Volume Changes in Porcelain Bodies During the Cooling Phase After Firing

Keywords: volume change, cooling, glass transition, thermal hysteresis, microcrack

DIL002

Traditional sintered ceramic bodies, like stone-ware or porcelain-ware, are primarily composed of clays, feldspars and quartz mixtures.

A number of novel non-contact optical dilatometric techniques and the new Optical Dilatometry Platform ODP 868 were used to measure thermal expansion, physical transformations as well as the deflection upon heating of samples obtained from two batches. This kind of procedure leads to fully appreciate the crucial role of quartz particles morphology and grain size on the sintering behavior and final microstructure of the samples.

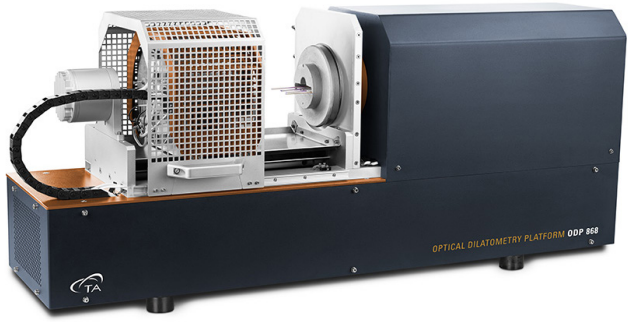

Figure 1. Optical Dilatometry Platform ODP 868

The observations of the material expansion, shrinkage, shape changes and deflection at high temperatures revealed also the crucial influence of quartz thermal inertia on residual stress development in ceramics. A considerable attention has been in fact paid to the hysteresis generated upon subsequent cooling.

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

The use of an optical dilatometer makes possible the identification of its transition temperature and effects of the cooling rate on the specific volume as well. 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.

INTRODUCTION

During firing, traditional sintered ceramic bodies develop abundant glassy phases, which are still well present in the body at the end of sintering.

The final product consists of a high percentage glassy matrix embedding crystalline phases, which can be new-formed (mullite) or residual (quartz).

These two main components greatly influences the final properties of the finished product. The glassy phase is intrinsically more brittle than crystalline phases, but it is also able to modify its specific volume depending on the cooling rate.

The origin of the hysteresis appears to be related to microcrack formation in the tile during cooling in the kiln, since the quartz coefficient of expansion is larger than that of the other existing phases. As a result, during heating of the fired piece in a dilatometer, only a fraction of the quartz present in the compact, namely the quartz joined to the matrix, contributes to overall expansion since many quartz particles are separated from the matrix by microcracks, which accommodate particle expansion.

While thermal expansion/contraction implies transitory volume changes, the volume changes induced by the cooling rate are permanent. This means that a state of stress between two adjacent areas with different specific volume will yield a permanent state of stress.

Volume changes due to different cooling rate, will remain frozen into the body and generate a permanent state of stress.

The volume contraction during the cooling stage is usually evaluated as the reverse of the thermal expansion. Therefore the measurement is done with the assumption that the porcelain body behaves exactly in the same way during heating and during cooling.

This assumption proved to be true only if the thermal expansion is measured up to a temperature lower than the glass transition temperature of the glassy phases which are still present in the body after sintering.

The permanent volume changes during cooling are difficult to be investigated by traditional single pushrod dilatometry, because it would require to record a calibration curve for each thermal cycle. Furthermore, the pressure of the pushrod limits the study of the thermal expansion of a sample up to a temperature where the specimen it is rigid enough not to

be deformed by the pressure of the rod, thus below the glass transition temperature range.

EXPERIMENTAL

Thermal expansion and flexion tests were performed on porcelain body samples to investigate the amount and effects of their volume changes during cooling.

Due to the high percentage of glassy phase, the porcelain body samples could be successfully investigated with optical no-contact instruments.

The optical dilatometer mode of ODP 868 allows to carry out thermal expansion measurements with no contact and no interference caused by the measuring system. This method thus provides an absolute measurement. Two beams of lights illuminate both the ends of the specimen, which is placed horizontally into the furnace, and two digital cameras capture the images of the last two hundreds microns of each tip.

