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DIL005

## ABSTRACT

Pyroplasticity is the gravity-driven viscous deformation of a ceramic material during firing and can affect the productivity of a production plant. It determines the relationship between the thickness and the strain rate of the material as a function of firing temperature. This pyroplastic deformation can be quantified by measuring the bending of a body sample during heating. In case of manufacturing process with industrial roller kiln, the stress on the sample inside the analytical instrument is typically greater: as the material moves over the rollers, the supporting points shift continuously across the entire width of the piece, whereas in the laboratory instrument the material is suspended on two static supports. However, qualitatively the results are fundamental to have a comprehension of the behavior of the glassy phases during sintering and to optimize the firing cycle.

## INTRODUCTION

This measurement is particularly important for those 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. The primary deformation mechanism is viscous flow, therefore having a time-dependence for the bending deformation. The first derivative of the bending curve represents the deformation speed and is a function of the material viscosity within the limit of small deformations. In fact, during the final stage of firing an abundant vitreous phase is developed with a sufficiently low viscosity to cause rapid deformation of the material. Pyroplasticity can be measured directly with the optical Fleximeter mode of the ODP 868, produced by TA Instruments. The sample is suspended between two support rods 70 mm apart, while a camera frames the centre of the sample, which moves during heat

treatment (Figure 1). Pyroplastic viscous flow produces a downward movement at the sample midpoint. Glazed and other multi-component systems can also exhibit upward motion caused by the mismatch of thermal expansion and resulting internal stresses within the specimen.

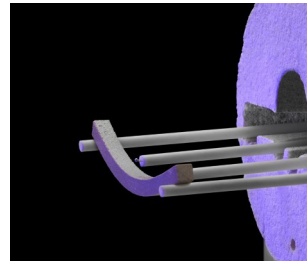


Figure 2: ODP 868 FLEX green specimen (80x5x5 mm) obtained from the ceramic body layer of a porcelain tile

## EXPERIMENTAL

In Figure 3 the two possible behaviours of pyroplasticity are demonstrated. Two samples of green bodies were heated at 30°C/min and then treated isothermally for 5 minutes at 1220 °C and again for 5 minutes at 1230°C (red curve). Sample 1 (green curve) shows a final bending of more than 6 mm, and the maximum deformation rate (dotted green line) occurs at the maximum temperature (1230 °C). Sample 2 (dotted blue line) shows a final bending of less than 3 mm and the maximum deformation rate (blue curve with circles) occurs at the beginning of the first isothermal segment at 1220 °C. Sample 1 deformation curve reaches a maximum deformation of 6401 μm at 1230 °C, reaching a speed of deformation equal to  $dy/dt = 28.71 \times 10^{-3} \text{ mm} \cdot \text{s}^{-1}$  while Sample 2, at 1230 °C, reaches a maximum deformation

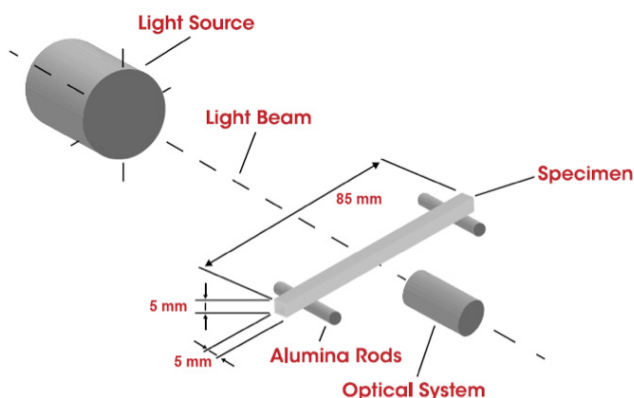


Figure 1: Measuring scheme of the non-contact optical fleximeter mode of the Optical Dilatometry Platform ODP 868 from TA Instruments

