



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

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Abstract

Generally, the deformations of ceramic materials during and after firing may have a complex origin. If the products are made up of a single material, such deformations are mainly due to pyroplastic phenomena. In the case of glazed materials, two further factors must be considered: the state of tension established between glaze and body, and their differences in behaviour during sintering. A novel optical technique is described to measure the state of tension of ceramic glazed bodies and applied to the study of delayed crazing and pyroplastic deformation of the body. This article outlines how can ceramists avail themselves of new optical equipment in order to design high quality products and avoid ordinary defects. Combining dilatometric tests and bending analysis, a full study of residual stresses on glazed ceramic can be performed; therefore, this is how planarity problems can be solved. Furthermore the Optical Fleximeter MISURA® is able to get information about viscosity changes during firing process in porcelain stoneware tiles: study of pyroplastic behaviour.

Keywords: Traditional ceramic materials, Deformations, State of tension, Flexion curve

BADANIA EKSPERYMANTALNE DEFORMACJI I STANU NAPRĘŻENIA W MATERIAŁACH CERAMIKI TRADYCYJNEJ

Ogólnie rzecz biorąc deformacje materiałów ceramicznych w trakcie i po wypaleniu mogą mieć złożone pochodzenie. Jeżeli produkty są wykonane z jednego materiału, takie deformacje związane są głównie ze zjawiskami piroplastyczności. W przypadku materiałów szklwionych należy wziąć pod uwagę dwa czynniki: stan naprężenia powstałego pomiędzy szklwem i czerpem, oraz różnice w ich zachowaniu podczas spiekania. Opisano nową optyczną technikę pomiaru stanu naprężenia szklwionych materiałów ceramicznych oraz jej zastosowanie do badania opóźnionego pęknięcia i deformacji piroplastycznej wyrobu. Artykuł ten pokazuje jak ceramicy mogą skorzystać stosując nowy sprzęt optyczny w celu opracowania wysokiej jakości produktów i uniknięcia pospolitych wgnęć. Połączenie testów dylatometrycznych i analizy zginania umożliwia całkowite zbadanie naprężeń resztkowych w ceramice szklwionej, i dlatego pokazuje jak można rozwiązać problemy płaskości. Ponadto Optical Fleximeter MISURA® umożliwia uzyskanie informacji o zmianach lepkości podczas procesu wypalania płytek z kamionki porcelanowej – badania nad zachowaniem piroplastycznym.

Słowa kluczowe: tradycyjne materiały ceramiczne, deformacje, stan naprężenia, krzywa zginania

1. Introduction

During firing, a glaze applied on a ceramic body undergoes some transformations which can be simply listed as: losing of the forming water of the clay components, glass transition and softening. In correspondence to this point, the glass part of the glaze starts to melt, giving as a result 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. Delayed crazing is due to the volume increase of the body, because of absorption of humidity after firing. The body, in fact, can show a slow but inexorable tendency to react with the water present as humidity in the air, which changes permanently its properties. This dimensional increase of ceramic bodies occurs in a period of time which can vary from some days to some years. In the past, this phenomenon was not understood and it was indeed the biggest problem of porous ceramic bodies. The solution looks easy at first sight: minimise the moisture

expansion and increase the compression of the glaze on the body. This approach indeed gave excellent results for many years, but nowadays the problem is showing up again in different circumstances. 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 wall 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 wall. The big problem now is planarity. 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 appears 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 [1]. Some experimental techniques were developed in the past with the purpose to study the compression level, [2] but due to their complexity in sample preparation (well shaped specimens designed specifically for the test), they had a moderate industrial consideration. Since all glazes, like glasses, are characterized by a very low resistance to traction stress, a little value of traction may cause their rupture. If the body expands, even if in a small percentage, 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 porosity. In case of low porosity bodies, another parameter turns into great technological importance: pyroplasticity. It describes the tendency of the body to deform plastically within a given temperature range, in fact during the final stage of firing an abundant vitreous phase with a sufficiently low viscosity flows and causes rapid deformation of the material. A body formulation and a firing cycle intended to avoid delayed crazing do not exist. 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. To solve planarity problems due to plastic deformations during firing additional investigations on the pyroplastic behaviour become indispensable.

