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Double Beam Optical Dilatometry

A Novel Tool f or the Ceramic Research.

Abstract

Thanks to the new double optical dilatometer, the ceramic scientist has the possibility to follow the behaviour of the sample during the heat treatment without interfering with the process. The applications brake the limits of traditional dilatometry in many fields of research:

- Incoherent materials, like the expansion and contraction of the raw glaze applied on the surface of a ceramic ware, or the behaviour of an incoherent granular flit
- Softened materials, like the behaviour of a glass above the transition temperature, where the surface tension starts to pull the edges and to make the sample shorter
- Sintering kinetics: studying the relationship between time and temperature during a sintering process
- Extremely thin samples, like tape cast substrates can be analysed with regard to thermal expansion and sintering behaviour.

Introduction

The thermo mechanical analysis plays a very important role in the ceramic field, and it is used to check the thermal expansion coefficient of bodies and glazes to ensure an optimal match of thermo mechanical behaviour. There are several! types of "Thermo Mechanical Analyser" for the measurement of different mechanical properties as a function of temperature.

The simplest ones, commonly called dilatometers, measure the dimensional changes as a function of temperature. The instruments of this family may differ in the way they measure dimensional changes of the sample. One very relevant difference is if there is contact with the sample or not.

Ali the mechanical or electronic dilatometers use a push rod in touch with the sample to transfer the dimensional change of the sample from the internal of the fumace to the transducer (dial gauge, differential transformer, capacitive) (Fig. 1).

The use of a push rod in mechanical contact with the sample requires to correct the measured data to take in account the expansion of the push rod, but now a day, with computerised systems, this operation is carried out automatically. As long as the System is kept calibrated, the measurements are very reliable, even if sometimes the correction amounts for twice as much as the measured value.

The push rod dilatometer can follow the sample only as long as it is rigid enough not to be deformed by the pressure of the rod. When a sample is too thin to be pushed or loo fragile to be pulled, or it is almost incoherent or softened, it cannot! be measured using this kind of dilatometer. it is necessary to use a non contact measuring system,

Optical dilatometers use a beam of light to measure the dimensional changes and so the sample is not in touch with the measuring system. There are several methods for measuring the dimensional changes of the sample with a beam of tight and they can be summarised in two categories: reflected beam and direct beam. The first optical dilatometer was invented by Abbe and Fizeau in the second half of the 19th century. This design uses a reflected beam of monochromatic light and the measurement of the displacement is carried out by courting the interference fringes between the forward going beam and the reflected team. After the Abbe invention, many improvements were achieved on the original design and now a day there are many models on the market, which use new optics and design. But in order to measure thermal expansion up to high temperatures the sample has to be set on a sample holder inside the fumace and also the sample holder has its own thermal expansion. In order to achieve a good accuracy it is necessary to measure the expansion of the sample holder and to subtract it from the actual expansion of the specimen.

The best way to do is to split the laser beam into two beams of light, which are reflected by the top of the sample and by the sample holder or by both ends of the specimen (Fig. 2). Measuring the sample from both ends the measure is absolute and there is no need for any correction. This is the most accurate way of measuring thermal expansion and it may reach a nano-metric resolution. This is the type of instrument used by the suppliers of standard materials for the thermal expansion. For example, the National Institute for Standards and Technology (NIST) uses a Fizeau double beam interferometer to certify the thermal expansion of their Standard Reference Materials for thermal expansion.

This method proved to be very accurate, with a resolution of a fraction of the wave length of the incident light, but it is limited by the reflectance of the surface of the specimen, if the specimen is not reflective, or it becomes not reflective during the test, it is then necessary to use a mir-

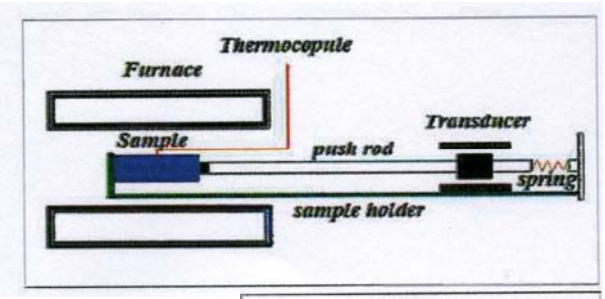


Fig. 1 (Lop)
Scheme of a traditional Dilatometer With a push-rod and A displacement transducer

