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EXPERIMENTAL STUDY OF DEFORMATIONS AND STATE OF TENSION IN TRADITIONAL CERAMIC MATERIALS

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Abstract: Deformations of traditional ceramic materials after firing may depend on several factors and are in general too complex to be studied theoretically. The flexion curve obtained experimentally with optical techniques proved to be a valid help for the study of the deformations and state of tension in glazed ceramic materials.

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

Introduction

The deformations of ceramic materials after firing may have a complex origin. If the products are made up of a single material, deformations are mainly due to pyroplastic phenomena. In the case of multi-layer products (glazed or technical double layer tiles), the interactions between the various layers during the heating cycle and the state of tension established among them after firing must be considered [1].

Pyroplasticity

Traditional sintered ceramic bodies, like stone-ware or porcelain-ware, undergo a viscous flow sintering process, where the driving force is mainly given by the surface tension of the liquid glassy phase and the speed of the process is controlled by the viscosity of the glassy phase [2]. The viscosity of the glassy phase decreases exponentially as the temperature increases according to Arrhenius law, accelerating the sintering process. On the other hand, the effect of a low viscosity is to increase the material tendency to deform under its own weight (pyroplastic deformation).

The measurement of pyroplasticity is particularly important for bodies that have to be completely sintered because during the final stage of firing they develop an abundant vitreous phase with a sufficiently low viscosity to cause rapid deformation of the material. Unfired ceramic materials may behave in very different ways when subjected to the thermal firing treatment. In some cases, the higher deformation speed is found at the maximum temperature reached inside the kiln. In other cases, the highest bending rate occurs when the melting of the feldspars takes place, then at higher temperatures the tendency to bend falls as the vitreous phase dissolves other mineral components of the body, becoming more viscous [3].

In Figure 1 these two possible behaviours are represented. Two samples of technical porcelain were subjected to a thermal treatment consisting of a heating rate of 30°C/min, a first permanence of 5 minutes at 1220°C and a second permanence of 5 minutes at 1230°C (red curve). The two curves obtained represent the flexion expressed in microns and are overlapped in the same graph in order to make a comparison.

Technical Porcelain 1 (green curve) shows a final bending of more than 6 mm, and the maximum deformation rate (green curve with circles) is found in correspondence of the maximum temperature (1230°C). Technical Porcelain 2 (blue curve) shows a final bending of less than 3mm and the maximum flexion speed (blue curve with circles) is at the beginning of the first permanence at 1220°C.

The producer should pay more attention to the problem of deformation at the beginning of the first permanence (1220°C) during the firing of technical porcelain 2, while in the case of technical porcelain 1, deformations must be taken under control at the maximum temperature (1230°C).

