Experimental Study of Deformations and State of Tension in Traditional Ceramic Materials

Keywords: traditional ceramic materials, deformations, state of tension, flexion curve, ODP 868

DIL001

ABSTRACT

The application describes the technique, the instrumentation and the tests necessary to develop an ideal body/glaze system for high quality ceramic tiles, and to optimize firing cycles so to avoid the most common product defects (as for instance poor planarity, chipping or crazing) that are the root-cause of signifcant losses in the manufacturing of traditional ceramic products.

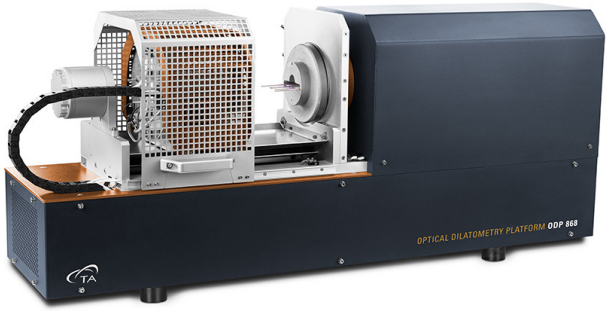

Figure 1: Optical Dilatometry Platform ODP 868

INTRODUCTION

During firing, a glaze applied on a ceramic body undergoes some transformations which can be simply listed as: loss of clay components' forming water, glass transition and softening. In correspondence of this point, the glaze starts to melt, giving rise to a continuous liquid layer. During cooling, the glaze viscosity increases until the glaze becomes rigid and it starts to contract simultaneously with the ceramic body, but not necessarily in the same way. A key further temperature should be defined to describe this locking phenomenon between the two materials during cooling, that is the coupling temperature. In correspondence of the coupling temperature, the glaze softens during heating (absorbing tensions) and solidifies during cooling (building up tensions).

In glazed or double layer tiles, deformations may be generated from the different behaviour of the two overlapped layers, both during heating and cooling phases. The coupling of materials with different thermal behaviours inevitably gives rise to a system of stresses due to the thermal incompatibility between the layers.

It is usual to study CTE differences just looking to the single thermal expansion curves of body and glaze, so neglecting that they constitute a unique mechanical system. This approach is mainly due to the poor analysis skills of traditional dilatometers in the viscous-elastic region of the two layers, when tensions are primarily established.

Two are the ways to accommodate tensions due to thermal expansion mismatch in this bilayer system: bending, up to a certain extent that is allowed by the mechanical strength of the materials, and finally cracking, when the fracture threshold is overcome.

However, it is a common practice in the ceramic tile industry to use differential cooling on the surfaces of a tile to control the planarity of the finished product. That is, depending on concavity or convexity of already fired tiles, glaze surface is cooled faster or slower than the substrate. CTE mismatch and interphase reactions are the key parameters that have to be controlled during the firing cycle. In more detail, two are the potential situations:

- CTE differences lead to a concave tile, so the correction to adopt is to apply a faster cooling on the glaze, that will be then in compression, but the tile will be finally flat.
- CTE differences lead to a convex tile, so the correction to adopt is to apply a slower cooling on the glaze, that will be then in tension, but the tile will be finally flat.

This is a completely random and not methodic approach, only depending on the visual evaluation of the kiln technician. In the meanwhile a certain amount of tiles are lost. And this approach, should be repeated every time a different tile is produced, since body and glaze CTE can change according to the chemical composition. The key point is also that this kind of post-correction inexorably gives rise to a system of tensions that are needed to keep the system planar thus overcoming the effects of the CTE differences.

This behaviour can not be characterized by any dilatometer, regardless if push-rod or optical.

This is the key of the whole analysis and the importance of running this test with the fleximeter mode of ODP 868: with this data both QC and R&D become aware of what could go wrong during the manufacturing process. Hence have a solid, scientific base to work on.

Fast firing is now the dominating technology and the time available to reach an optimal stabilisation of the body is reduced to few minutes. The size of the tiles is growing quickly: now the market is asking for tiles up to one meter in size and above. Thickness is down to the minimum, to save in cost and transportation. The value of the product lays in the richness of the surface and the thickness of the glazes is rising.