The specimen, completely free to expand or contract, is measured by the image that it projects on an image sensor. The practical applications of this kind of dilatometer are varied and they include all fields in which it is important to know the thermomechanical behaviour of the materials even when the sample has a viscous behaviour.

On the other hand, the fleximeter mode of ODP 868 allows to perform flexion measurements with no contact with the samples tested. During the analysis, 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 without applying any external load.

RESULTS AND DISCUSSION

The Optical Dilatometer provides the means to identify transition temperatures and effects of the cooling rate on the specific volume as well.

The magnitude of the volume change is directly linked to microcracks formation, to the amount of glassy phase in the porcelain body and to the original cooling rate in the industrial kiln.

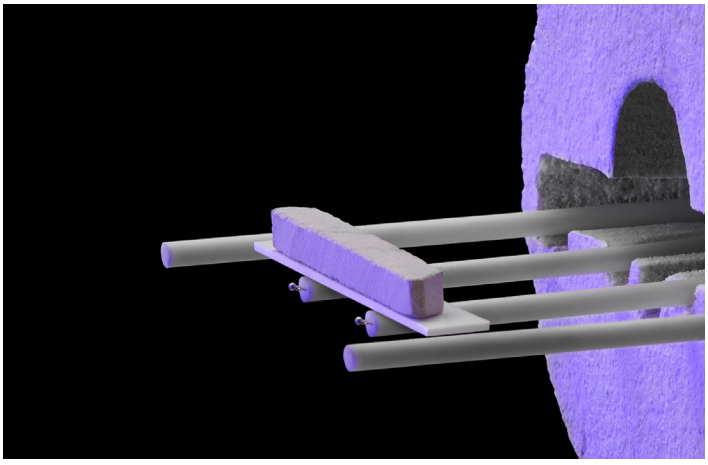

Figure 2. Specimen (50x5x5 mm) of body layer only of a glazed porcelain tile (glaze was removed with an electric saw) prepared for horizontal dilatometry test

Microcracking can be correlated with the hysteresis of the coefficient of thermal expansion during heating and cooling. At dilatometer peak test temperature (1000 °C), which is higher than the transformation temperature of the glassy phase in the matrix, the quartz particles bind again to the matrix.

During cooling (Figure 3), the existing phases remain bonded until the temperature of 573 °C where the coefficients of thermal expansion of all phases are similar and the cooling rate is slow.

When the quartz shrinks abruptly at 573 °C, almost all the quartz is chemically bound to the matrix and contributes to overall tile shrinkage. As a result, at this temperature, the test piece coefficient of thermal expansion during cooling must be greater than that found during heating. In accordance with this assumption, the magnitude of the hysteresis, must be directly related to microcrack concentration, or to the quartz content detached from the matrix. These cracks, acting by themselves or in combination with large pores, constitute fracture-initiating flaws that contribute to body failure.

Figure 4 shows the result of the application of a slow cooling to a porcelain tile specimen taken from industrial manufacturing to investigate the effects of the amount of glassy phases.

This test was carried out heating the specimen at 10 °C/min up to 1000 °C and then cooling it slowly at 2 °C/min down to 500 °C, reheating at 5 °C/min up to 1000 °C and cooling again at 2°C/min down to room temperature.

The analysis of the behavior is very interesting: during the first heating at 10 °C/min, the curve apparently does not show

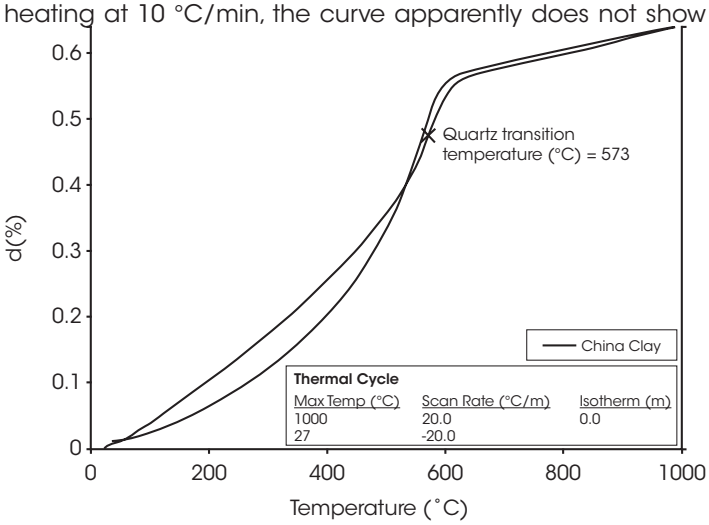

Figure 3: thermal hysteresis during the optical dilatometer test.