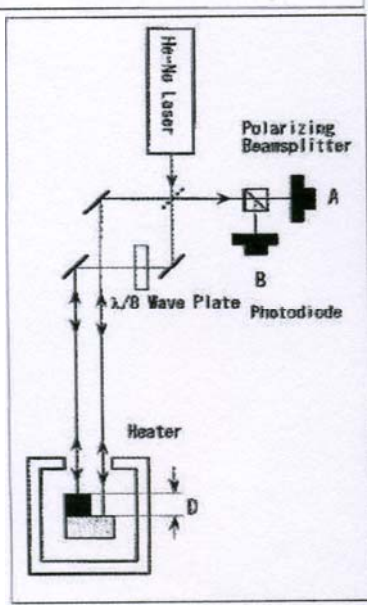


Fig. 2
Scheme of a double Beam interferometric dilatometer

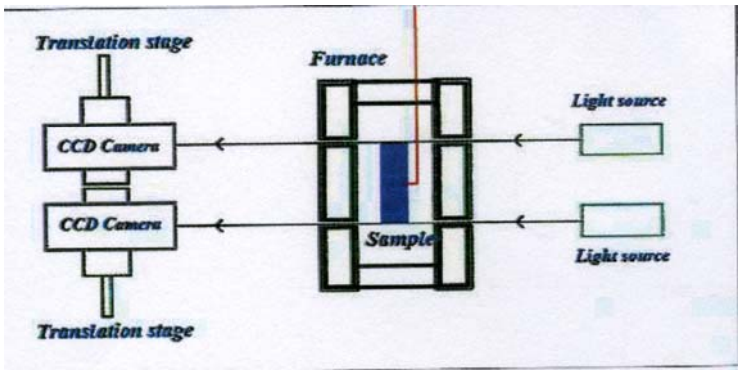


Fig. 3 (left)
Scheme of a double beam optical dilatometer with two direct beams of light

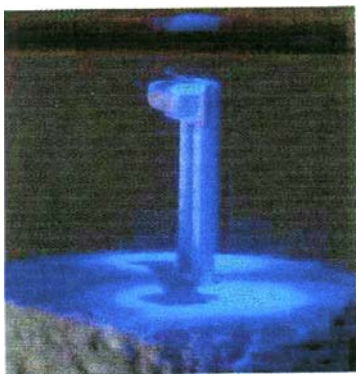


Fig. 4 (right)
Picture of a sample of molten glaze on the measuring system of the "Misura ODLT" double beam horizontal optical dilatometer. The sample is completely free to move and it is not in touch with anything.

ror, which is put in touch with the specimen using a refractory push rod. Managing in this way, this method looses the advantage of being non contact and becomes substantially similar to the electronic dilatometer.

The direct beam measuring System overcomes this problem because the specimen is measured by the image that it projects on a CCD when it is lighted by a direct beam of light. Using a beam of light with short wave length and a very high resolution CCD it is possible to achieve a good resolution. For example, using a blue light with a wave length below 0,5 µm, it is possible to have an image with an actual resolution of 0,5 µm per pixel of the camera (not an interpolated resolution but an actual resolution). With a sample of 50 mm of length the resolution becomes one part over 100 000.

Using two beams of light, which illuminate both the ends of the specimen it is then possible to achieve an absolute measurement of the dimensional changes of the sample during the heat treatment (Fig. 3).

The specimen is completely free to expand or contract, there is no measuring System in touch with it, but only a sample holder, to keep it in place inside the fumace. The displacement of the sample holder is not relevant for the result of the measurement because the optical system is watching both the ends of the sample (Fig.4)

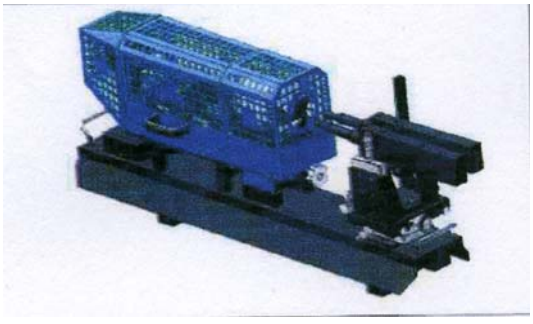


Fig. 5
Scheme of the double beam vertical Optical dilatometer "Misura ODHT"

The Double Direct Beam Optical Dilatometer

The idea of a double beam optical dilatometer is not new, but many attempts made in the past flailed because of the limitation imposed by the image production and image processing technology. Now a day, the performance of digital cameras and personal computers enable the design of double beam optical dilatometer at competitive cost.

