STUDY OF SURFACE POROSITY IN CRYSTALLINE GLAZES

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ABSTRACT

A study has been undertaken of the evolution of surface porosity in transparent glassy crystalline glaze coatings, consolidated at different heat-treatment temperatures, and its influence on the quality of the glassy coating. The study was conducted on a crystalline glaze used in the manufacture of fast double-fired wall tiles. The evolution of the resulting porosity in the different glaze sintering stages has been characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Key words: *crystalline glazes, sintering, porosity*

1. INTRODUCTION

The glaze application systems and decorating techniques used in the manufacture of ceramic floor and wall tiles have evolved significantly in recent years. The most recent technological advances pursue new finishes and aesthetic effects, which until recently were difficult or impossible to achieve. On the other hand, certain widely used technologies in the manufacture of advanced ceramics offer new possibilities of great interest for research into the glazes used in ceramic floor and wall tiles[1]. The manufacturing process of these coatings is complex and requires control of the uniformity of thickness and the absence of defects.

Various defects may be encountered in the glaze surface, the most common being *waves*, owing to lack of time or temperature for the glaze to level; *pinholes*, caused by gases evolving from the body; and *craters*[2,4]. The origin of these defects may vary: frit particles of a size comparable to coating thickness, crystalline particles that do not enter the melt, occluded bubbles in the glassy matrix, etc. These treatment temperature-dependent defects can give rise to pinholing or pores in the surface of the glassy coating.

In glassy materials, sintering develops by a viscous flow mechanism [3,4,5]. Viscous flow sintering begins at glass softening temperature and is encouraged by increasing temperature. During the sintering process, the glassy particles soften and begin to generate liquid phase. The liquid begins to flow and drags along rests of unmelted material. The pores are transformed and lose the characteristic interconnection of the unfired material on developing a system of closed pores. As temperature rises, the quantity of liquid phase increases and its viscosity decreases. Once the glaze has melted, the surface stretches and the pores practically disappear. When the ceramic glaze contains crystalline particles that do not melt during firing, the sintering rate decreases and can be arrested when the inclusions enter into contact with each other and form a rigid structure. This process can occur in an analogous way as a result of the devitrification of crystalline phases in the melt [5].

In this paper, the evolution of crystalline glaze porosity with heat-treatment temperature is studied.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

The study has been carried out on a crystalline glaze with an industrial composition, which is used in the manufacture of fast double-fired wall tiles. The bodies glazed in the line underwent subsequent heat treatment in an electric laboratory kiln, according to an industrial firing cycle of ~ 45 minutes. The peak firing temperature was 1142 °C. At lower treatment temperatures, the residence time at the temperature was 10 seconds and the samples were then cooled according to the same cooling cycle.

The crystalline glaze samples were studied by hot stage microscopy with a Leika microscope. The samples used were cylinders 3 mm high x 2 mm in diameter[6]. The test was run at a heating rate of 20°/min.

Differential thermal analysis (DTA) of the samples was performed with a Netzsch instrument.

Surface analysis of the samples was performed by scanning electron microscopy (SEM, with a Carl Zeiss DSM-950 microscope.

Topographic analysis of the samples was conducted by atomic force microscopy (AFM) with a Burleigh SPM microscope. The atomic force microscope (AFM) is a basic research tool for surface analysis on an atomic level. It is a non-destructive technique that allows visualizing the general characteristics of a sample surface. The samples used corresponded to as-fired surfaces.

3. RESULTS

Figure 1 shows the evolution of crystalline glaze shrinkage by hot stage microscopy (HSM) together with DTA. Glaze shrinkage begins at ~ 850 °C and the sintering stage governed by the viscous flow mechanism commences. In the 1025 °C to 1050 °C temperature range, densification slows. At 1050 °C the glaze has melted, in accordance with the DTA curve.

The results obtained in the glaze characterization show that glaze sintering begins at 950 °C by the appearance of liquid phase, while after 1050 °C glaze melting is less effective in the porosity elimination stage. In order to study this in further detail, we analysed the surface porosity of samples fired at temperatures of 950, 1000, 1050, 1100 and 1142 °C.

