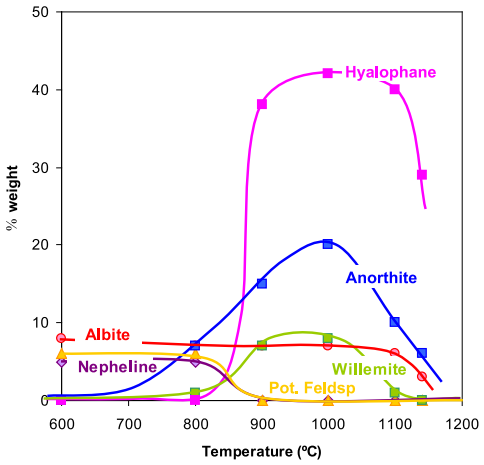
The volume shrinkage (ε_d) and the sintering rate ($d\varepsilon_d/dT$) with temperature of glaze A exhibited the typical behaviour of glasses that crystallise abundant crystalline phases in the range of sintering temperatures (Figures A1 and A2). The sintering halt corresponded to the DTA peak assigned to the crystallisation of the phases that appear in Figure A2. Sintering was only reinitiated when a high percentage of crystalline phase dissolved in the melt and melt viscosity decreased, mainly owing to the rise in temperature. Sintering then continued until it was completed at temperatures of about 1100ºC.



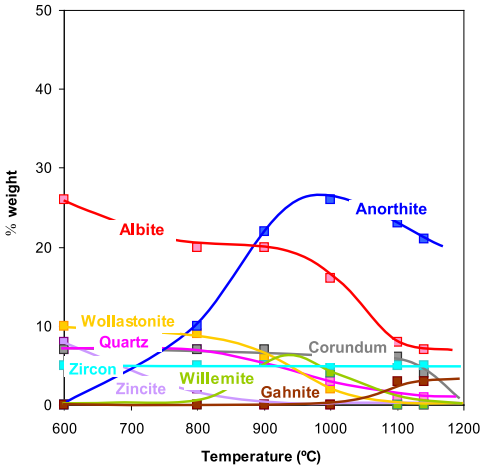
A1



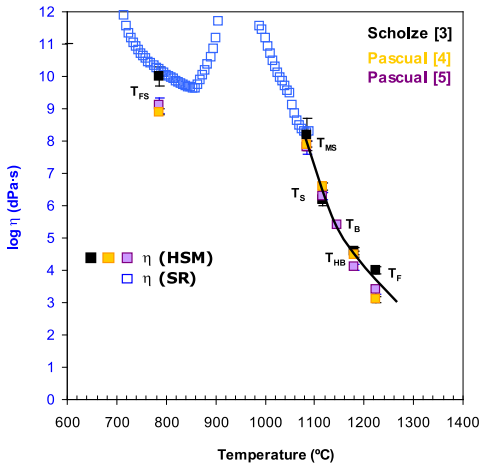
B1



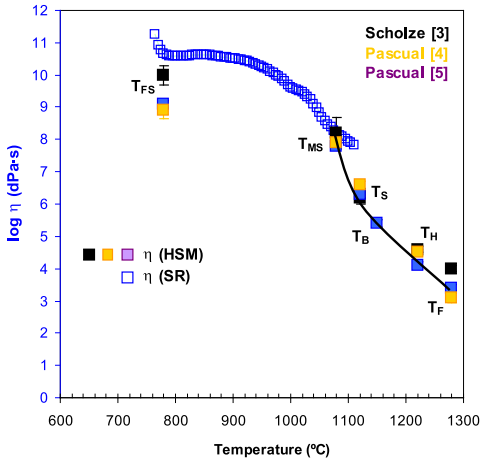
A2



B2



A2



B3

<u>Glaze A</u>. Sintering and crystallisation (A1). Variation of crystalline phases with temperature (A2). Fusion (A3).

<u>Glaze B</u>. Sintering and crystallisation (B1). Variation of crystalline phases with temperature (B2). Fusion (B3).

The thermal behaviour of glaze B (Figures B1 and B2) differed from that of A, mainly because in this glaze the unfritted starting components partly melted concurrently with anorthite crystallisation. As a result, only a slight slowing of the sintering process was noted, which coincided with the DTA peak. At higher temperatures, the progressive increase in liquid phase resulting from the partial fusion of the starting components and the anorthite and from the reduction in melt viscosity, produced by the rise in temperature, led to the complete sintering of the glaze at temperatures of about 1100ºC.

Plots are shown in Figures A3 and B3, for glazes A and B respectively, of the variation of their viscosity calculated from the sintering model (equation 3), in the range of sintering temperatures. The characteristic viscosity points, according to different authors, have also been plotted. It may be observed that the effective viscosity found in the sintering tests perfectly matched the results obtained using the characteristic points technique, thus completing the viscosity curve of a glaze.

5. CONCLUSIONS

The sintering, crystallisation, and fusion of two glazes with similar (technical and aesthetic) properties, but having different compositions, were studied. Once they had been fired at the appropriate firing temperature, both were found to display very similar microstructural characteristics. The simultaneous determination of the sintering rate–temperature curves, obtained by HSM, and of the DTA curves was confirmed to be a suitable procedure for studying glaze sintering. It was verified that the determination of the effective viscosity–temperature curve of a glaze from the sintering experiments, applying the proposed model, is very satisfactory.

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