1.1. 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 [3]. 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 [4]. As proposed by Sang-Ho Lee, Gary L. Messing and David Green [5] and Auree Butchtel, Hyojin Lee, W.M. Carty [6],

viscosity may be calculated using the formula that defines the deflection of a beam supported at the ends and subjected to its own weight (formula valid when deformation is purely elastic), where y_{\max} = deflection, ρ = density, g = acceleration of gravity, L = distance between supports, E = elastic modulus, h = beam thickness.

$$y_{\max} = \frac{5\rho g L^4}{32 E h^2} \quad (1)$$

When the deflection of the beam is caused by viscous flow, it increases as a function of time and the ratio of deformation is therefore a function of viscosity (for small deflection values the elastic modulus E can be replaced by the viscosity η and the deflection y_{\max} replaced with the deflection rate. Considering the solely maximum value of deflection at the centre of the beam, the viscosity results:

$$\eta = \frac{5\rho g L^4}{32 \dot{y}_{\max} h^2} \quad (2)$$

On the basis of the dimensional variations (to be measured by means of a sintering dilatometric test) and knowing the loss of ignition, the correct value of density can be calculated and inserted in this viscosity formula. It describes the inverse relation between the viscosity of glassy phases developing and reacting during the sintering process and the bending rate (first derivative of the absolute bending) of a suspended specimen.

1.2. Deformations in glazed tiles

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. This problem was tackled by Timoshenko in 1925, when he developed 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 into account 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 (T_g) 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 (T_c), 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.

1.3. Theoretical deformations

Coupling between glaze and ceramic body was studied by Amoros, Negre, Belda and Sanchez, who 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 [6]. 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 [7]:

$$D = \frac{1}{8} \frac{L^2}{h} K_R \Delta C \quad (3)$$

where D = deformation intended as "deflection" [mm], L = length [mm], h = thickness [mm], C = 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

$$K_R = \frac{6(m+1)^2 m}{m^4 n^2 + 4m^3 n + 6m^2 n + 4m + 1} \quad (4)$$

with $m = \frac{S_g}{S_s}$ and $n = \frac{E_g}{E_s}$

where S_s = support thickness, S_g = glaze thickness, E_s = support elasticity modulus, E_g = glaze elasticity modulus.

The determination of the constant K_R is quite difficult, because it is necessary to know the values of the two elasticity moduli E_s and E_g , furthermore, the C value needs an experimental determination; however some interesting remarks can be made. With the same K_R and C (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 C , the deformation increases if the support elasticity modulus E_s and thickness S_s decrease, since K_R increases if m or n increase ($m < 1$) [8]. In a further publication, Amoros and Moreno 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 [9].

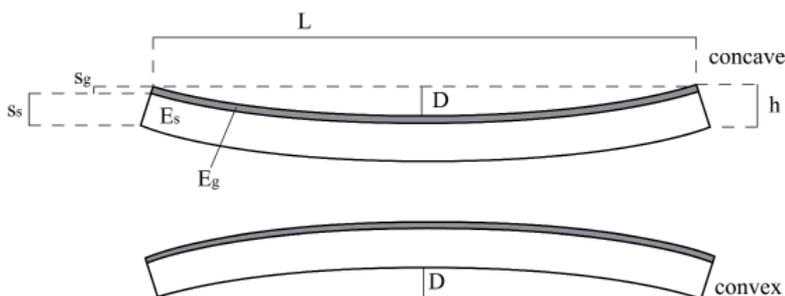


Fig. 1. Quantities used in equations (1) and (2).

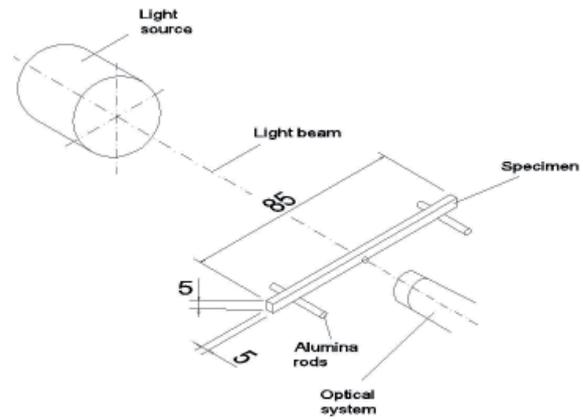


Fig. 2a. Scheme of the optical Fleximeter.