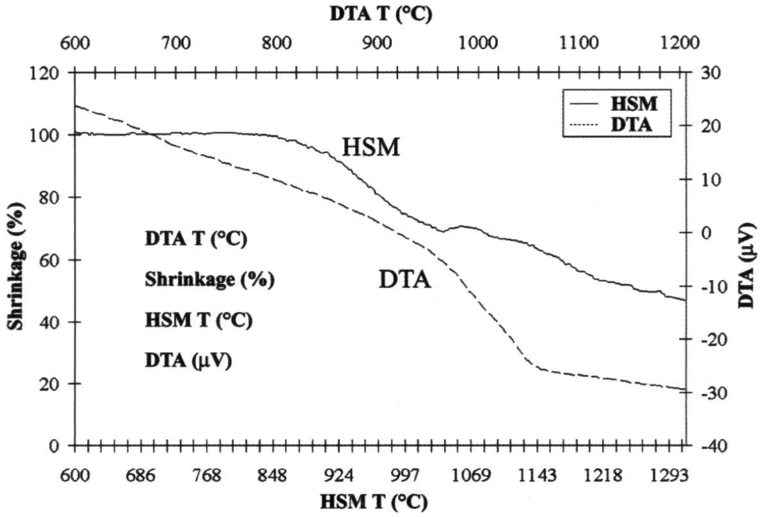
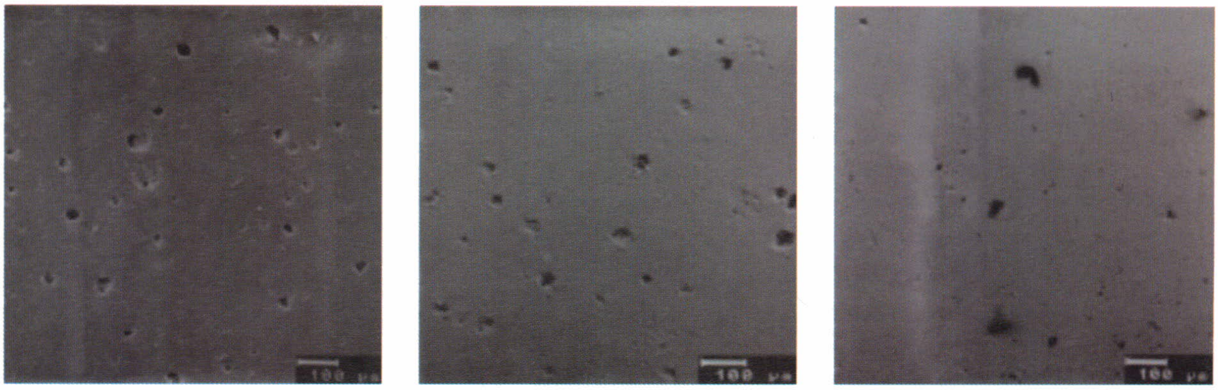
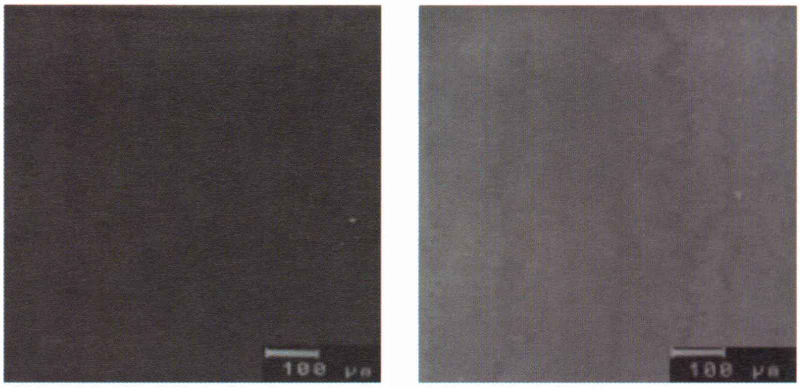


Figure 1. Curve of area variation and DTA as a function of crystalline glaze temperature.

