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NEW APPLICATIONS OF THE THERMODILATOMETRY IN THE CHARACTERIZATION OF CERAMICS

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Thermodilatometry is widely used at high temperatures for studying ceramics. The sintering process can be monitored but if the rate of shrinkage is too high, it may produce a structure damage, therefore an adapted software is available to work at a constant sintering rate.

Structural changes can be studied as well as the expansion of ceramic fibres.

Keywords: ceramics, thermodilatometry

Introduction

Thermodilatometry is a technique which consists in measuring the length of a sample as function of the temperature.

When a ceramic powder is heated, the sintering process can be observed and studied.

Some sudden length variations can be observed when the phase transition (or glass transition) occurs inside a solid material: it corresponds to a change in the structure.

Experimental

The SETARAM DHT is a vertical type and differential dilatometer: two push-rods apply a constant load, one on the sample, one on the reference. The whole probe is located in a furnace with graphite heating element (Fig. 2).

Two models of dilatometer may be used:

– DHT 2050 K with alumina probe can be used up to 1780°C under oxidizing and inert atmosphere

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– DHT 2400 K with graphite probe can be used up to 2100°C under inert atmosphere

Due to the differential layout, a good accuracy can be obtained: the resolution is 0.1 micrometer.

Different sample holders enable the analysis of samples

– in solid state
– in powder and
– in fibre form.

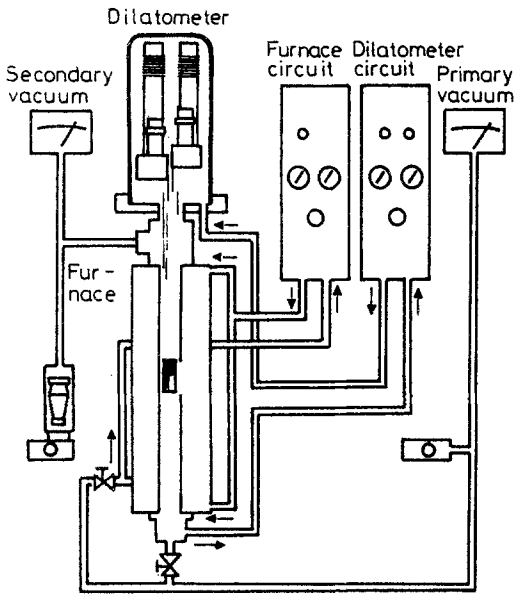

Fig. 1 Dilatometer layout

Results and discussion

Sintering of ceramics

Materials like ceramics are generally prepared by sintering: during this process the material shrinks (Fig. 3).

Dilatometry enables the investigation of the sintering process of ceramics:

– up to 1000°C: an expansion of 0.73% corresponding to the dilation of the sample

– from 1000°C up to 1750°C: sintering of the ceramics (– 15.3%) with a maximum sintering rate ($60 \mu m \cdot min^{-1}$) at 1450°C

– the cooling of the sample involving a small shrinkage

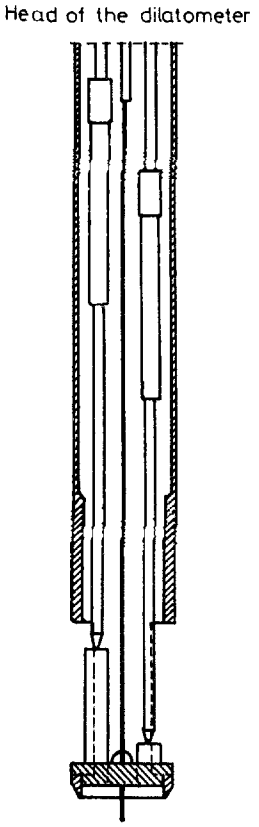

Fig. 2 Head of the dilatometer. Material: – alumina (1780°C) – graphite (2100°C);
Sample dimensions: – H 30 mm – Ø 12 mm;
Atmosphere: 1780°C version
– inert gas
– oxiding gas
– reducing gas
– vacuum
2100°C version
– inert gas
– vacuum

Sintering at controlled sintering rate

The sintering process is a rapid and important phenomenon even if the sample is heated slowly (5 $deg \cdot min^{-1}$), but if the rate of shrinkage is too high, stress may appear inside the material, it may involve a damage in the structure and here dilatometry can do more: with an adapted software package it

is possible to determine the temperature program which will produce a constant rate of shrinkage.