As a first approach it may seem reasonable to use only one camera with a large CCD to collect the image of the sample as a whole. This kind of design looks cheaper at a first sight but becomes immediately unfeasible thinking at the resolution required for a thermal expansion measurement on small size samples. In fact, to achieve a resolution of 0,5 µm on a sample 50 µm long, ensuring a resolution of the measurement of one part over 100.000 it would be necessary to use a CCD with 100.000 pixels per line, which is not yet available on the market and it may well not be available for a while.

The use of two beams of tight implies the use of two microscopes and two digital cameras. Focusing the image of the tip of the sample on the CCD of the camera with the maximum of the magnification achievable using visible light, means to be able to see only few hundred microns of the sample. A sample 50 mm or 50.000 microns long which reaches an expansion of 1 % will expand 500 micron. Using blue fight with wave length of 478 nanometres and magnifying up to 0,5 micron per pixel, the image will shift 1.000 pixel. Since the sample is free on the sample holder, it may move in one direction only, going out of the field of view of a video camera with 1 mega pixel (1.000 x 1.000). The use of line cameras is unfeasible because the measurement will be strongly affected by edge imperfection. The use of larger area CCD implies to be able to obtain a perfectly fiat filed over a large area CCD, and working with this magnification is close to impossible.

The solution to this problem is to move the optical path in order to follow the expansion or the contraction of the sample. In order to do this it is necessary to use two linear translation stages equipped with a step motor controlled by the computer and able to make the shift in a very short time with very high accuracy

This new design, patented by Expert System Solutions, allows to build optical dilatometers with unprecedented features: using a sample 50 mm long placed horizontally in the fumace it can measure expansion with a resolution of one part over 100.000, or using a sample 15 mm long placed vertically inside the fumace it can measure sintering or bioating process with no limitation in dimensional changes (Fig. 5).

One relevant feature of this kind of dilatometers is the fact that the calibration curve it is not necessary. Once the magnification of the two optical paths is carefully established, there b no need for further calibration, unless the instrument is mechanically taken apart. In fact, the magnification of the optical system does not change with time or with the number of test performed. To prove it, it is possible to check the calibration using a Standard Reference Material supplied by NIST.

Fig. 6 shows the perfect match between the curve measured on a certified sample and the curve obtained plotting the certified data from NIST.

New Fields of Research

Now the ceramic scientist has the possibility to follow the behaviour of the sample during the heat treatment without interfering with the process. The applications brake the limits of

traditional dilatometry in many fields of research:

* Incoherent materials, like the expansion and contraction of an Incoherent granular frit, as applied on a raw tile
* Softened materials, like the behaviour of a glass above the transition temperature, where the surface tension starts to pull the edges and to make the sample shorter
* Sintering kinetics; studying the relationship between time and temperature during a sintering process
* Extremely thin samples, like thermal expansion and sintering behaviour of the extremely thin layer of glaze as applied on a ceramic tile.

Thermal Expansion on Incoherent Materials

Ceramic is the science of sintering powders and powders can be incoherent. Optical dilatometry can be used to check the behaviour of uncompacted powders which have no mechanical strength, like a layer of granular frit.

Thermal expansion of a granular frit can only be measured with no contact because, with no addition of a binder, the material is completely incoherent. The thermal expansion test with traditional dilatometers on these raw materials is normally carried out adding a clay as binder, but managing in this way the behaviour changes completely. Using an optical dilatometer it is possible to get an accurate measurement of the thermal expansion even on a granular frit which was held together simply by wetting with a drop of water. Fig. 7 shows the samples before (in front) and after the thermal expansion test. The result of the measurement in Flg. 8 clearly shows the sintering and melting behaviour of the material.