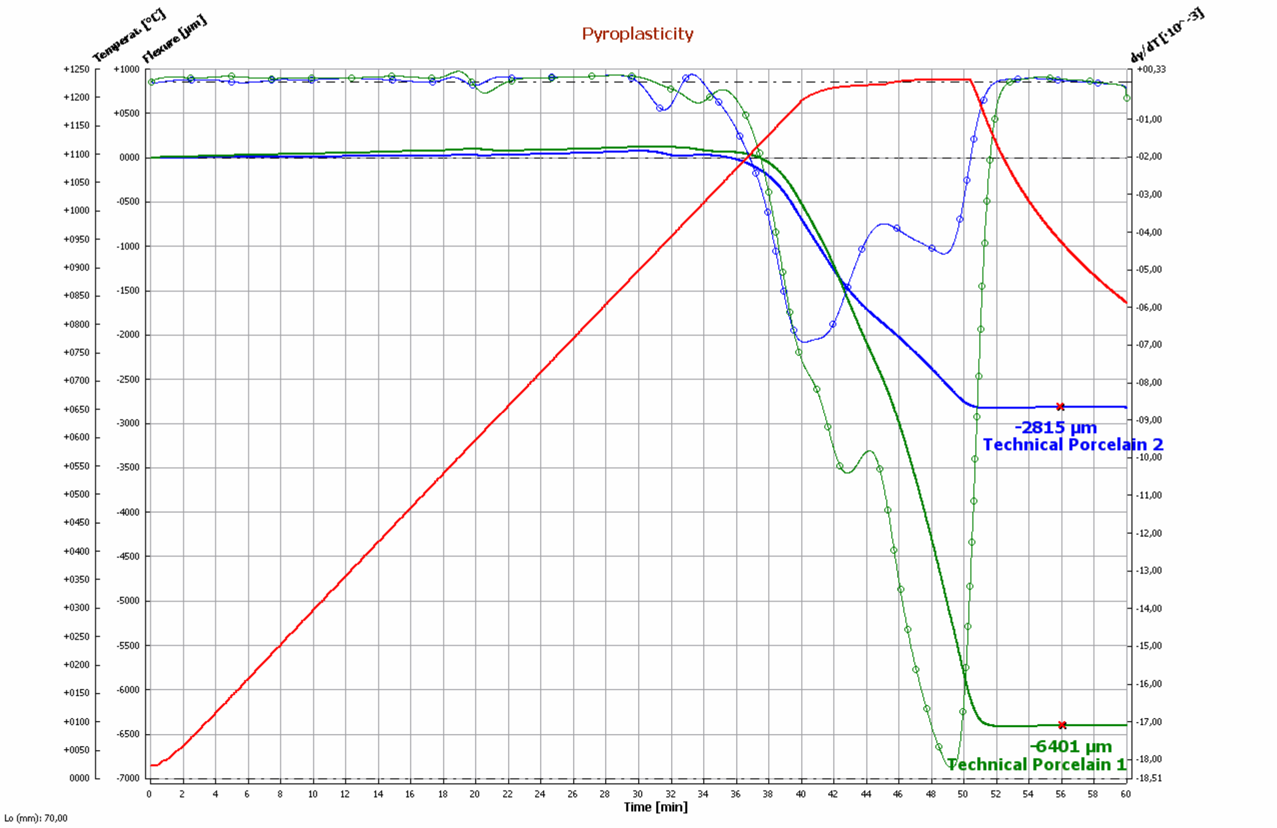

Figure 1: Flexion curves of two technical porcelain samples

Deformations in glazed tiles

In glazed or double layer tiles, deformations may be generated from the different behaviour of the two overlapped layers, during both 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.

This problem was tackled by Timoshenko in 1925, when he develops an equation that calculates the deformation of bimetallic strips as a function of the temperature.

Unlike bimetallic strips, that bend only because of the differences between the thermal expansion coefficients of the two metals overlapped, in the case of a glazed ceramic material it is necessary to take account of the physical transformations occurring into the ceramic body and the glaze.

The ceramic support shows the characteristics of an elastic solid, while glasses and glazes exhibit a strongly temperature-dependent mechanical behaviour. At room temperature, they behave as elastic solids, obeying Hooke’s law; at temperatures higher than their glass transition temperature (Tg) they behave as plastic fluids and their viscosity decreases as temperature rises, in accordance to Arrhenius’ law.

Another characteristic point of the glaze-body system is the coupling temperature (Tc), in correspondence of which the glaze softens during heating (absorbing tensions) and solidifies during cooling (building up tensions). As a direct consequence, after cooling a system of tensions may originate inside the material, giving rise to defects such as crazing, peeling or planarity defects.

The study of the deformations and state of tension in a glazed ceramic material may be tackled from different points of view, both theoretical or experimental.