Geometrical perfection is a must: tiles are mechanically squared to give a marble-like look to the surface. The big problem now is planarity. If we consider porous wall tiles, the old trick of increasing the state of compression of the glaze onto the body to avoid delayed crazing was working well on the old thick and small tiles. Now the same level of compression on the very same body and glaze but with a much larger size, has a nasty side effect: bending. To reduce the bending there is only one solution: reduce to the minimum the amount of compression. A second defect could appear in case of too high compressive tension in glaze: peeling. In some cases the tendency of the glaze to peel off the body appear in the sharp corner of three-dimensional products, such as kitchenware. The problem, now, is to know how much it is the minimum amount of compression. Since all glazes, like glasses, are characterized by a very low resistance to tractions stress, a little value of traction may causes their rupture. If the body expands even if in a small percentage, for example because of moisture absorption, the glaze may easily crack, unless it is in a state of compression with respect to the body. In this case, a little expansion of the body reduces the state of compression, without generating a dangerous traction. This tendency to react with water in the course of time cannot be completely eliminated: all glazed bodies show this problem. The only type of body that can be considered stable during the time is the completely sintered body, characterized by a lack in porosities. The problem, however, can be successfully tackled by studying the state of tension between glaze and body, by means of thermal expansion and bending tests.

Theoretical deformations: coupling between glaze and ceramic body was studied by Amoros, Negre, Belda and Sanchez, which used a formula derived from Timoshenko equation to calculate theoretically the curvature induced in a glazed ceramic tile by the state of tension (compression/traction) of the glaze. They introduced some simplifying

$$D = \frac{1}{8}\frac{L^2}{h} K_R \Delta c \qquad (1)$$

hypotheses: isotropic, homogeneous, perfectly elastic materials, no interface development between support and glaze, same temperature among the layers, elasticity moduli ratio constant during cooling.

Where

D = deformation intended as "deflection" [mm],

L = length [mm], h = thickness [mm],

ΔC = percentage difference between the single dilatometric curves of the ceramic body and the glaze at room temperature (after translating the glaze dilatometric curve so that it coincides with the body dilatometric curve in correspondence of the coupling temperature), and

$$K_R = \frac{6(m+1)^2 mn}{m^4 n^2 + 4m^3 n + 6m^2 n + 4mn + 1} \text{ with } m = \frac{s_g}{s_s} \text{ and } n = \frac{E_g}{E_s} \qquad (2)$$

Where

S_s= support thickness,

S_g= glaze thickness,

E_s= support elasticity modulus,

E_g= glaze elasticity modulus.

It should be pointed out that ΔC value needs an experimental determination; however some interesting remarks can be made. In a further publication, Amoros and Moreno clarified that, during firing, diffusion and dissolution phenomena between glaze and support layers occur and a glaze-body interphase develops. Thus, glaze and body do not behave as independent layers because of the presence of such interphase, which affects the properties of the final product, including planarity. For this reason, they state that coupling between glaze and support should be investigated experimentally, using the experimental conditions which better reproduce the industrial ones.

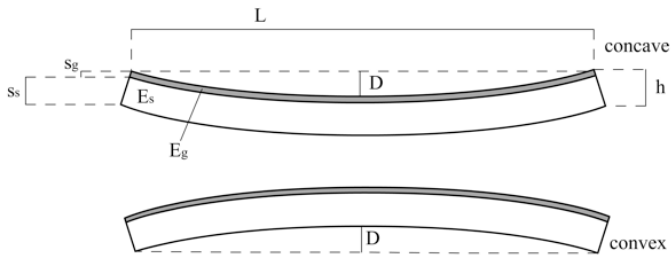

Figure 2: Quantities used in equations (1) and (2)

EXPERIMENTAL METHOD

Considering the limits to determine theoretically the flexion behaviour of a glazed ceramic material, experimental methods are of fundamental importance for studying the deformations induced by the state of tension established between graze and ceramic support. Optical techniques allows to characterize the material behaviour during firing and cooling without entering in contact with the specimen and thus with no interference caused by the measuring system, obtaining a good comprehension of the material real behaviour in an actual industrial firing cycle. The instrument used in this paper to study the deformations and the state of tension in ceramic materials is the Fleximeter mode of ODP 868. A small sample bar is suspended between two holding rods 70 mm spaced, while a camera frames the centre of the sample, which moves downward or upward during the heat treatment (Figure 3). The beam of blue light which lights the centre of the specimen has a wave length of 478 nanometres and enables to reach the optical resolution of 0,2 micron per pixel of the digital camera. Until now, the instrument used to measure the coupling temperature was the Steger tensiometer and the analysis was quite problematical. The

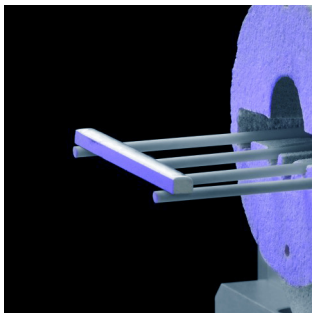

Figure 3: ODP 868 FLEX specimen (80x5x5 mm) obtained from a glazed porcelain tile

test was performed with very long (30 cm) specimen which was not placed completely inside the kiln, with consequent lack in homogeneity in sample temperature.