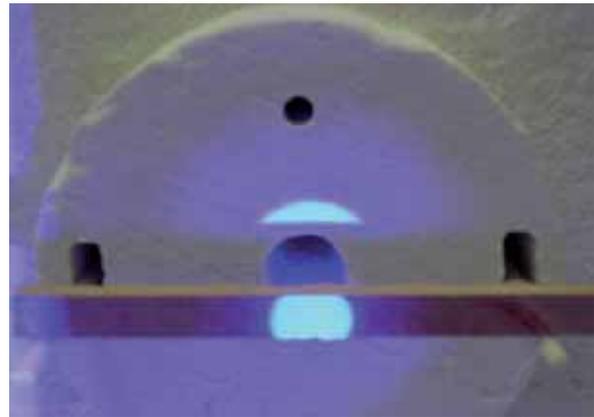


Fig. 2b. Sample inside the kiln.

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 glaze and ceramic support. Among them, optical techniques allow 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 (Figs. 2a and 2b). The back lighted optical system, provides images of the last few hundreds microns of the sample central portion through an high magnification microscope and a digital camera. 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.

The curve obtained with this instrument allows the coupling temperature between glaze and ceramic body to be identified, to

obtain information about the sample planarity and pyroplastic behaviour, to study qualitatively the state of tension established between glaze and body.

3. Results and discussion

The aim of the experimental procedure proposed is the application of this new optical technique to investigate the thermal behaviour of some porcelain stoneware bodies during firing and to present a complete stress level study on a double layer ceramic. Specimens are 85x5x5 mm in side bars made of green pressed bodies (400 Kg/cm²) for the pyroplastic analysis, and fired glazed monoporosa samples, directly cut from industrial pieces. Green samples have been initially dried at 150°C for 2h. In Fig. 3, the effect of a different body composition on the pyroplastic behaviour appears evident. 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. 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 shows a final bending of more than 6 mm, and the maximum deformation rate (a curve with circles) is found in correspondence of the maximum temperature (1230°C). Technical Porcelain 2 shows a final bending of less than 3 mm and the maximum flexion speed (a 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