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 hypotheses: isotropic, homogeneous, perfectly elastic materials, no interface development between support and glaze, same temperature among the layers, elasticity moduli ratio constant during cooling [4]:

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

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)

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

Where:
S_s= support thickness
S_g= glaze thickness
E_s= support elasticity modulus
E_g= glaze elasticity modulus

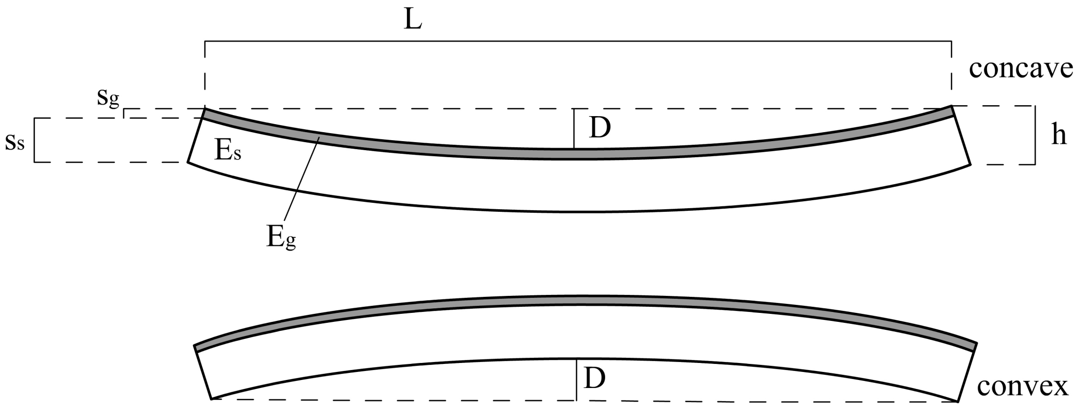

Figure 2: Quantities used in equations (1) and (2)

The determination of the constant K_R is quite difficult, because it is necessary to know the value of the two elasticity moduli E_s and E_g, furthermore, the ΔC value needs an experimental determination; however some interesting remarks can be made.
With the same K_R and ΔC (same glaze and ceramic support), the deflection is directly proportional to the square of the tile length (L) and inversely proportional to the tile thickness (h). With the same tile length (L), tile thickness (h) and ΔC, the deformation increases if the support elasticity modulus E_s and thickness S_s decrease, since K_R increases if m or n increase (m<1) [4].

In a further publication, Amoros, Moreno, Negre and Orts point out 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 [5].

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. Among them, 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 optical Fleximeter. 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 (Figures 3a and 3b). 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 0,5 micron per pixel of the digital camera.

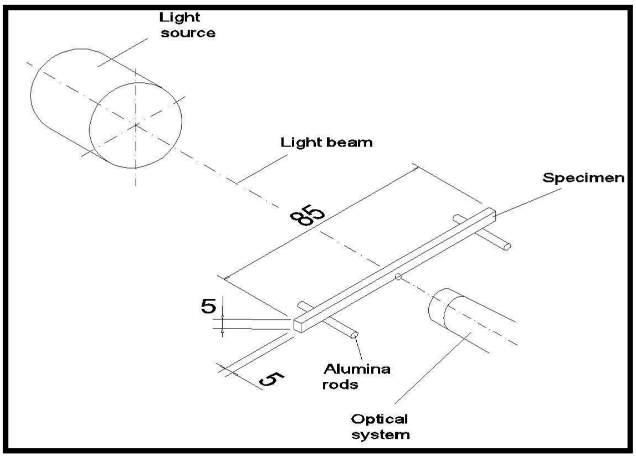

Figure 3a: Scheme of the optical Fleximeter

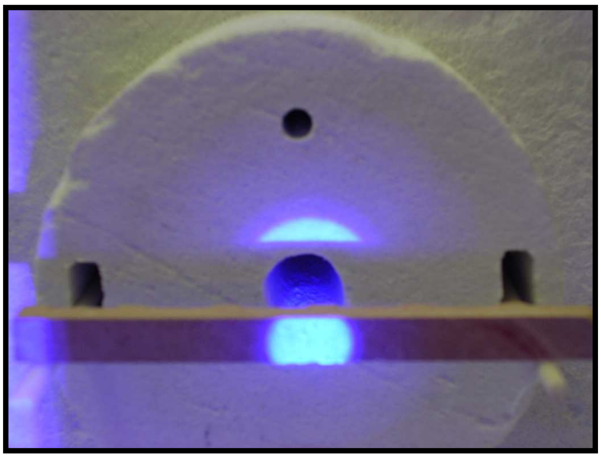

Figure 3b: Sample inside the kiln

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 to study qualitatively the state of tension established between glaze and body.