Measurement of Thermal Expansion above the Glass Transition Temperature up to Melting

Most of the sintering mechanisms which evolve during the heat treatment in traditional ceramics imply the development of a liquid phase. The presence of the liquid phase during sintering makes the material substantially viscous. The dimensional changes during the sintering process can be studied only if the measuring system does not interfere with the sintering mechanism itself. The non contact measurement ìs ideal for the study of the transition from solid to liquid even in the glassy state. The measurement of thermal expansion is substantially identical to the measurement obtained with a push rod dilatometer as long as the sample is still rigid. When the temperature overcomes the glass transition, the viscosity drops exponentially and the sample becomes soft. With a non contact system it is possible to continue

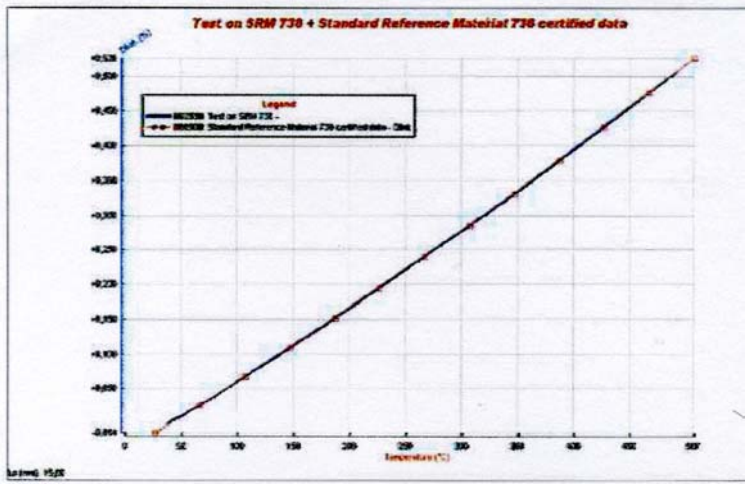


Fig. 6
Thermal expansion of the Standard Reference Material SRM 738 from NIST as measured with a double beam optical dilatometer (blue line) in comparison with certified data (red dotted line).

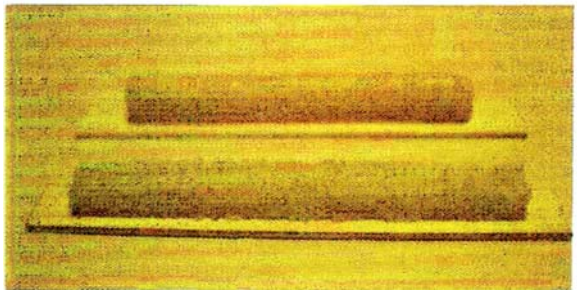


Fig. 7 (below)
Samples of incoherent granular frit: before (in front) and after the thermal expansion and sintering test.

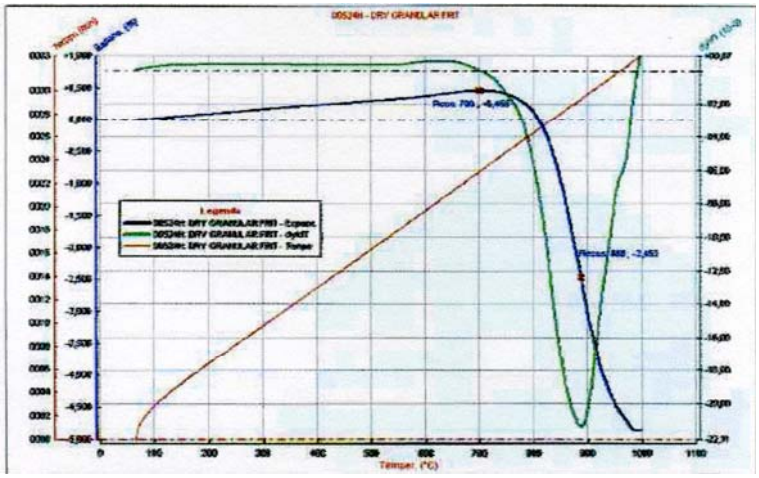


Fig. 8
Thermal expansion and sintering of an incoherent granular frit (blue curve), derivative (green), time (red).