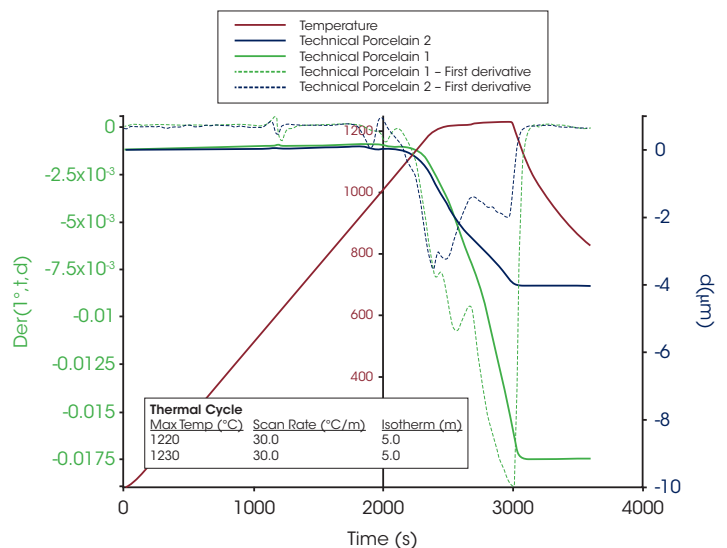


Figure 3: Bending deformation and bending deformation speed curves of two samples of green body

of 2815  $\mu\text{m}$  and a speed of deformation equal to  $dy/dT=4,7 \times 10^{-3} \text{ mm} \cdot \text{s}^{-1}$ . Surprisingly, Sample 2 reduces the speed of deformation while the temperature increases: this is a clear sign that the glassy phases are changing their compositions, becoming more viscous. The addition of glassceramic materials to bodies, for example, can reduce bending, indicating an increase in modulus of elasticity caused by the transition from the vitreous phase to the crystalline phase.

Today's needs of R&D laboratories in tiles manufacturing plants are also focused on understanding the inherent mechanisms that govern the bonding process between two overlapped green layers.

In the case of double layer materials that have to undergo sintering, understanding the origins of the deformation developed during firing can be very worthwhile. Usually the main targets are:

1. Measuring the bending deformation caused by differences in dilatometric/sintering behaviour of the different layers;
2. Determine the pyroplasticity onset;
3. Quantify the amount of all these bending deformation.

The results obtained from only one bending test are not enough to discriminate the deformation causes. In fact, it is necessary to carry out two bending tests, with the same layer placed first upward and then downward on the support. If these two curves are specular, the deformations have not a pyroplastic origin, but they are due to a difference in sintering of the two different bodies that constitute the double layer material. On the contrary, the bending deformation will be caused by pyroplasticity.

Figure 4 shows the results of two tests aiming to study the pyroplastic behavior of a bilayer constituted by two different green bodies (named layer 1 and layer 2).

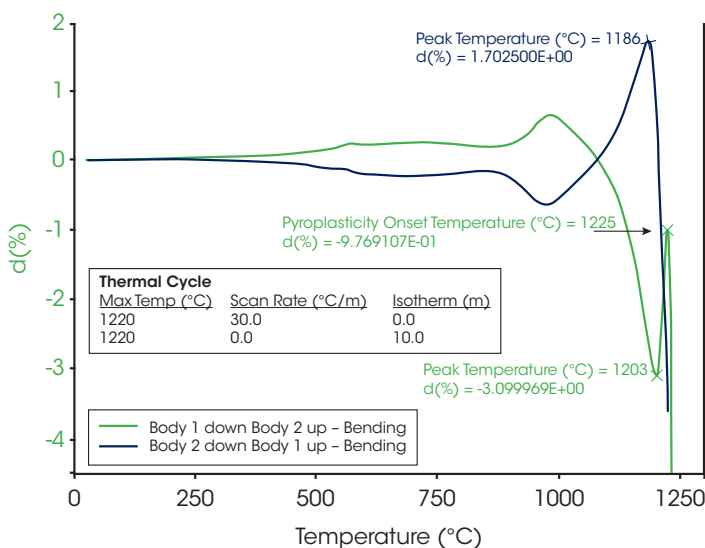


Figure 4: Bending curves of a double layer material, with layer 1 on the top (blue curve) and on the bottom (green curve)

As it is possible to see in figure 4, the two bending curves are specular up to a temperature of 1200 °C. Bending deformations experienced in the relatively low temperatures range (up to about 900 °C) are caused by differences in the dilatometric behaviour of the two raw bodies. The more evident deformation occurs between 900 and 1200 °C and it is due to a difference in the onset of sintering temperature of the two layers.