In Figure 4 the flexion curve obtained for a specimen cut directly from a fired glazed tile and subjected to a heating cycle with a heating speed of 20°C/min up to 1100°C is represented.

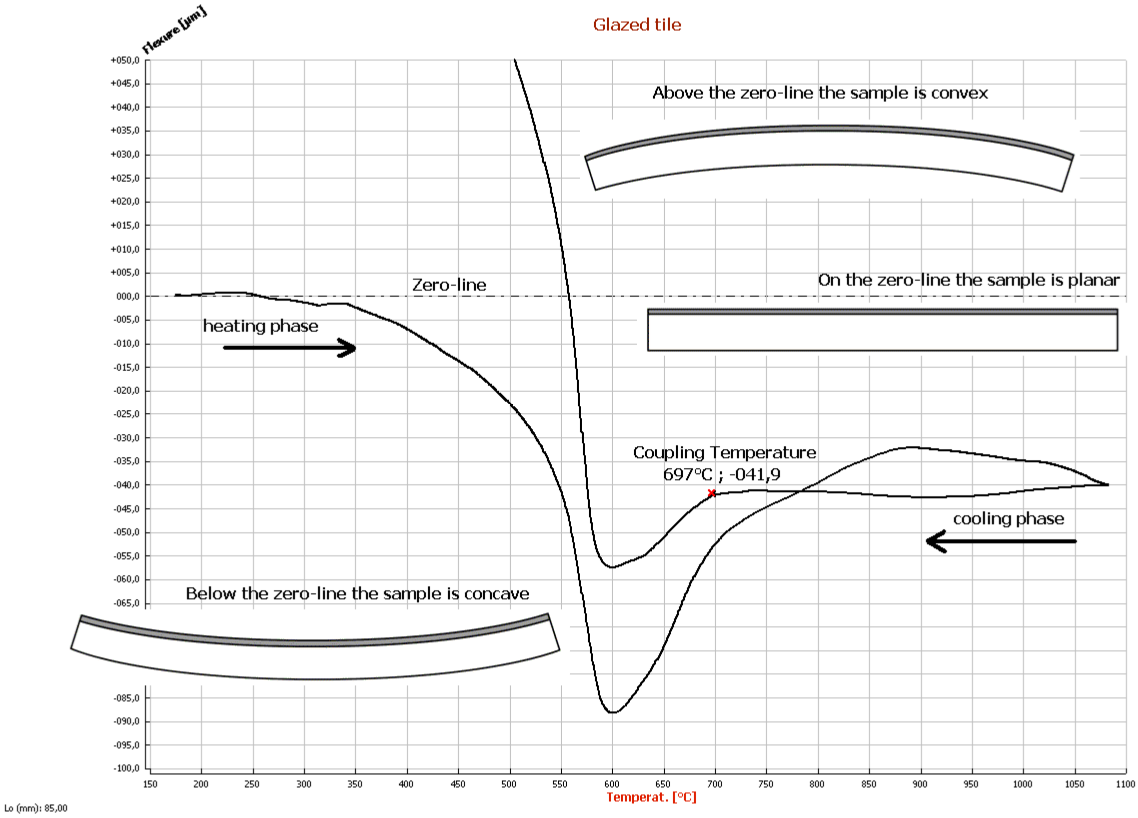

Figure 4: Flexion curve interpretation

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 – β 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 697°C it is possible to identify the coupling temperature (Tc). 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.