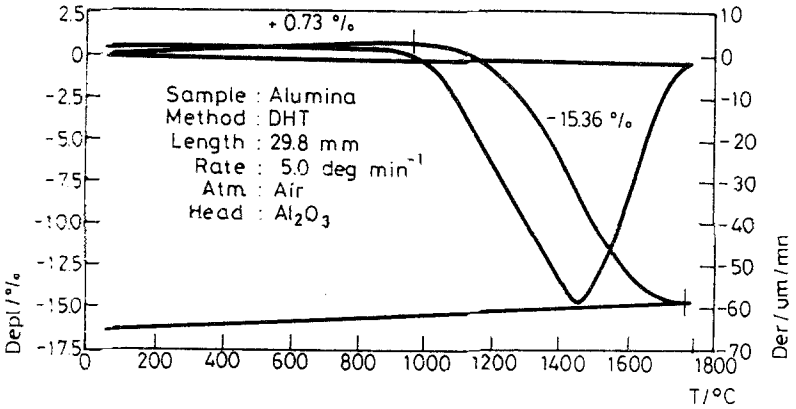

Fig. 3 Sintering of alumina at 5 deg·min^{-1}

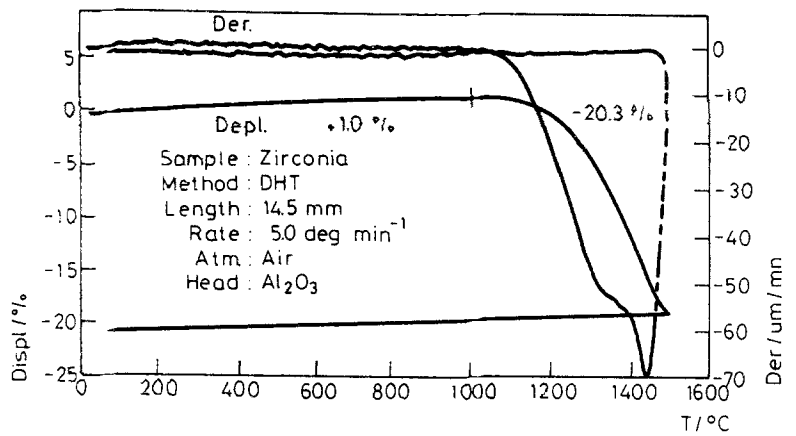

Fig. 4 Sintering of zirconia at 5 deg·min^{-1}

To demonstrate this possibility, two experiments have been carried out:

– the first experiment was the sintering of zirconia at a constant heating rate (5 deg·min^{-1}). Figure 4 shows that the shrinking rate passes through a maximum of 70 μm·min^{-1} at 1440°C.

– in the second experiment (Fig. 5) the heating was programmed at 5 deg·min^{-1}, provided that the shrinking rate is <20 μm·min^{-1}, which means that if the shrinking rate tends to be higher than the set value (20 μm·min^{-1}) the temperature scanning rate will be less than 5 deg·min^{-1}. Figure 6 which is

an enlargement of Fig. 5 illustrates what the temperature program should be in order to have a shrinking rate never exceeding 20 μm/min. This temperature program can be used for the industrial production of ceramics.

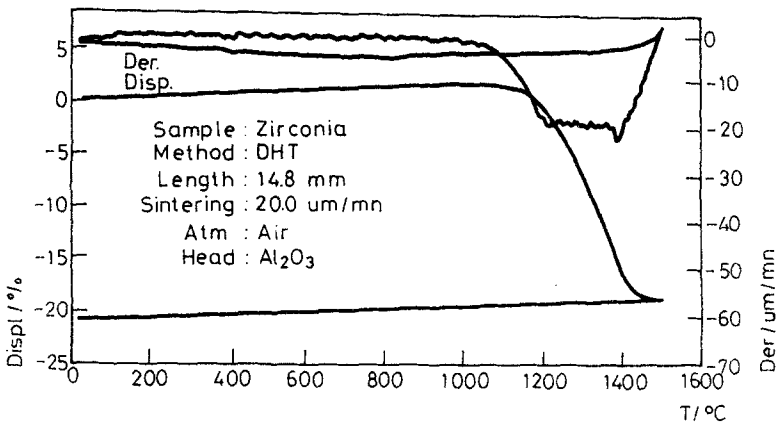

Fig. 5 Sintering of zirconia R < 20 μm/min

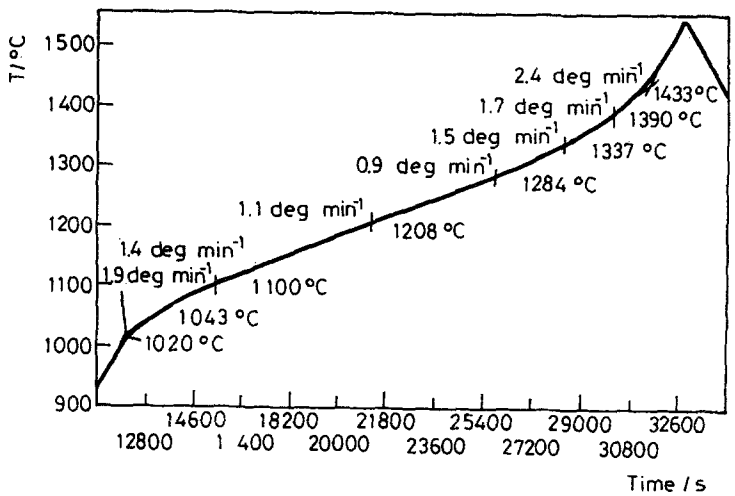

Fig. 6 Sintering temperature program

Phase transition

Phase transition corresponds to a change in structure which can be detected by dilatometry.