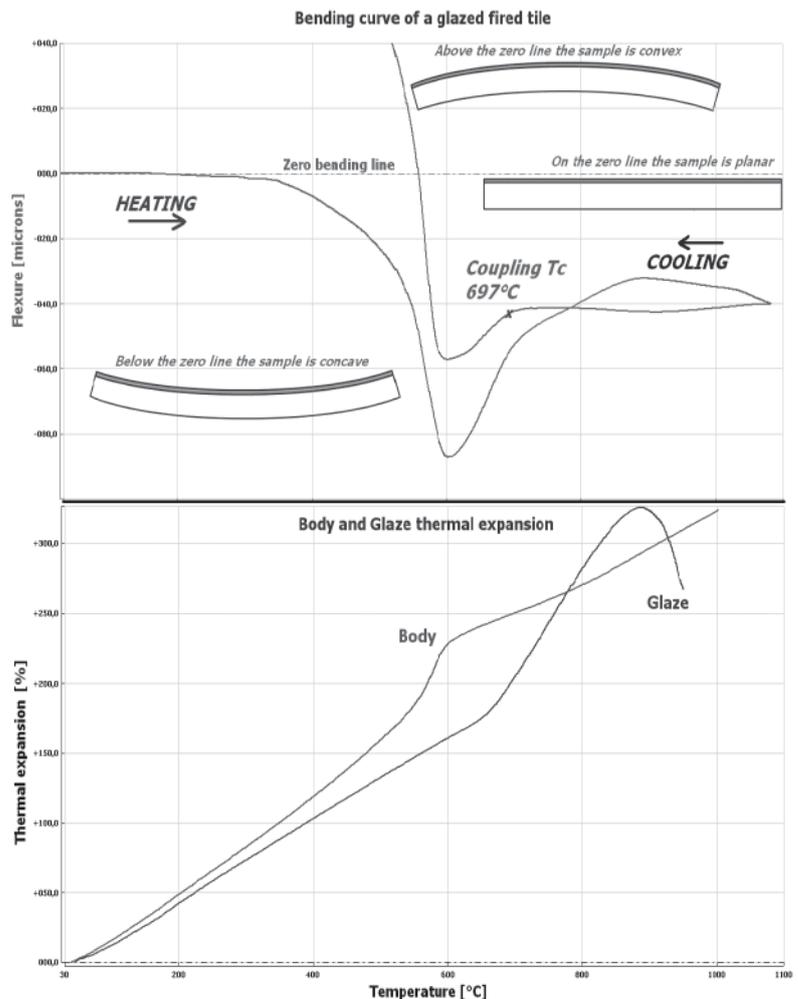


Fig. 4. Flexion curve interpretation.

control at the maximum temperature (1230°C).

Different information is available in Fig. 4, 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 higher CTE compared to the glaze, it is subjected to 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 to 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

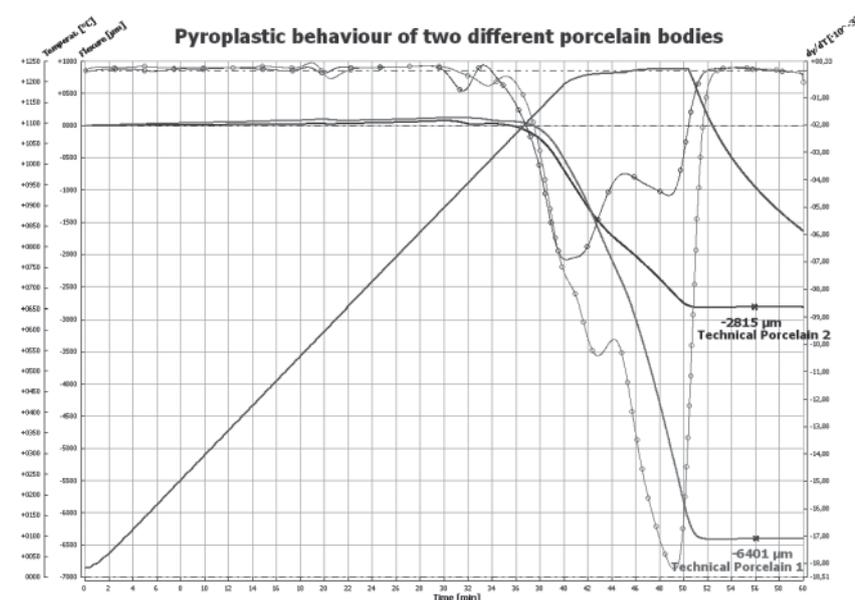


Fig. 3. Flexion curves of two technical porcelain samples.