The curve obtained with this instrument allows to identify the coupling temperature between glaze and ceramic body, to obtain information about the sample planarity and pyroplastic behaviour, to study qualitatively the state of tension established between glaze and body.

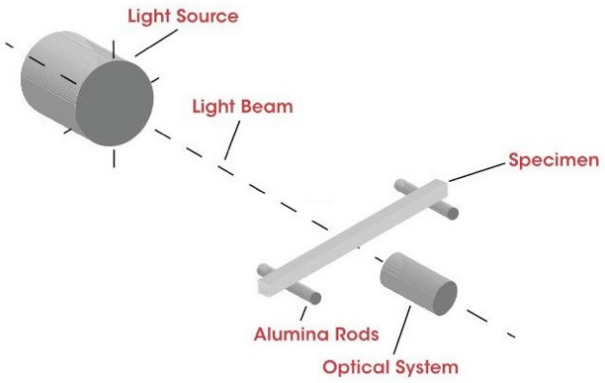

Figure 4: Scheme of the optical Fleximeter

RESULTS AND DISCUSSION

Different information are available in Figure 5, where a two ways heating cycle (with 20°C/min as heating rate and slow cooling) has been applied on a glazed monoporosa sample: absolute bending values remains within one hundred microns because up to the glaze melting (during heating) and from coupling temperature (during cooling), bending occurs mainly owing to a difference in thermal expansion (that is elastic deformation) between layers. The downward flexion in the initial part of the curve is due to the differences between the coefficients of thermal expansion of glaze and body: having the body an higher CTE compared to the glaze, it is subjected to an higher expansion, becoming longer than the glaze. The specimen appears concave. The curve shows a negative peak at 600°C, after the transition α quartz to β

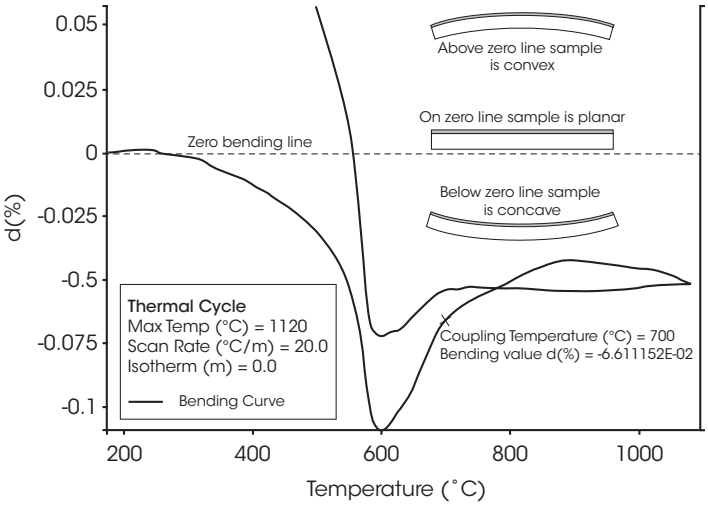

Figure 5: bending curve of a glazed monoporosa sample

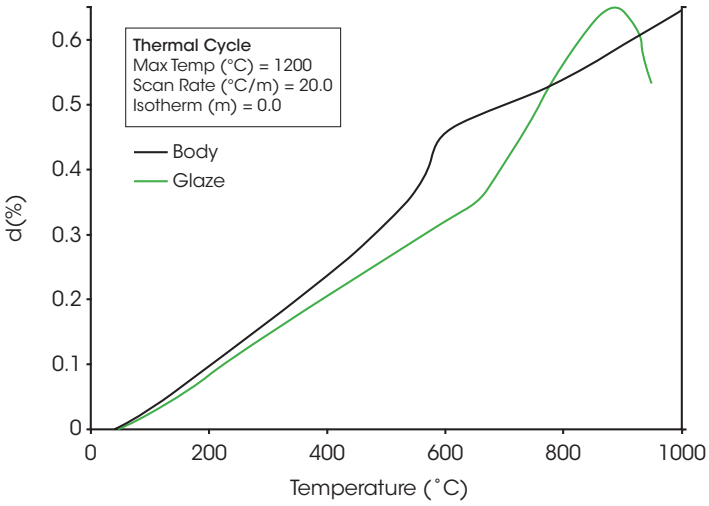

Figure 6: expansion curve of glaze and body constituting the glazed monoporosa sample