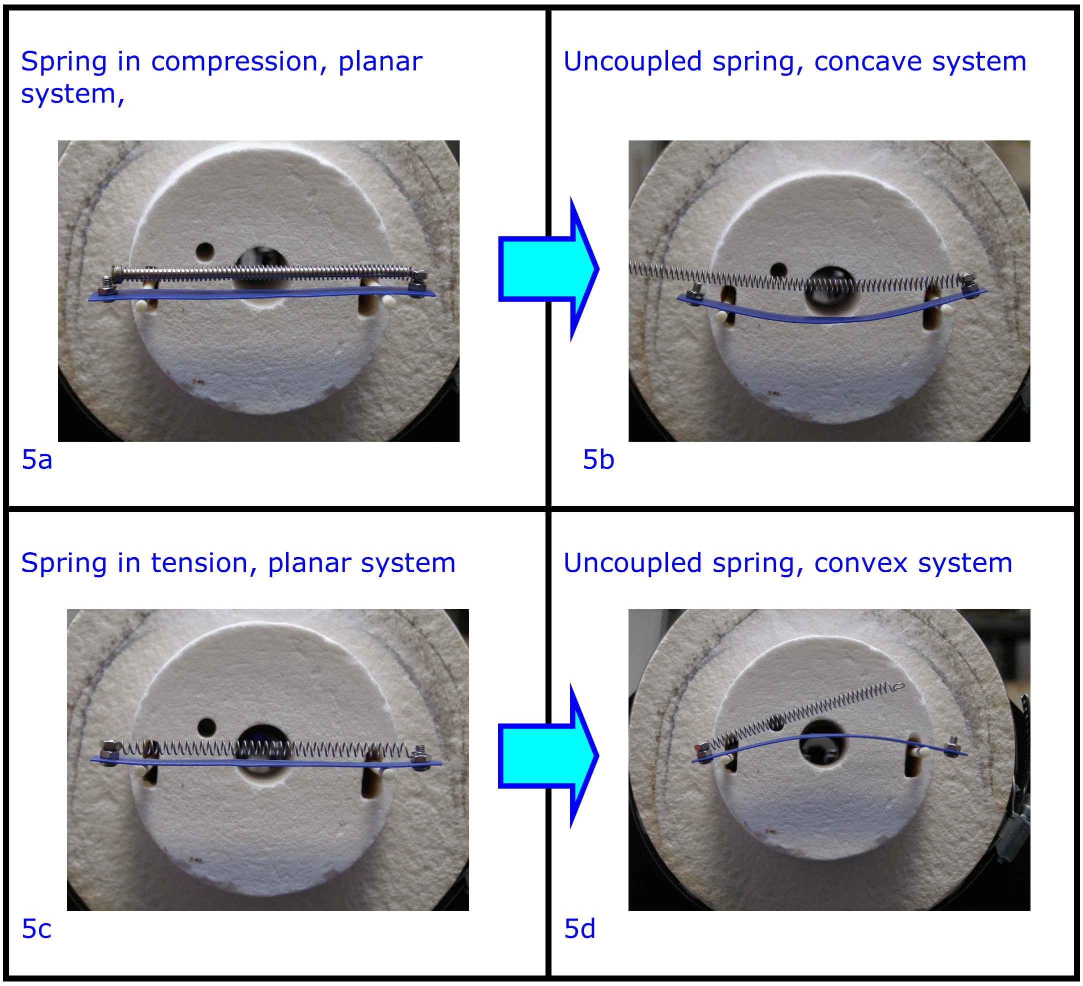

Figure 5: The spring-plate model associated to the glazed tile

Observing Figure 5, 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 that kept 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, a concave deformation occurs in the tile; if the glaze is initially in a state of traction, when the fired glazed tile sample is subjected to temperatures higher than the Tc, a convex deformation occurs in the tile.
Figure 6 represents the comparison between two flexion curves obtained for two different glazed tile samples. For T>Tc, the blue curve is surely above the zero-line: this means that the glaze was in a state of traction. The red curve, for T>Tc, is below the zero-line: the glaze was in a state of compression.
Observing the two curves at room temperature it is possible to complete the qualitative study of the state of tension. The blue curve is below the zero-line: this mean that the support is longer than the glaze, which is in a state of traction and may be subjected to crazing immediately out of the kiln. The red curve, instead, at room temperature is above the zero-line: the glaze is in a state of compression, being longer than the support.