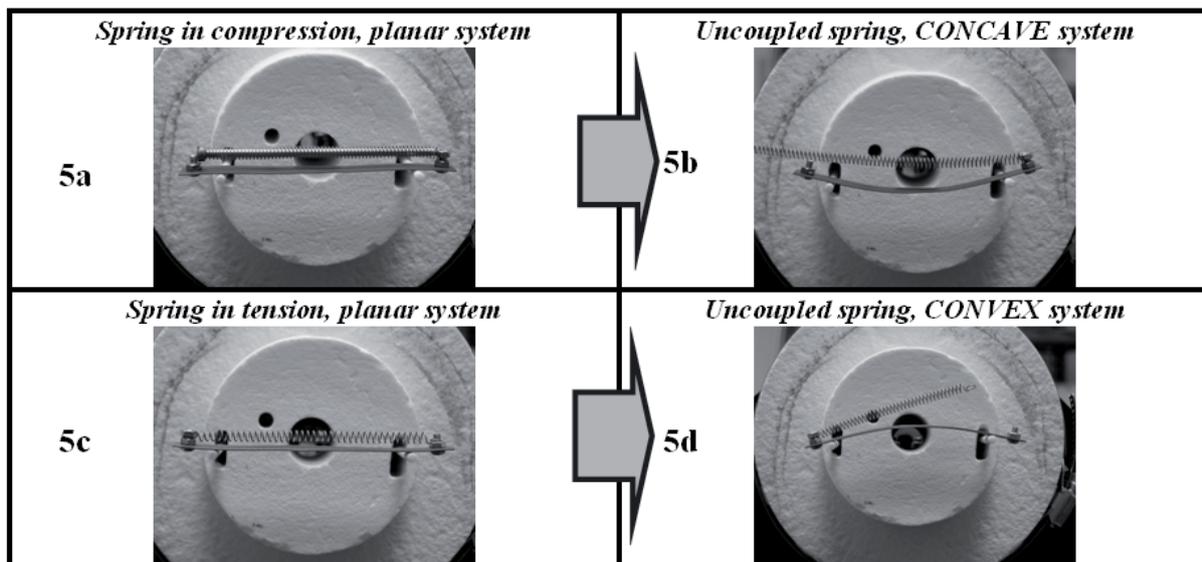


Fig. 5. The spring-plate model associated to the glazed tile.

and follows the body contraction without developing tensions. At 697°C it is possible to identify the coupling temperature (T_c). 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 T_c 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 of 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.

Observing Fig. 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 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 T_c , 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 T_c , a convex deformation occurs in the tile. Fig. 6 represents the comparison between two flexion curves obtained for two different glazed tile samples. For $T > T_c$, the dark grey curve is surely above the zero-line: this means that the glaze was in a state of traction. The light grey curve, for $T > T_c$, is below the zero-line: the glaze was in a state of compression. 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 translate

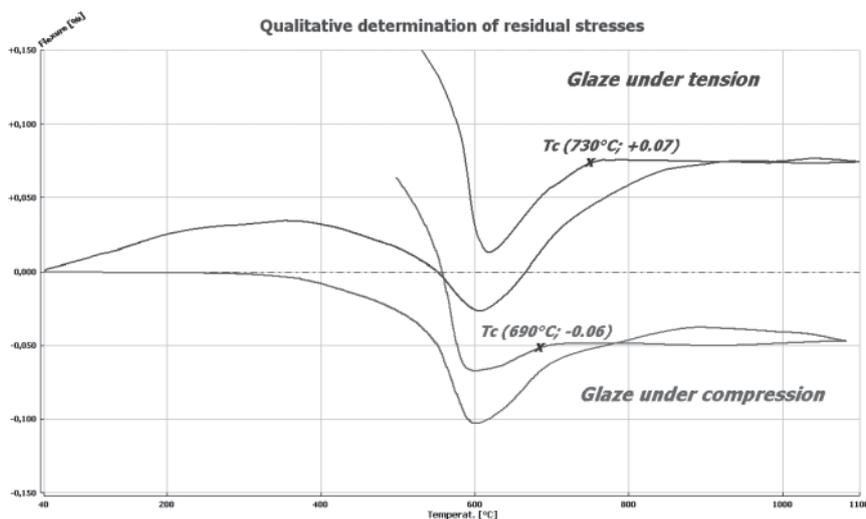


Fig. 6. Comparison between the flexion curves of two fired glazed tile samples to study qualitatively their state of tension.

the glaze thermal expansion curve so that it coincides with the body thermal expansion curve in correspondence of the coupling temperature [10]. The two curves, after the translation, do not coincide anymore at the origin (room temperature). This difference is indeed the traction or compression which has established between glaze and body immediately after firing. From this moment, the body starts to react with the air humidity, increasing its volume. This is a hydrothermal phenomenon, which is favoured by the presence of humidity and high temperatures. This process of rehydration, in the case of tiles already placed on the floor, may require some years, but can be also artificially accelerated by increasing

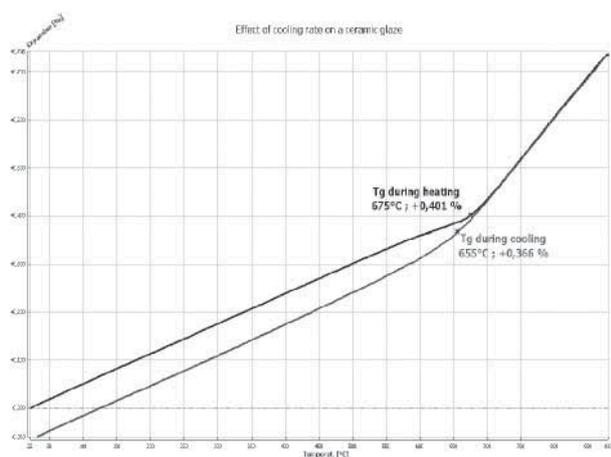


Fig. 7. Effect of the cooling rate on the specific volume and T_g of a ceramic glaze.

