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HIGH TEMPERATURE DILATOMETER STUDY OF SPECIAL CERAMICS AND THEIR SINTERING KINETICS

W.-D. EMMERICH, J. HAYHURST and E. KAISERSBERGER
NETZSCH-Gerätebau GmbH, P.O. Box 1460, D-8672 Selb (F.R.G.)

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ABSTRACT

Many properties of special ceramic materials, often closely related, such as sintering temperature, shrinkage in firing, mineral reactions and strength can be studied by thermal analysis. Also the influence of the type, structure and preparation of raw materials, plasticizers and binding materials for forming and compressing, as well as their compatibility with protective coatings (glazes, varnishes, metal films) are investigated by thermal analysis. Computerization of the routine application of important TA methods has opened up new horizons for exact quantitative evaluation due to considerable savings in time and man-power.

During the recent development of rutile ceramics the sintering process at approximately 1100°C was studied with dilatometry. Using a rapid, high temperature dilatometer the sintering kinetics at different heating rates (5–50 K min^{-1}) were determined and the activation energy for the sintering process computed. From expansion of the curve section up to 1000°C in the computer version, the anatase–rutile transformation can be clearly seen between 800 and 900°C, i.e. a small change can be evaluated as well as the larger sintering process. Sintering studies on lead zirconate titanate (PZT) ceramics are also described.

INTRODUCTION

In the field of technical ceramics, by which we mean electro-ceramics, oxide ceramics and other special materials such as silicon nitride, silicon carbide and ferrites ("the black ceramics"), high-accuracy analysis is of increasing importance. Applications of special ceramics are very widespread from the high technology of space research, turbines and engine components to a normal, everyday fuse.

Electro-ceramics include an enormous variety of materials, typically steatite, cordierite, rutile and titanates. Oxide ceramics are mainly mixtures of silicon, magnesium, zirconium and aluminium oxides and silicates. The main feature which sets these materials apart from "normal" ceramic materials, e.g. porcelains and clay systems, is the low plasticity and workability of the material. This can be increased in two ways: grinding to reduce particle size and/or addition of binders and plasticizers; a combination of both often being used.

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These processes have a great influence on the production parameters, such as firing temperature, rate and degree of sintering and mechanical strength. The gaseous products of the firing process are also changed by these processes and here thermal analysis, especially in combination with evolved gas analysis systems, lends itself very well to environmental studies.

The varying pretreatment of raw materials before firing necessitates the analysis of an increasing number of parameters. To illustrate this we have chosen titanium oxide and lead zirconate titanate ceramics as examples.

EXPERIMENTAL AND RESULTS

The samples of raw materials measured were compressed powder, containing plasticizer and additives. To study the sintering behaviour of TiO_2 material (rutile ceramics), measurements were made in a high temperature, horizontal, single push-rod dilatometer having a transducer with 5 mm linear range and a temperature range of 25–1600°C, with control, data acquisition and evaluation via a personal computer. The sample holder system used for these measurements was dense sintered alumina of high purity.

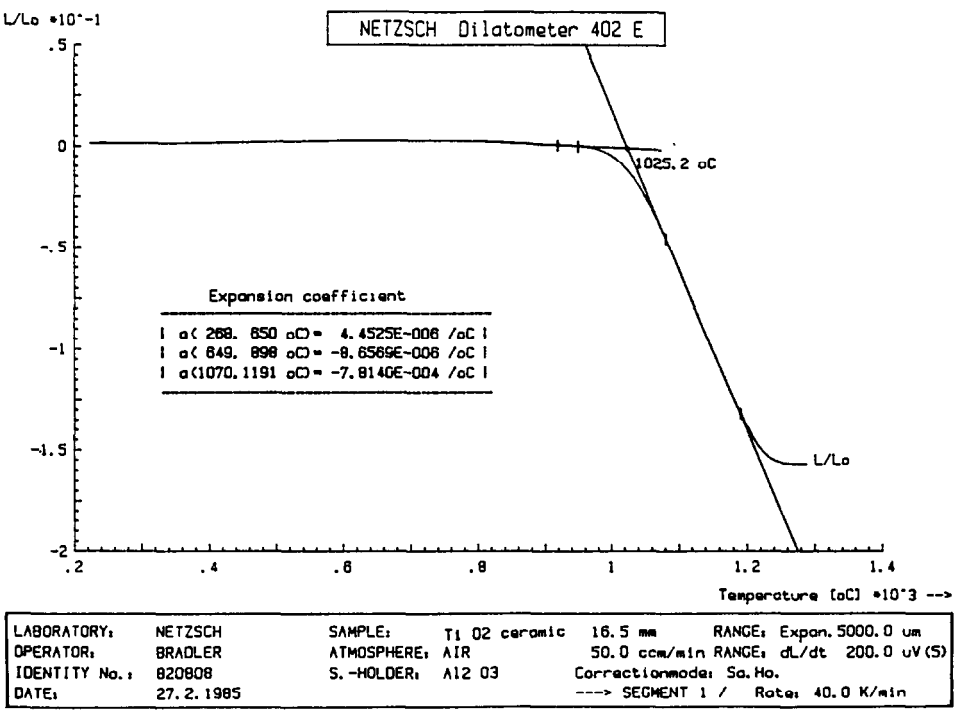

Fig. 1. Sintering curve of TiO_2 ceramic.