Figure 2 shows glaze surface porosity. In the micrographs of the samples treated at 950 and 1000 °C abundant porosity can be observed at the sample surface. This porosity has an irregular shape and is generalized across the entire glaze surface. Average pore size (assimilating pore shape to spherical pores) is less than 50 µm. The structure of these surface pores exhibits a crater-type nature with crystalline particles along the edge (Figure 3). These particles act as diffusion limiters for very high viscosity liquid phase. With the rise in temperature, liquid phase viscosity decreases and contributes to the reduction in pore size at the surface just as in the interior. The existence of particles that do not enter the melt maintains the irregular pore structure.



950 °C 1000 °C 1050 °C



1100 °C 1142 °C

Figure 2. SEM micrographs of the crystalline glaze surface.

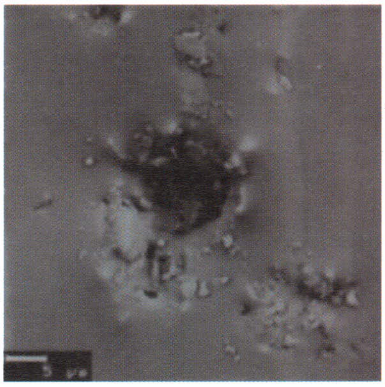
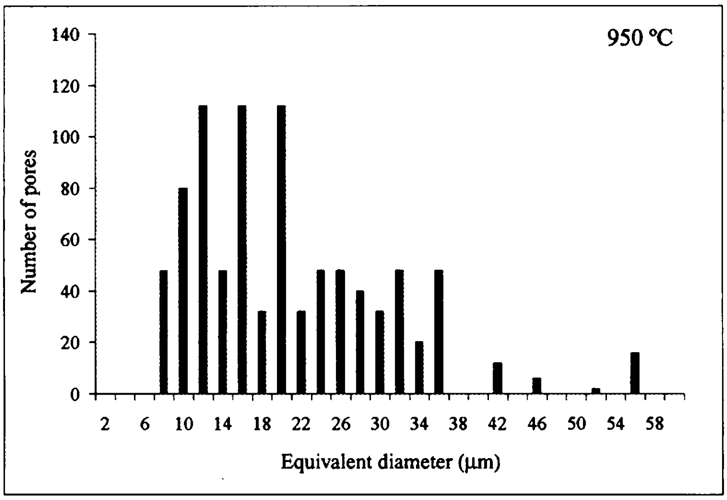


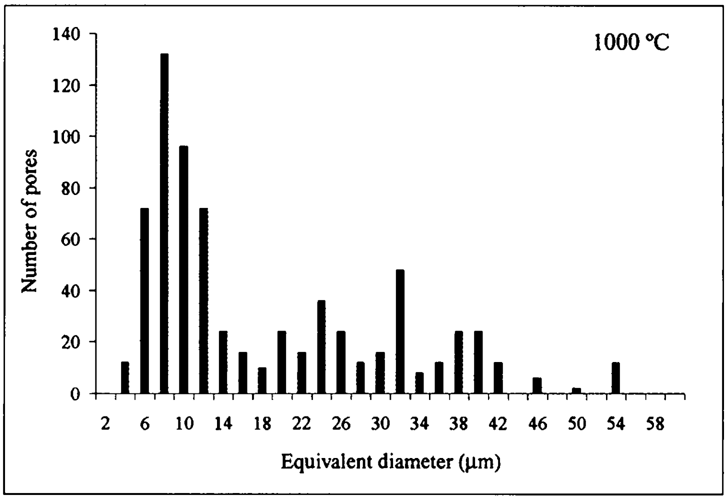
Figure 3. Surface micrograph of a pore of a crater-type nature (1000 °C).

At 1050 °C the pores have decreased considerably. As the glassy mass has not yet melted completely and surface stretching has therefore not taken place, the pores decrease in size owing to mass transfer from the surface inwards into the pores.

At temperatures of 1100 °C or higher, the glaze has melted and the surface has stretched. Inside the glaze the pores have consolidated as bubbles (not shown), whereas at the surface only isolated pores are detected. No rests of unmelted material are observed.

Figure 4 shows the distribution of surface porosity evaluated by image analysis techniques.





