Thermal Expansion Study of a β-Eucryptite-Based Glass-Ceramic by Means of Optical Dilatometry

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The main application of optical dilatometers is found when the material under investigation cannot withstand any external force to be properly studied. Two are the major reasons for this particular situation: the state of aggregation of the material itself and its geometric shape.

The study of the thermal behaviour of glass ceramic materials is one of this case, the transitions between the glass and crystalline phase occur at temperatures beyond the glass transition temperature (Tg), where the viscosity is low enough to allow the growth of the crystal nuclei. The other case is represented by the measurement of thermo-mechanical behaviour of specimens with a very low thickness. Even reducing to the minimum the force applied by the push rod of a standard dilatometer it is close to impossible to get a reliable measurement on thin sheets and on viscous materials, because they get deformed too easily.

The horizontal dilatometer mode of Optical Dilatometry Platform ODP 868 solves completely these problems thanks to the optical non contact measuring system. Since any pressure is applied on the sample, the entire process can be monitored even if the materials begin to develop liquid phases during heating. This kind of information can be useful in the development of new materials, since the actual expansion of the material in the crystallizing or re-crystallizing phase can cause deformation phenomena which otherwise could not be understood.

Figure 1: Optical Dilatometry Platform ODP 868

Glass-ceramic materials are conventionally obtained through the controlled crystallization of solidified glass melts and transparency is achieved through the controlled nucleation and growth of extremely fine crystals (much smaller than the wavelength of visible light).

RESULTS

In this paper, the thermal expansion behaviour of a commercial β-eucryptite-based glass ceramic is investigated by means of the optical non-contact dilatometry.

The dilatometric test of Figure 2 was carried out with a heating rate of 20 °C/min, up to the complete melting of the sample. The curve is characterized by an initial negative thermal expansion phase, from room temperature up to 850 °C, which is just the glass transition temperature of the glassy phase present inside the sample. Beyond this temperature, a positive thermal expansion phase occurs up to 969 °C, the softening point of such glassy phase. After the first glass shrinkage caused by the surface tension, the sample undergoes a strong expansion starting at 1017 °C. This indicates that a phase transition phenomena is occurring within the material.

This phase transformation is identified as the transition from β-eucryptite (richer in lithium and aluminium) to β-spodumene (less rich in aluminium and lithium). The maximum speed of this phase transformation is found at 1046 °C (point of flex in the thermal expansion curve), while at 1066 °C there is a sharp increase in the expansivity that is due to the increased degrees of freedom of the molecular groups into the liquid state. When the temperature increases, the viscosity drops according to the Arrhenius law and, at a given temperature, the surface tension starts to pull the edges of the specimen. As a consequence the sample tends to minimize its external surface and assume a sphere shape. The process also

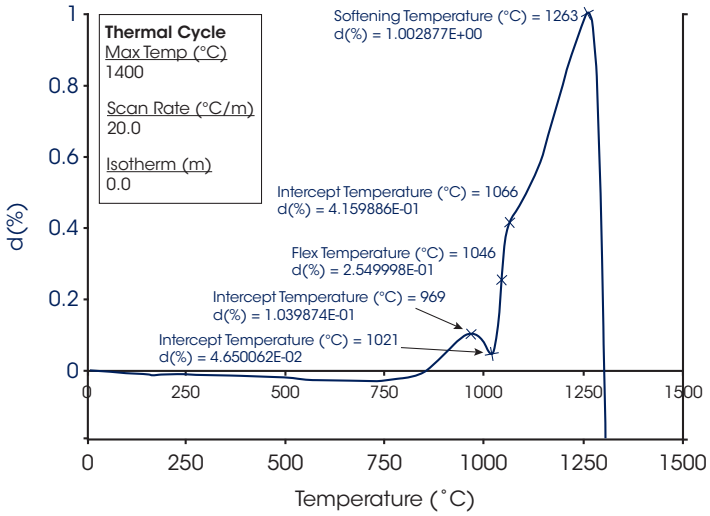

Figure 2: Thermal expansion curve of the β-eucryptite-based glass-ceramic studied

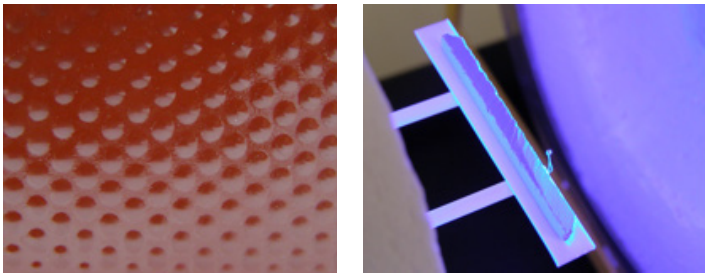

Figure 3: Left – Sample before the test: brown and transparent. Right – Sample after the test: opaque and pale grey.

involves a volume rearrangement: the initial rectangular-bar-shaped sample has to shrink along the length axis, and expand along the other two. As a matter of fact, the optical horizontal dilatometer measured only the fast contraction starting at 1263°. It is worthwhile to note that testing the same sample with a push rod dilatometer, once in the visco-elastic state the material becomes soft enough to be deformed by the applied load. The deformation so measured, as the temperature at which this would be recorded, would not be representative of an actual dimensional change but the mere result of the push rod squeezing the specimen itself.