At 1200 °C the sample with layer 1 on the bottom shows an inversion (positive peak): it represents the onset of pyroplastic deformation. In the test with the layer 1 on the top (blue curve) the effect of pyroplastic deformation is superimposed to the effect of differential sintering, because they have the same sign. When the layer 1 is on the bottom (green curve), the two effects are subtracting, because they have opposite signs.

Since it is not possible to determine "ab initio" the bending behaviour of a material, the analysis performed with the ODP 868 in Fleximeter mode is of fundamental importance to characterize the material behaviour during heat treatment. In this regard studying the bending deformation of a double layer sample is crucial not only when constituted by traditional ceramics, but also when multi-layer advanced ceramics are investigated.

Figure 6 reports the bending deformation of a sample that is constituted by a Nickel based layer and Zirconia based (YSZ) substrate. The blue curve is the result of the configuration with the YSZ layer on the bottom, while the green curve represents the bending deformation of a sample placed with the YSZ layer on the top. The results are expressed as a function of the time. The temperature curve is represented in red.

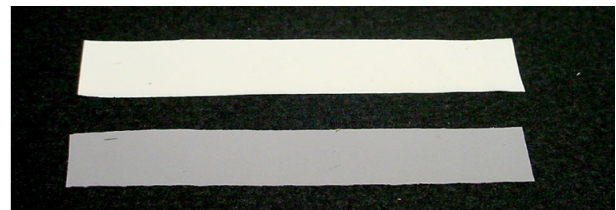


Figure 5: Ni-YSZ cermet layer (grey) and YSZ layer (white)

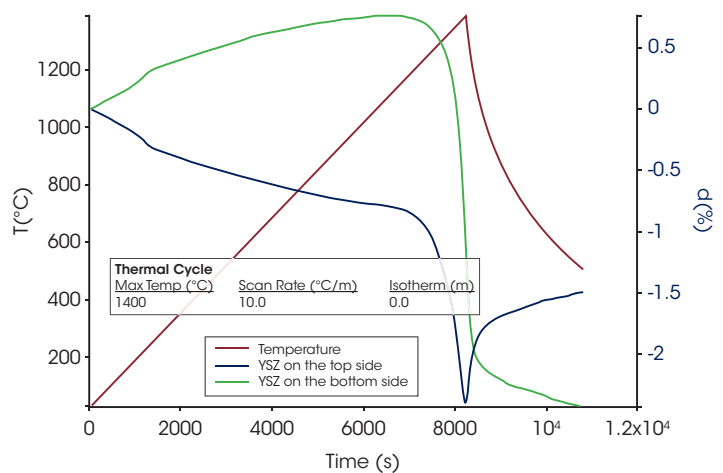


Figure 6: Bending curves of a multilayer material constituted by a Nickel based layer and a Zirconia (YSZ) based substrate, with YSZ on the bottom (blue curve) and on the top (green curve).

The two bending curves are specular up to a temperature of about 1150 °C, onset of pyroplastic deformation. The bending deformation occurring at temperatures lower than 1150 °C are caused by differences in the dilatometric behaviour of the two different layers. In particular, the NiO-YSZ cermet layer has a higher thermal expansion than the YSZ thin layer: at lower temperature the NiO-YSZ cermet results longer and causes a bending upward.



Figure 7: Optical Dilatometry Platform ODP 868

## CONCLUSIONS

The optical, non-contact measuring approach is extremely effective for the optimisation of industrial processes, making it possible to get reliable measures of the thermal behaviour in terms of sintering speed, bloating, pyroplastic deformation speed and bending. This study is yielding extremely valuable information which can be used to define the best heat treatment for each specific material. Considering the various experimental results it is easy to understand that it is very difficult to solve the various problems of deformation without the support of complete laboratory data. The ODP 868 was designed to meet this requirement.

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