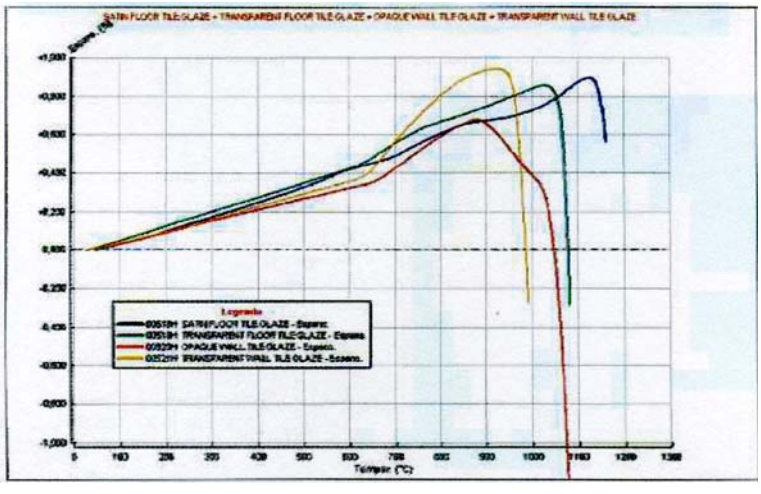


Fig. 9
Thermal expansion up to the malting of part of the curve above the glass transition temperature keeps going up to the melting of the sample.

Fig. 10
Glaze samples after the thermal expansion test: the edges of the samples become round because the glaze is melting.

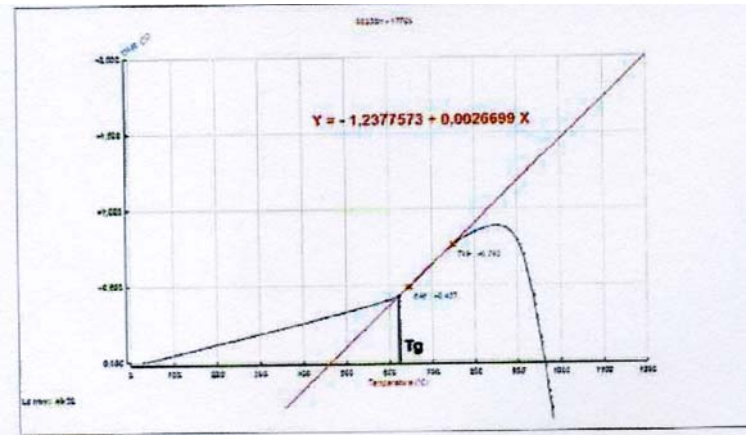


Fig. 11
The slope of the curve above the transition temperature is the thermal expansion coefficient of the liquid phase. Extrapolating this part of the curve it is possible to know the increase in volume of the glass at any temperature.

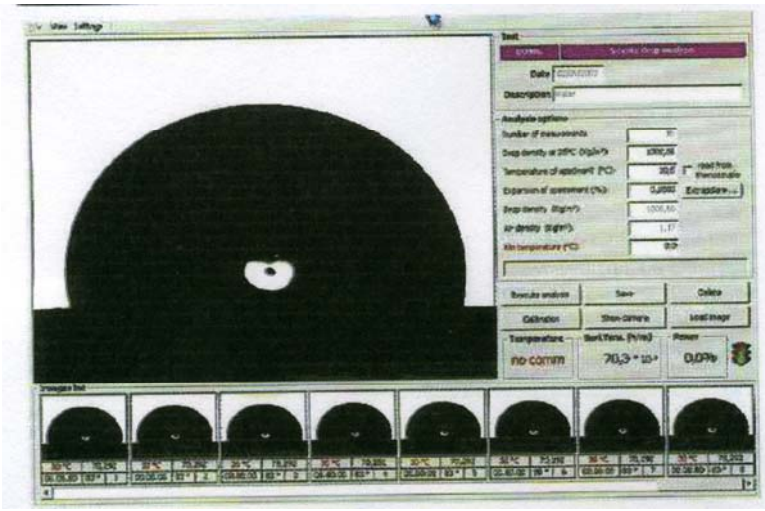
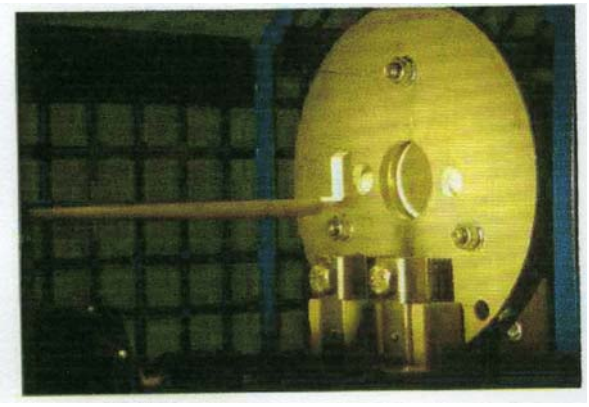


Fig. 12
Dialog window of the drop analysis instrument developed by Expert System Solution, which apply the Young-Laplace method to measure the surface tension of liquid from room temperature up to 1600°C.