any unusual behavior. In fact, it is possible to clearly see the quartz transition, but after that, there are other two changes in slope at 764 °C and 904 °C. Above this temperature, the expansion curve keeps rising, but reducing the rate of

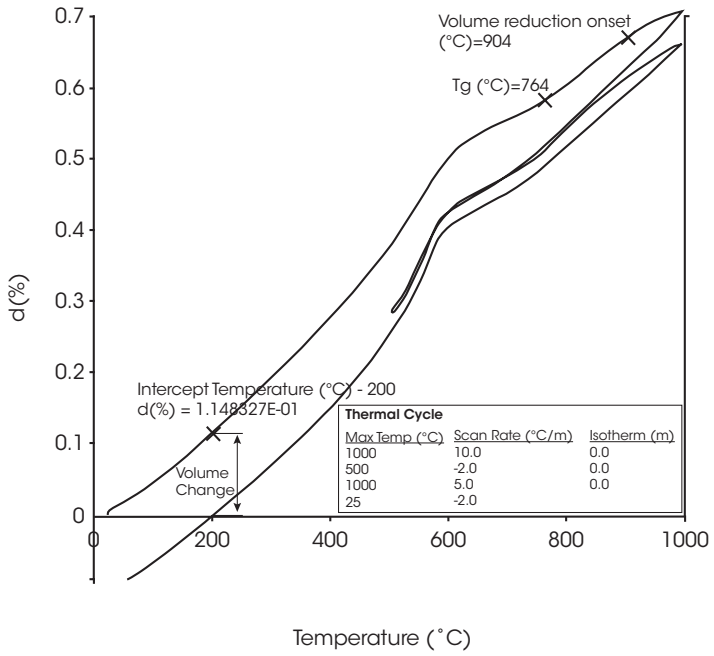

Figure 4. Thermal expansion curve of a porcelain tile sample, effects of the application of a slow cooling

expansion.

The change in slope at 764 °C is indeed the glass transition of the glassy phase, while the decreased rate of expansion above 904 °C is due to the volume reduction of the glassy phase. At these temperatures (more than 100 °C above the Tg), the viscosity of the glassy phase is decreasing exponentially according to the Arrhenius law and the glass rearranges it lattice to a smaller volume.

This volume reduction is due to the fact that the specimen was cooled very quickly in the industrial firing kiln, and the volume of the glass is the one corresponding to a fast cooling. Reheating the specimen, overcoming the Tg, the glassy phase is rearranging to a lower volume state.

In fact the reduction in volume takes place even during the subsequent cooling stage at 2 °C down to Tg.

The following part of the graph is a reheating at 5 °C/m, which follows the same path of the cooling at 2 °C/min up to the Tg. Above the Tg, the reduction in the rate of expansion, which gives rise to a volume reduction, is again apparent.

The last cooling at 2 °C per minute down to room temperature is parallel to the curve recorded in the first heating at 10 °C/min, but is quite lower on the Y axis.

Comparing the dimension of the sample on the Y axis at zero expansion, it is possible to see that the change in volume due to slow cooling is equivalent to the expansion over occurred in the temperature range 25- 200 °C.

Despite the fact that the slope of the two curves is the same, i.e the thermal expansion coefficient does not change, the volume may undergo permanent changes. A permanent state of stress may build up between different areas of the ceramic ware that have been cooled at a different rate, even if they have the same thermal expansion coefficient. The situation become 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.