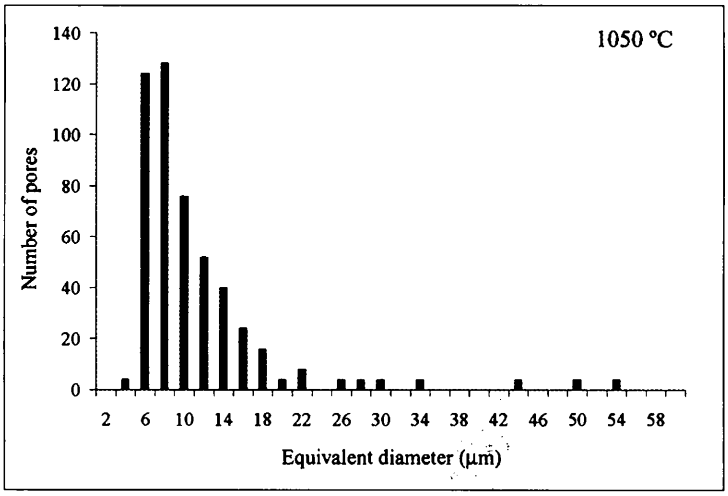


Figure 4. Porosity histograms.

An irregular and very wide pore distribution can be observed at the surface at 950 ºC. Increasing firing temperature to 1000 ºC causes a slight reduction in average size. A distribution appears, which centres around ~ 6 - 8 µm equivalent pore diameter, while the wide initial distribution still remains. At 1050 ºC, most of the pores are observed to close and they display a distribution centring around 4 - 6 µm, while pore rests of sizes exceeding 20 µm are still found.

The AFM micrographs in Figure 5 show that at 950 ºC, glaze surface porosity stems from the difficulty of packing the material, and is irregular, displaying a crater-type structure with crystalline particles along the edges, which form peaks surrounding valley regions. The dimensional differences between the highest regions (peaks) and the deepest ones (valleys) are ~ 0.1 µm. This value causes surface topography to be imperceptible to the SEM techniques in cross sections.