A further test at lower temperature was performed on another sample of the same material in order to follow the dimensional variations taking place during the cooling phase. The maximum temperature reached, in this case, is 1200 °C. The results are shown in figure 4.

This graph shows that from 1200 °C down to 1050 °C, the cooling part of the curve is almost perfectly overlapped with the part of the curve acquired during heating.

It is quite clear from the difference between the heating and the cooling sections of the curve, that there is an irreversible change of volume due to the transformation of β-eucryptite into β-spodumene.

Finally, the last test (Fig 5) was performed to compare the thermal expansion curve of a fired sample (green curve) with that of a not-fired sample (black curve).

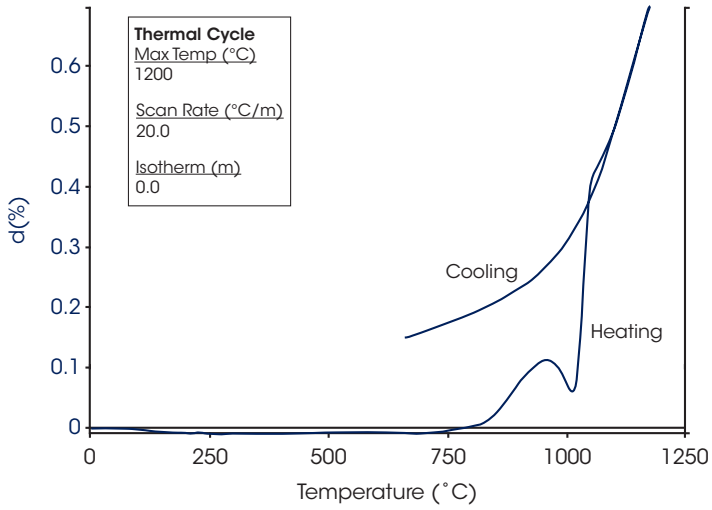

Figure 4: Thermal expansion curve of the β-eucryptite-based glass-ceramic studied, with cooling down to 700 °C

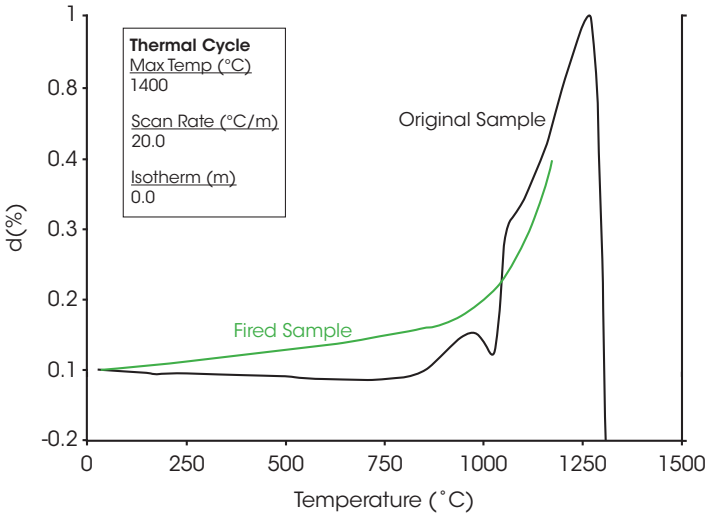

Figure 5: Thermal expansion curves of a fired samples and the original one.

The fired sample, that during heating underwent the phase transformation from β-eucryptite towards β-spodumene, has always a positive, even if low, thermal expansion coefficient. The not-fired sample, as seen previously, as a negative coefficient of thermal expansion up to 850 °C. The phase transformation alters strongly the CTE properties.

THERMAL EXPANSION MEASUREMENT ON ULTRA THIN SPECIMEN USING THE OPTICAL DILATOMETER

In this case, as the specimen is very thin and unable to stand alone, the sample is placed horizontally on a special sample holder (Fig 6).

Measuring both ends of the specimen at the same time without making contact provides an absolute measurement. There is nothing interfering with the measurement itself, so there is no need for a calibration curve and so it is possible to perform actual heat treatment curves.

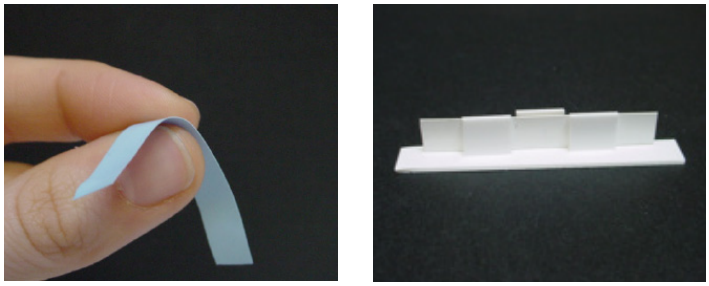

Figure 6: Thin green ceramic tape (aluminium oxide) unable to stand on its own, can be tested with fixture for thin samples.