This difference in glassy phases density justifies the hysteresis shown by the bending curve in Figure 5. The optical fleximeter, in fact, allows the analysis of differential state of stress built up during the cooling on the upper and lower side of the ware. It is a common practice in the ceramic tile industry to use differential cooling to control the planarity of the finished product. High amount of stress in the final product may result in difficulties in cutting and it may lead to reduction in toughness. Figure 5 shows the result of a fleximetry analysis on a specimen cut from a typical glazed porcelain tile.

The behavior of the curve under heating is as expected: the glaze is under compression, then the specimen upon heating become concave, so the curve goes down. This is because the thermal expansion coefficient of the body is higher than the thermal expansion of the glaze, then, upon heating, the body becomes longer than the glaze and the specimen becomes concave. The flexion curve reaches a minimum in correspondence of the quartz transition, because at this temperature the body reaches its maximum thermal expansion coefficient. After the minimum, the bending starts decreasing and the curve starts rising upward, up to the point it stabilizes below the zero line. This is the typical behavior of a correct state of compression of the glaze onto the body: above the coupling temperature the compressive stresses between the glaze and the body are released and the specimen is still slightly concave.

The cooling curve is expected to show the reverse behavior, but instead the flexion follows a different path. The cooling curve in Figure 4 is all below the curve measured during the heating.

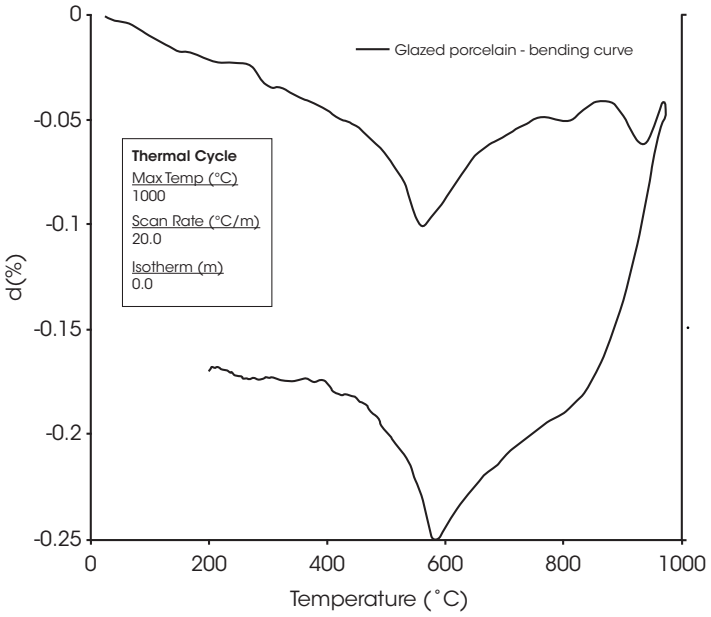

Figure 5. Flexion curve of a glazed porcelain tile, heating and cooling

The reason for this is the different cooling of the two opposite surfaces (upper and lower surface) of the tile.

The symmetrical cooling in the fleximeter changes the planarity of the specimen, because now both sides are cooled with the same rate.This would be the shape of that tile if cooled symmetrically: the tile would have been concave and it was made flat cooling the upper side faster that the bottom side.

The side effect of this differential distribution of stresses is the fact that the tile may become difficult to cut, because inside of the ceramic body there is elastic energy stored as tensile or compressive stresses. This energy may interfere to the propagation of cracks during the cutting and lead to uncontrollable cutting paths.

CONCLUSIONS

Optical dilatometry and optical fleximetry analyses allowed to investigate the volume changes induced by the cooling rate in porcelain bodies.

The common practice in the ceramic tile industry to use differential cooling to control the planarity of the finished product induces permanent changes of volume in different areas of the ceramic ware, which give rise to permanent states of stress. Interesting results obtained with this study come from the application of forming and firing techniques realized on a small scale by using laboratory equipment but are completely reproducible at industrial level. ODP 868 allows to reproduce exactly thermal cycles which are usually set up in the rolls industrial kilns and represents excellent analysis instruments which allow to realize customized thermal treatments, designated in conformity with materials to study and able to perform a very precise measurement of the sintering process.

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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