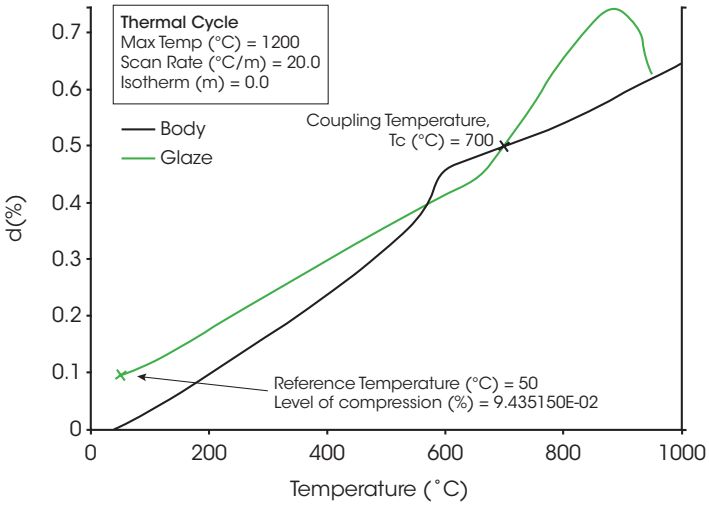

Figure 7: After synchronizing the two expansion curves at the coupling temperature, they don't coincide anymore at the origin. The difference between them is the level of compression established in the glaze.

quartz occurring into the ceramic body: in correspondence of this point the difference between the thermal expansion curves of glaze and body is maximum, also because the glaze is about to undergo the glass transition.

At the beginning of the cooling phase, the glaze is liquid and follows the body contraction without developing tensions. In correspondence of 700°C it is possible to identify the coupling temperature (Tc). Glaze and the body chemically interact and are bonded together. Above Tc tensions are released, below Tc, during cooling inside the kiln, tensions are built up. Then it can be argued that during cooling the curve should be symmetrical with the one in heating: wishful thinking because instead the flexion follows a different path, and the system does not come back to planarity. This phenomenon is primarily due to the differences between glaze's and body's CTEs that are greatly enhanced by the new formed interface. The glaze has become rigid enough to build up tensions, causing the flexion of the sample. In this example, it is easier

to identify the coupling temperature during cooling, because a rapid variation of inclination in the flexion curve occurs. During the heating phase, the coupling temperature is less evident and more difficult to be identified. It is also possible to see that the curve is below the zero-line (concave specimen) during the whole heating phase and for a part of the cooling phase (from 1100 down to 550°C). At this point one might ask why, if we assume that for temperatures higher than the Tc the glaze is not able to build up tension, in such interval the tile is concave and not planar as it may be expected. To give an answer to this question, a simple model has been developed: a planar system composed by a spring (glaze) and a thin plate (body) is associated to the glazed tile bar. Two cases (spring in tension and spring in compression) were analyzed.

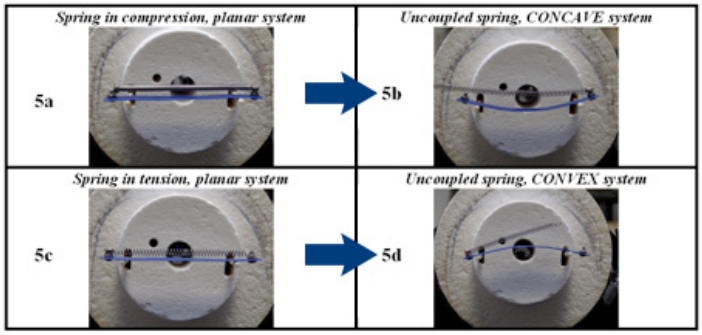

Figure 8: The spring-plate model associated to the glazed tile

Observing Figure 8, it is possible to see that, if the spring in compression is uncoupled from the plate, the plate bends downwards (concave system) because it was the spring compression keeping the system planar. If the spring in tension is uncoupled from the plate, the plate bends upwards (convex system) because it was the spring tension that kept the system planar. By analogy with this system, if the glaze is initially in a state of compression, when the fired glazed tile sample is subjected to temperatures higher than the Tc, the tile will undergo a certain deformation leading to a concave shape. On the other side, if the glaze is initially in a state of traction, when the fired glazed tile sample is subjected to temperatures higher than the Tc, the tile will undergo a certain deformation leading to a convex shape.

CONCLUSIONS

A quantitative study of the state of tension established between glaze and body after firing is however fundamental in order to prevent some frequent problems occurring in glazed products, for example delayed crazing or serious planarity defects. To obtain the final result, it's necessary to move the glaze thermal expansion curve so that it coincides with the body thermal expansion curve in correspondence of the coupling temperature (see figures 6 and 7). The two curves, after the change, do not coincide anymore at the origin (room temperature). This difference is directly proportional to tensions (either traction or compression) established between glaze and body immediately after firing.

The Fleximeter mode of ODP 868 is then crucial to post-analyze products that are prone to have planarity defects after firing. A sample can be directly taken from production, and analyzed above its coupling temperature: the bending curve during cooling will reveal how much the mechanical system was tensioned.

For more information or to place an order, go to http://www.tainstruments.com/ to locate your local sales office information.