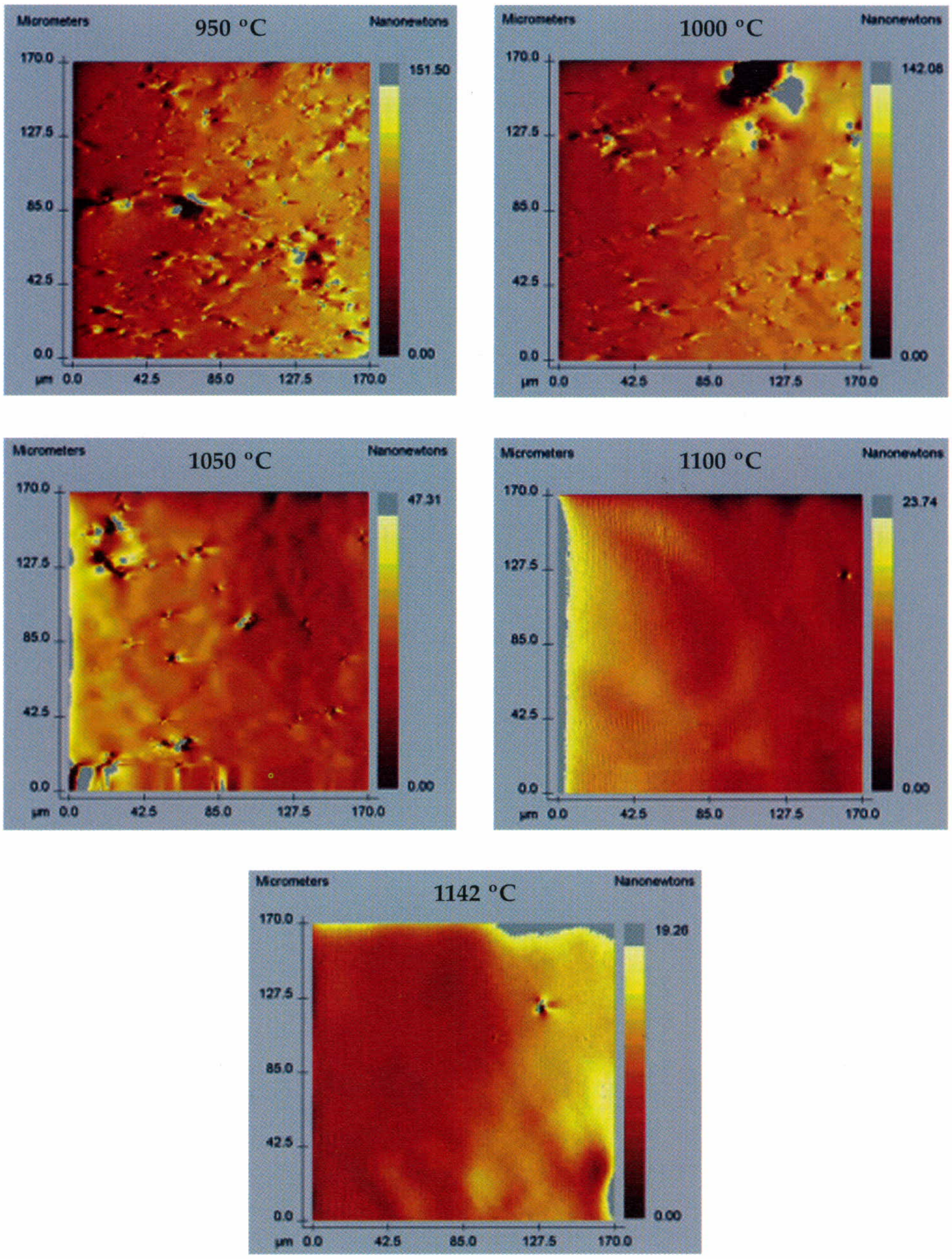


Figure 5. AFM micrographs of the crystalline glaze surface.

When temperature increases, particles continue to exist that do not enter the liquid phase and act as flow movement inhibitors. The existence of non-dissolved particles in the melt helps maintain the structure of irregular valleys which progressively close, with decreasing differences in heights.

At 1050 °C the glaze begins to melt, and the valleys and peaks progressively disappear, while some rests corresponding to former pores that have been unable to close are left. The valleys have not been completely covered and glaze surface stretching has not occurred here. At 1100 °C the glaze melts and the surface stretches. The troughs lose their irregular shape and start forming deeper, rounded valleys. However, there are still certain incidental unmelted particle rests at the peaks. At 1142 °C the glaze has stretched completely. The residual porosity that is encountered is incidental and is attributable to the existence of pores with a critical size that have not been eliminated.