Fig. 13
Pressed sample of recycled glass powder on the sample holder of the "Misura ODHT" double beam vertical optical dilatometer.



the measurement up to the complete melting of the glass. Fig. 9 shows the measurement on different glass and glaze samples while Fig. 10 shows the samples after measurement.
The graph reaches a peak point and then starts falling down. The reduction in size of the samples is given by the surface tension of the glass which makes the tip rounded and the sample shorter.
The part of the curve above the transition point is hundreds of degrees long and this allows the extrapolation of the thermal expansion of the molten glass (Fìg. 11). Knowing this it becomes possible to calculate the density of the molten glass at any temperature and this is a crucial Information for the calculation of the surface tension of the molten glass using the method of the sessile drop analysis. This instrument, developed by Expert System Solutions is the only one available on the market which can perform the measurement of the surface tension using the sessile drop analysis up to 1600°C. Fig. 12 shows the dialog window of the software which performs the analysis of the profile of the sessile drop according the equation written by Young and Laplace at the beginning of the 19th century.

Sintering of a Class Powder

The study of the sintering kinetics is an ideal application for the optical dilatometer. The relationship between sintering speed at constant heating rate versus temperature or shrinkage versus time at constant temperature can be exactly determined. Only with a non contact dilatometer it becomes possible to follow the sintering behaviour of a ceramic material when the driving force of the sintering process is the surface tension of a liquid phase. This study is yielding extremely valuable information which can be used to define the best heat treatment for each specific material.
The sample of compacted glass powder (Fig. 13) was first heated with constant heating rate up to complete melting. This test allows to define the temperature of maximum sintering speed, calculating the derivative of the sintering curve. Designing a second heat treatment with a permanence at that temperature the time necessary can be identified to achieve a stable condition of sintering, preventing the melting or the bloating of the material (Fig. 14).As expected, the sintering speed ìs decreasing exponentially against time at constant temperature, while ii is increasing exponentially versus temperature at constant heating rate.

Extremely Thin Sample: Layer of Glaze as Applied on a Ceramic Tile

The behaviour of the raw glaze can be followed up to complete

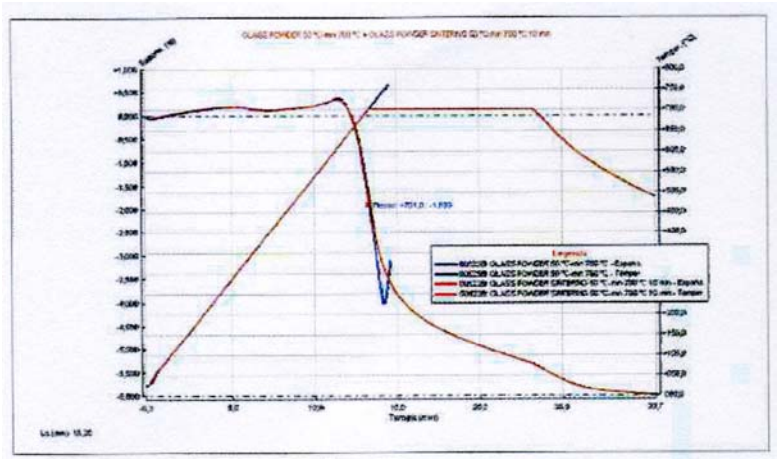


Fig. 14 Sintering of a glass poder. The blue curve is the first, carried out at constant heating rate up to bloating. The maximum sintering rate is identified at 701°C. the red curve is a second test carried out with the same heating rate up to 700°C, then holding this temperature for 10 minutes. The sintering proceeds with no sign of bloating.