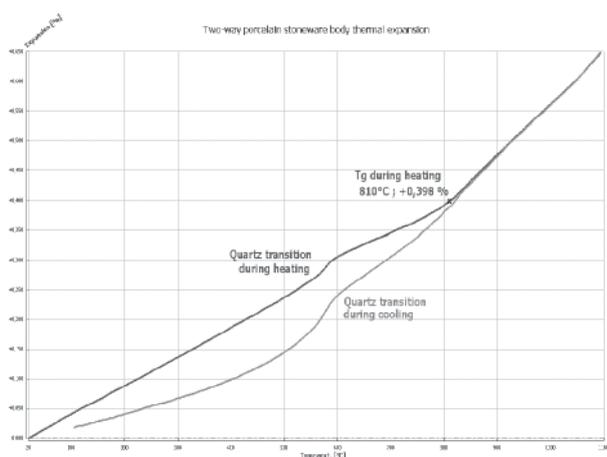


Fig. 8. two-way dilatation of a porcelain stoneware fired body; the optical dilatometer Misura® detects the T_g of the glassy phase and the increase in density.

the water vapour pressure and the temperature. Performing an autoclave test at high temperature and pressure, the process can be completed in few hours.

The measurement of the percentage of expansion due to the adsorption of water should be compared with the measurement of the percentage of compression of the glaze layer with respect to the body. If the value of expansion after the autoclave test is lower than the level of compression established between glaze and body, then the product will not be at risk of delayed crazing. Both bending curves in Fig. 6 show, during the cooling process, an increase in convexity that clearly describes the final non zero inter-layer stress. In fact a zero stress situation would be achieved for bending curves giving a zero bending at the end of the cooling process also. An in-depth study of phenomena involved with the final stress level, especially required for big size and with reduced thickness tiles, should take into account the effect of the cooling rate on the specific volume of glassy phases [11]. Fig. 7 shows expansion data of a ceramic glaze melted during an industrial process, subjected to a two-way dilatation test at $10^\circ\text{C}/\text{min}$ (both for heating and cooling). During glass cooling, a contraction takes place due to rearrangements of individual structural elements; this proceeds rapidly as long as the viscosity is low. In the region of the transformation temperature, however, rearrangements require measurable

times and if the cooling rate is high (as that occurred during the fast melting cycle of this glaze), the larger structural elements cannot follow even earlier, and even the smaller ones become immobile sooner: the transformation region is shifted towards higher temperatures. During the second cooling at a low rate, the transformation is located at a lower temperature. This difference in glass density justifies the hysteresis recorded in bending curves. The situation becomes even more complicated in case of glazed porcelain stoneware bodies, where a nearly 50% of feldspars is used in fast firing compositions and a plentiful glassy phase is therefore produced during sintering. The use of an optical dilatometer makes it possible to identify its transition temperature and effects of the cooling rate on the specific volume as well. It appears evident in Fig. 8 how this measuring technique is able to show the actual thermal behaviour of the glassy phase contained in a fired porcelain body; traditional dilatometers cannot push above the glass transition range and precisely measure the two-way hysteresis (specific volume variation due to different cooling rates) in case of viscous deformations in the sample. During heating the body expands linearly up to the quartz α - β transition, whose effect has been recorded at 573°C , then it continues expanding along a straight line. In case of porous bodies, having no viscous phase as sintering promoter, the CTE would change not much above the quartz transition but for the more dense and liquid sintered porcelain body, the glass transition is effectually recorded. During the following slow cooling the effect of the prior fast firing cycle appears evidently as a decrease on the specific volume on the final glass.

4. 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. The increased tile dimensions, the reduction of their thickness and the use of fast firing cycles are all factors which require 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. 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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