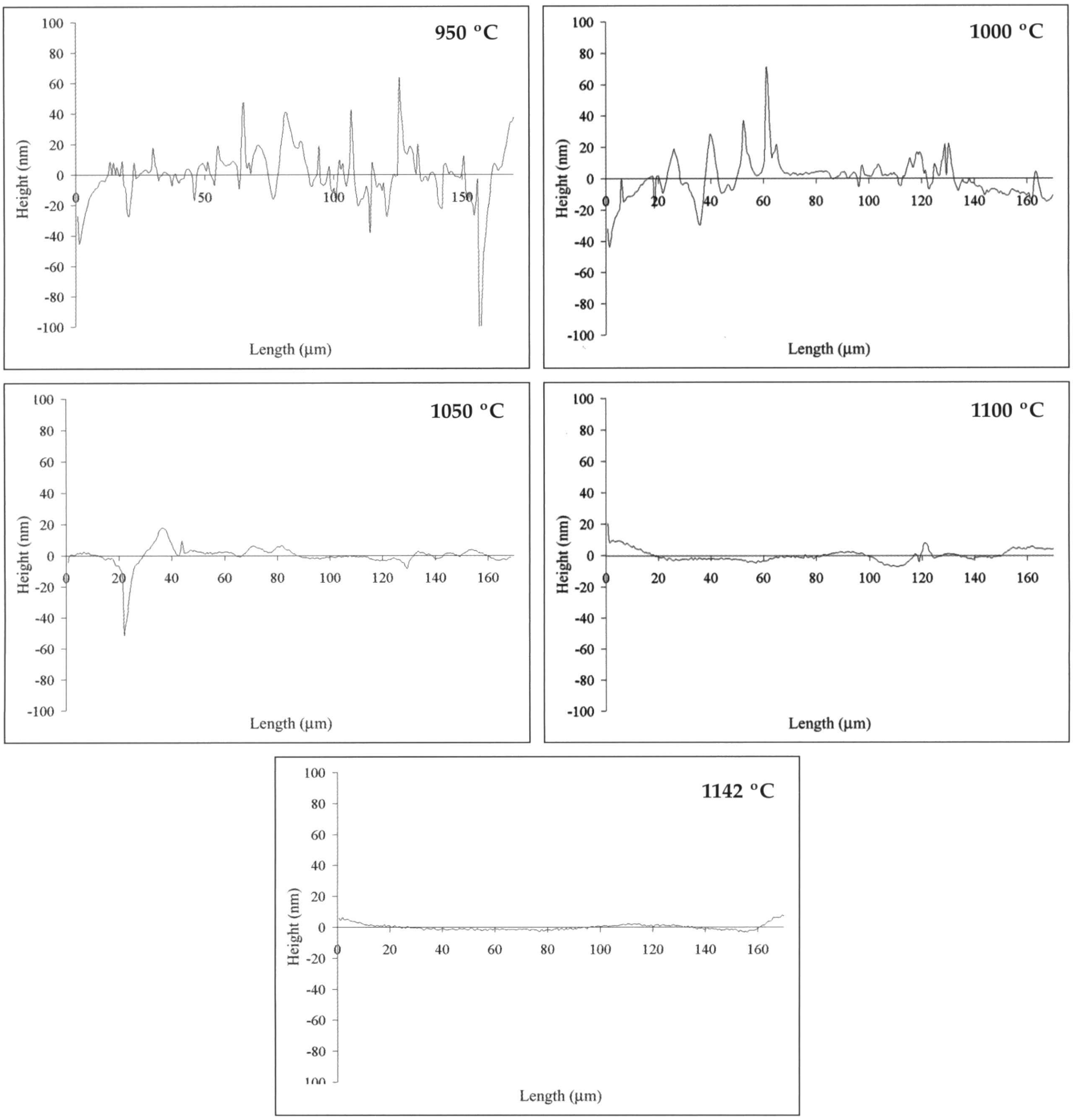


Figure 6. Profile curve.

Analysis of the characteristic profiles of the AFM micrographs of the fired sample surface, depicted in Figure 6, shows that increasing firing temperature notably reduces sample roughness. Two aspects may be noted; in the first place, the valleys (pores) are not deep, generally being less than 100 nm (0.1 μm) and, secondly, the presence of peaks is observed next to the valleys. Valleys and peaks appear to be related, as shown in the SEM micrographs. The peaks are related to crystalline particles that have not entered the melt and can locally increase the surface tension of the liquid, preventing glaze stretching.

At 950 °C the average peak height and semiwidth of their distribution (Figure 7) is greater than that of the valleys, which indicates that the number of non-dissolved particles is high. At 1000 °C peak height decreases with regard to that of the valleys. When sintering temperature rises, the quantity of particles that dissolves increases, reducing distribution height and semiwidth. At 1050 °C, the relation between valleys and peaks is in equilibrium, consistent with the fact that the elimination of porosity has slowed down in the stage prior to glaze melting. At temperatures where the glaze has melted, it is really no longer possible to speak in general of valleys and peaks; instead waves appear in the surface. These waves have a slightly higher initial roughness than that of the material at lower temperatures. The waves originate as a result of differences in the coefficients of expansion of the surface regions.