The specific sample measured with the optical dilatometer is a 100 micron thick green ceramic tape, cast with doctor blade technology. The material is electronic-grade aluminium oxide, used for electronic substrates. The first curve (Fig.7) was recorded with a heating rate of 20 °C per minute and shows the actual behaviour of the material during the sintering up to 1150 °C.

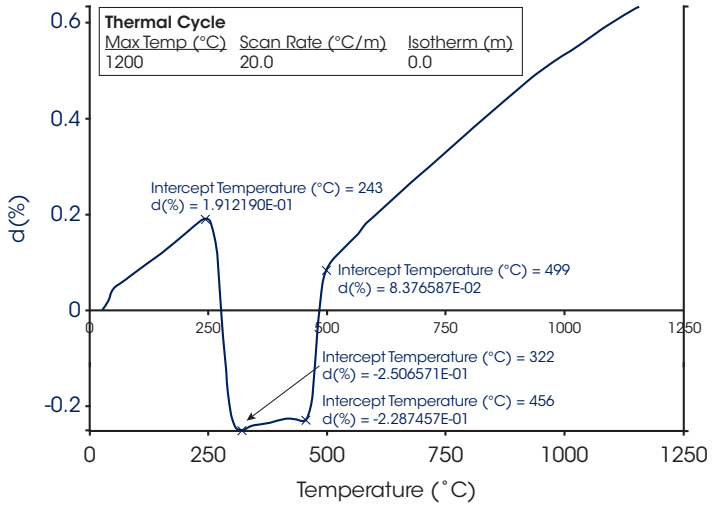

Figure 7: Thermo-mechanical behaviour of a 100 micron thick green ceramic tape with a heating rate of 20 °C/min

The curve shows a quite complex behaviour highlighting a shrinkage phase which starts at 243 °C and ends at 322 °C, corresponding to the burn out of the binder (in this case PVA).

Then the expansion process continues with a sharp change between 456 and 499 °C. After that, the material keeps expanding with constant thermal expansion coefficient up to 1150 °C where the actual sintering starts. The second curve shown in Fig. 8 was recorded with a complex heating cycle, to allow more time for the burn out of the binder. In this case the heat treatment was conceived with a low heating rate of up to 240 °C and an isotherm of 10 minutes at 240 °C.

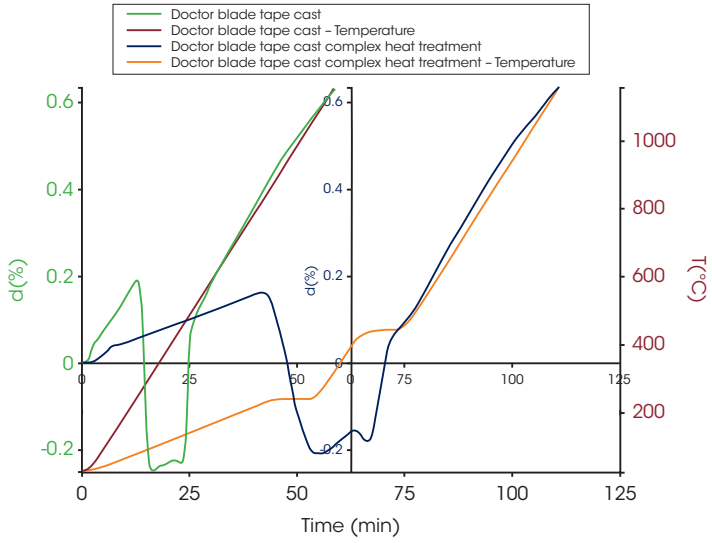

Figure 8: Thermo-mechanical behaviour of the green ceramic tape with different heating cycle, time base

After the burnout, the heating rate was increased to 20 °C/min up to 440 °C, which was followed by a second isotherm, to minimize the stresses caused by the second phase transition. After this rest at constant temperature, the heating rate was again set to 20 °C/min up to 1200 °C. Plotting the curve with time on the X axis it is then possible to appreciate the temperature profile with time: the main difference with the previous curve is the fact that during the permanence at constant temperature, the contraction at 240 °C and the expansion at 440 °C reach completion during the stasis at their correspondent temperature.

The different heating cycle and the permanence at constant temperature did not change much the behaviour of the material during the heat treatment, proving that these volume changes are not affected by time or speed of heating.

CONCLUSIONS

The possibility to carry out high temperature and high resolution measurements without making contact widen the field of research on ceramic materials. The dilatometer mode of ODP 868 proved to be reliable, reproducible and extremely easy to use. The measurement of the thermo-mechanical behaviour of extremely thin specimen can be carried out even above the softening temperature, enabling ceramic research to follow the actual behaviour of materials during the heat treatments. But even greater importance is for glass ceramics, where glassy and crystalline phases interact, develop and disappear during heating cycles. The availability on the international market of new equipments making easy and reliable measurements of thermal dilatations on materials up to their melting temperatures gives a new research tool to the scientific community.

For more information or to place an order, go to http://www.tainstruments.com/ to locate your local sales office information.