The silica powder is shaped by hot sintering. With dilatometry it is possible to follow the sintering of a quartz powder sample containing 2 to 4%

feldspar (Fig. 7). The curve shows the sample expansion (1.44%) up to 900°C.

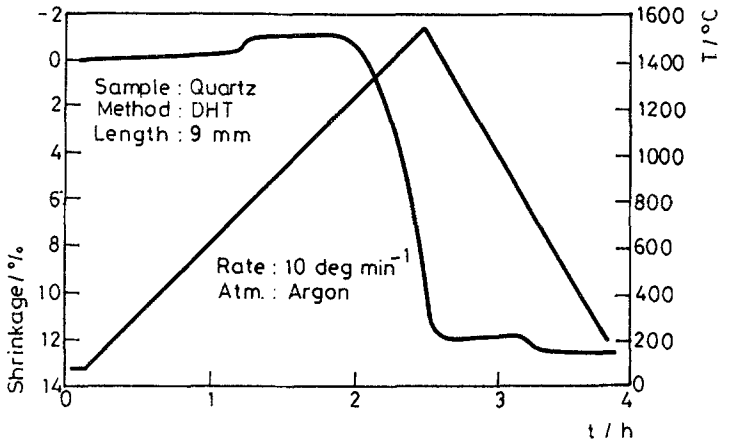

Fig. 7 Transition of quartz

The $\alpha \longrightarrow \beta$ transition of quartz is detected at 573°C.

From 900°C up to 1485°C an important contraction is measured (12.7%) corresponding to the sintering of the powder.

During the cooling the reversible transition $\beta \longrightarrow \alpha$ is observed again.

Expansion of fibres

Thanks to a modified device, the expansion of fibres can also be investigated.

Two clamps apply a slight tension (1g) at the ends of the fibre (Fig. 8).

The study of a TORAYCA carbon fibre shows (Fig. 9):

- an expansion of 0.04% between room temperature and 1100°C
- a shrinkage of 0.59% between 1000°C and 1650°C
- an expansion of 0.24% between 1650°C and 2100°C

During the cooling no significant variation in length but a thermal contraction is observed.

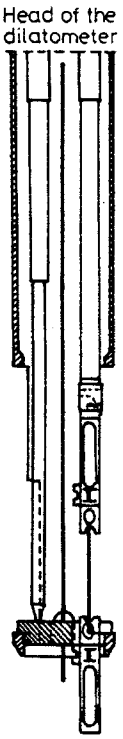

Fig. 8 Fibre accessory. Material: – graphite (2100°C); Sample dimensions: – H 30 mm; Atmosphere: – inert gas, – vacuum

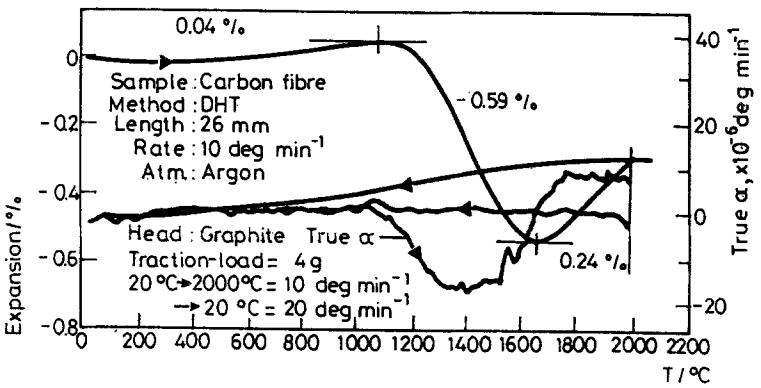

Fig. 9 Dilatometry of a fibre

Conclusion

The progress in thermal analysis techniques enables the optimization of material processing and enables to have a better knowledge of the thermal behaviour of ceramics at high temperature.

References

1 J. Rouquerol, Thermochim. Acta, 144 (1988) 209.
2 P. L. Husum and O. T. Sørensen, Thermochim. Acta, 144 (1987) 131.

Zusammenfassung — Zur Untersuchung von keramischen Substanzen bei hohen Temperaturen ist Thermodilatometrie ein weitverbreitete Methode. Der Sinterprozeß kann verfolgt werden, ist jedoch die Schrumpfgeschwindigkeit zu hoch, kann es zu Strukturschäden kommen, deshalb ist eine angeglichene Software erhältlich, die das Arbeiten bei konstanter Sintergeschwindigkeit ermöglicht.
Es können sowohl die strukturellen Veränderungen als auch die Ausdehnung von Keramikfasern untersucht werden.