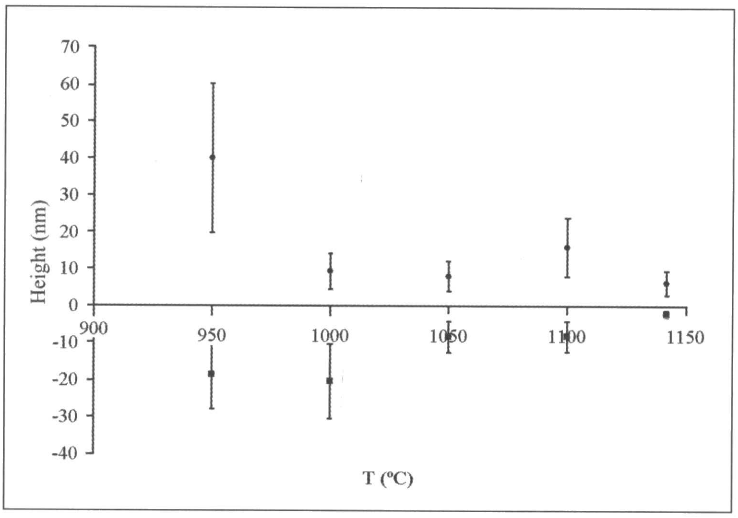


Figure 7. Curve that represents average size and semiwidth of the standard distributions of the valleys (▪) and peaks (•) with firing temperature.

Figure 8 schematically illustrates the effect of the peaks and valleys on mass transport at the glaze surface. The refractory particles are added to the glaze to reduce the sintering rate in the glaze mass and encourage the elimination of porosity in the mass before this closes. The presence of refractory particles in the peaks delays the glaze stretching temperature and therefore the elimination of porosity. Peaks form along the edge of the valleys owing to the existence of rests of unmelted material that prevent mass transport to regions of lower chemical power. It has been observed that

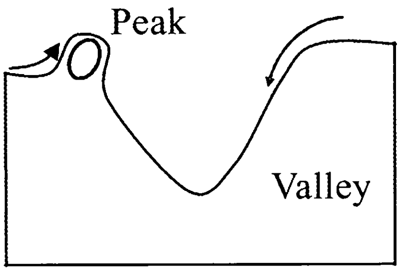


Figure 8. Diagram of crater and valley formation. The arrows indicate the mass transport direction.

if the troughs reach a critical size, they subsequently generate pinhole defects in the glaze.

Craters have traditionally been believed to be due to large bubbles bursting without time to level again. Bubbles are the result of the growth of gaseous nuclei, whose formation is encouraged by rough surfaces, edges and/or small particles in contact with the liquid phase. The porosity in the unfired glaze that has not been eliminated ends up as bubbles when the glaze melts, which explains the lesser effectiveness of melting as a porosity elimination process. The pores coalesce in bubbles that are in equilibrium in the glaze melt. The non-dissolved particles favour bubble formation because they are possible sites of gas nucleation and because they weaken the glaze structure in their proximity. The bubbles that burst and produce craters do not come from the body, but swell until their diameter exceeds the thickness of the glaze. The gases evolving from pores in the biscuit seem to be the most current cause of crater formation. Although a bubble that evolves from inside, forming craters at the surface[2] can contain particles suspended in the glaze, the evolution of pores in the unfired material and the effect of particles demonstrate that the craters observed in this crystalline glaze originate according to the mechanism described.

The phenomena observed suggest that some of the arising surface defects in the crystalline glaze occur as a result of the existence of non-dissolved material in the fluid, which is dragged along and forms a valley in equilibrium. These processes encourage the formation of wavy regions and defects which, though of very minor depth, are stress points for the glaze.

4. CONCLUSIONS

To sum up, the following stages occur during the glaze sintering process:

1st stage (900 - 1000°C). Sintering occurs in the presence of liquid phase by the viscous flow mechanism. The glaze begins to flow and drags along rests of unmelted material.

2nd stage (1000 - 1050°C). The elimination of porosity slows down owing to the existence of crystalline particles in the regions of peaks which are able to control the mass transport.

3rd stage (> 1050°C). The completely molten glaze dissolves crystalline particles.

It has been observed that the presence of crystalline particles in the sintering stage by the viscous flow mechanism is responsible for the defects in the form of surface pores, which give rise to pinholing after the coating has stretched. These surface pores display a crater-type structure with crystalline particles along the edges.

A valley completely surrounded by peaks (crystalline particles) will not close, even though the firing temperature increases, giving rise to surface defects known as pinholes. These defects are not associated with bubbles that migrate towards the surface.

5. ACKNOWLEDGEMENTS

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