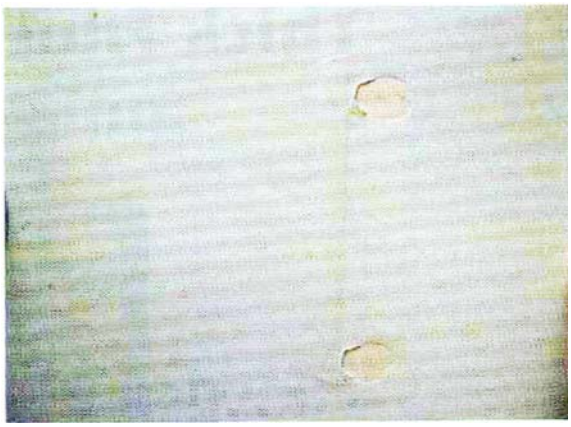


Fig. 15 Experimental lethod to collect the glaze layer as applied on the glaze line. A small ape of ashless laboratory filter is set on the tile before the application. After the application it is visible the relied given by the paper under the glaze.

melting, up to the point it becomes shorter because the surface tension is rounding the edges of the sample.

The samples were obtained laying an ashless filter for chemical analysis on the ceramic tile before the glaze application, directly on the glazing line Flg. 15. The amount of glaze and the nature of the deposit of glaze particles is exactly the same as in the industrial application.

The filler is then removed from the surface of the tile and it is cut in a suitable size for the measurement inside the optical dilatometer (typically 50 mm long, 5 mm wide). The sample is then set on the special sample holder for thin samples (Fig. 16) and the measurement is started. The filter paper will burn out leaving no ashes and with no interference with the measurement. From the result of the test (Fig. 17) we can clearly see that the layer of glaze undergoes a sudden shrinkage in the initial phase of sintering. Since the material is incoherent and not viscous, this shrlnkagemay produce an extensive microcracking on the surface of the glaze. The scars of these small cracks will make the surface of the glaze slightly hammered, even thought the application was perfectly smooth.

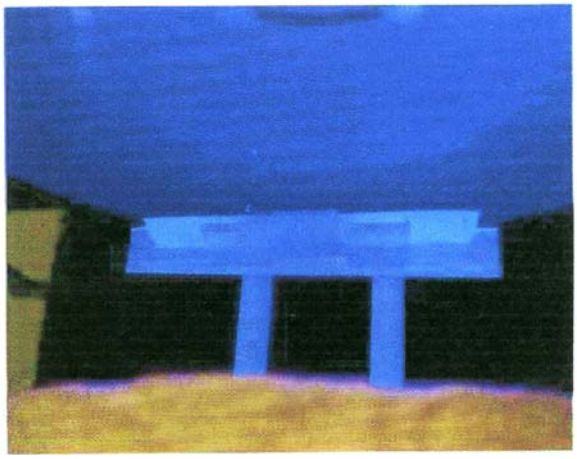


Fig. 16 The layer of glaze is carefully removed from the surface of the tile, still on the filter paper. The sheet is set on a sample holder inside the fumace of the double beam horizontal optical dilatometer.

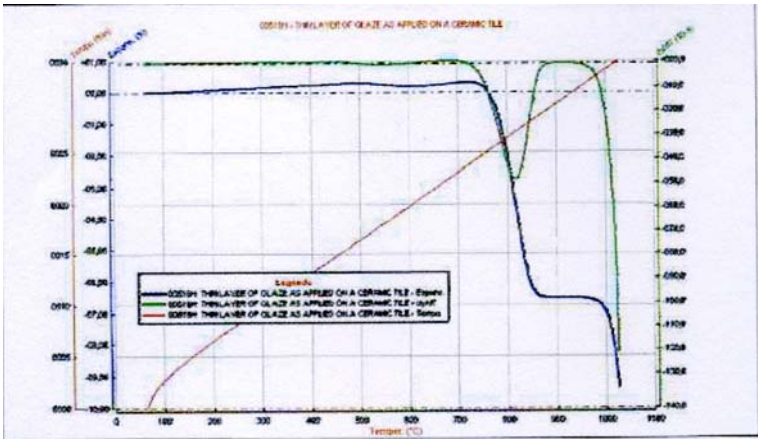


Fig. 17 Thermal expansion and sintering of an extremely thin layer of glaze as applied on a ceramic tile (blue curve), derivative (green), time(red).

Conclusions

This is only overview of the new research possibility made available by the new technique of double direct beam optical dilatometry. Ceramic science is the ideal field of application of this testing method because of the specific characteristic of the ceramic materials. It is now possible to follow all the stages of the ceramic process with no interference due to the presence of a measuring system in touch with the material.

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