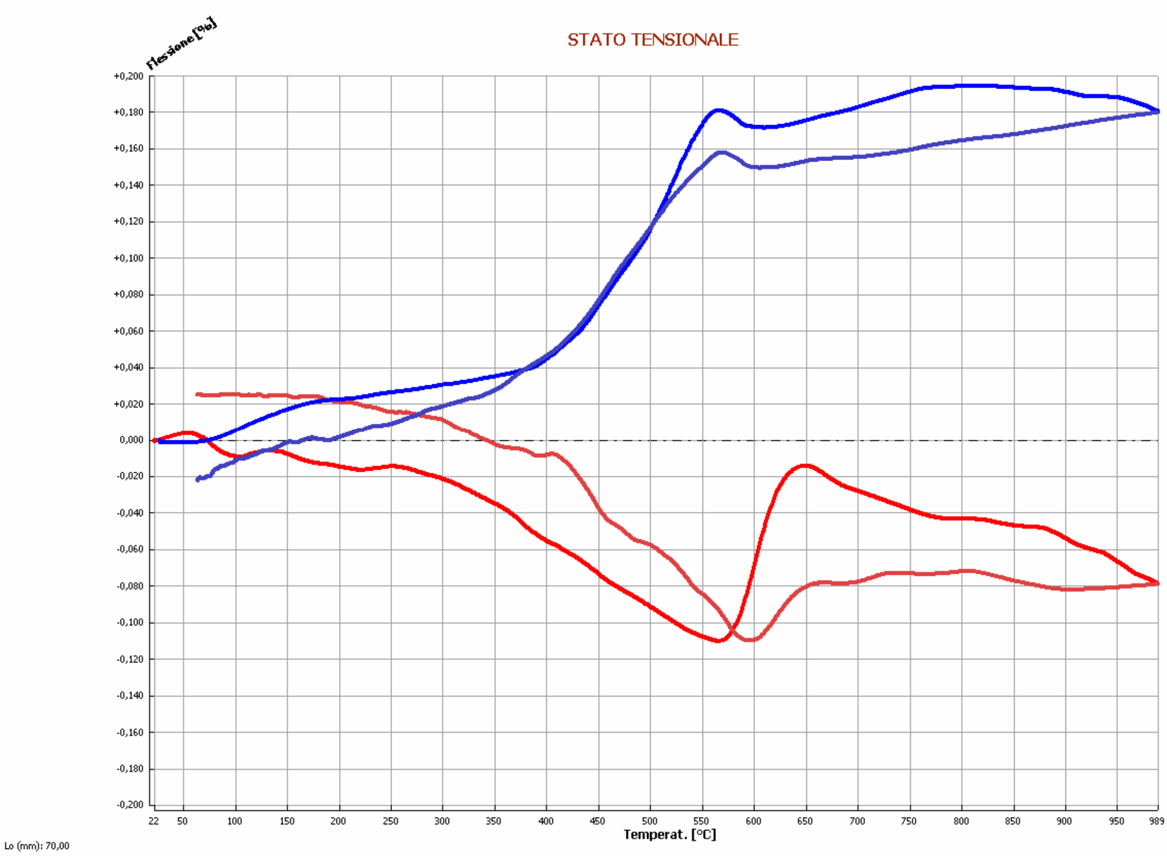

Figure 6: Comparison between the flexion curves of two fired glazed tile samples to study qualitatively their state of tension

The 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.

The increased tile dimensions, the reduction of their thickness and the use of fast firing cycles are all factors which required an accurate planarity control. In porous glazed tiles, the amount of compression of the glaze should be reduced to the minimum, in order to avoid problems of crazing and at the same time prevent the nasty side effect of bending.

For a more detailed discussion, see the article "Delayed crazing resistance of glazed ceramic materials" written by M. Paganelli e D. Sighinolfi and published on cfi/Ber. DKG 85 (2008) No. 1-2

Conclusions

The behaviour of traditional ceramics is often too complex to be understood theoretically, starting from the thermo-physical parameters of the single components, since there are many difficulties, like the development of new phases during the process. In this field, the experimental method based on the optical Fleximeter results proved to be a valid help for the study of the deformations and state of tension in glazed ceramic materials.

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