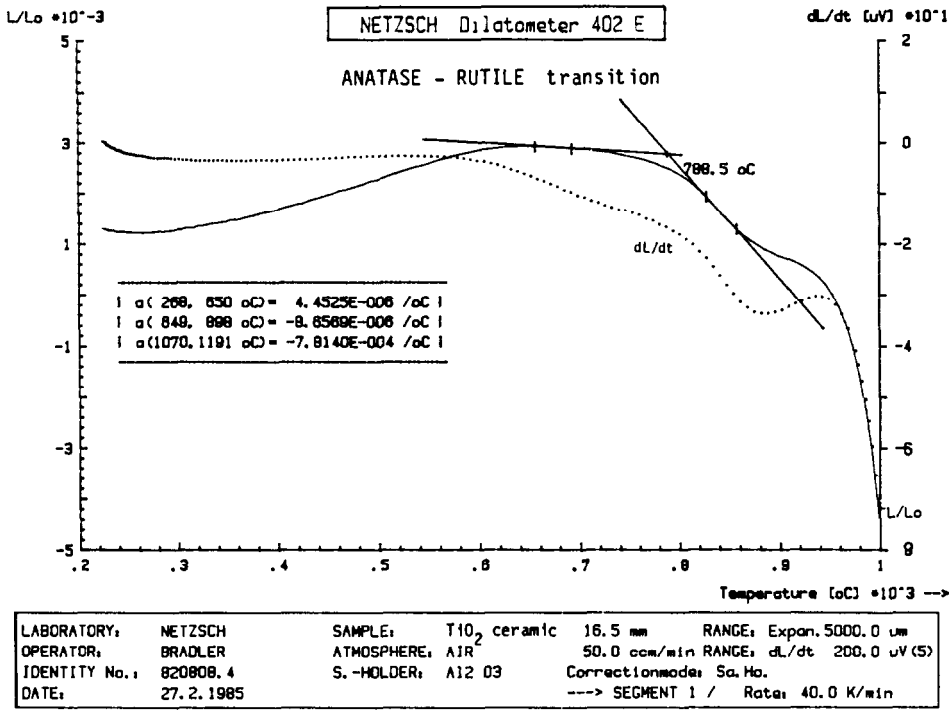

Fig. 2. Expansion curve for TiO_2 ceramic up to 1000°C.

The computer printout in Fig. 1 depicts the complete sintering from 1025 to 1240°C at a heating rate of 40 K min^{-1}: 16.1% shrinkage in length occurred during sintering with 0.24 N force on the push-rod. The measurement was made in flowing air (50 ml min^{-1}) to burn off the binder material and flush out any volatile products. The α values for given temperature ranges, corrected for sample holder material, and system deviation are printed on the plot by the computer.

Enlargement of sections of the curve is possible with the computer, clearly showing the burning-out of the binder or the anatase–rutile transformation between 800 and 900°C (Fig. 2).

Particularly interesting in Fig. 2 is that the anatase–rutile transition, which is quite difficult to detect by DTA, is very clearly shown here from its influence on the expansion curve.

Several measurements were carried out on the same material at different heating rates. The results are summarized in Table 1.

Figure 3 shows the measurements plotted on the same axes for comparison. The reciprocal temperatures, at which a particular percentage of sintering corresponding to increasing density is reached, were plotted against the natural logarithm of the heating rate (see Fig. 4) [1].

TABLE 1

Sintering measurements on TiO_2 ceramic

Heating rate (K min^{-1})	Start of sintering (extrap. onset) (°C)	Total shrinkage (%)	Sintering rate (mean) (μm min^{-1})
5	977	15.9	151.7
10	990	15.2	253.2
40	1025	16.1	596
50	1050	15.3	1379

The plots calculated by linear regression are parallel straight lines, showing that the sintering is a random bulk single-step process independent of heating rate within the limits of these measurements. The activation energy can be calculated from the slope using the Arrhenius equation. It is also simple to predict at which temperature a desired degree of sintering at a given heating rate is achieved. Other parameters essential for production, e.g. maximum sintering temperature, can also be predicted from a single further measurement.

Other thermal analysis methods would also be of value, particularly simultaneous thermal analysis (TG/DTA), to control the production and use of binder materials.

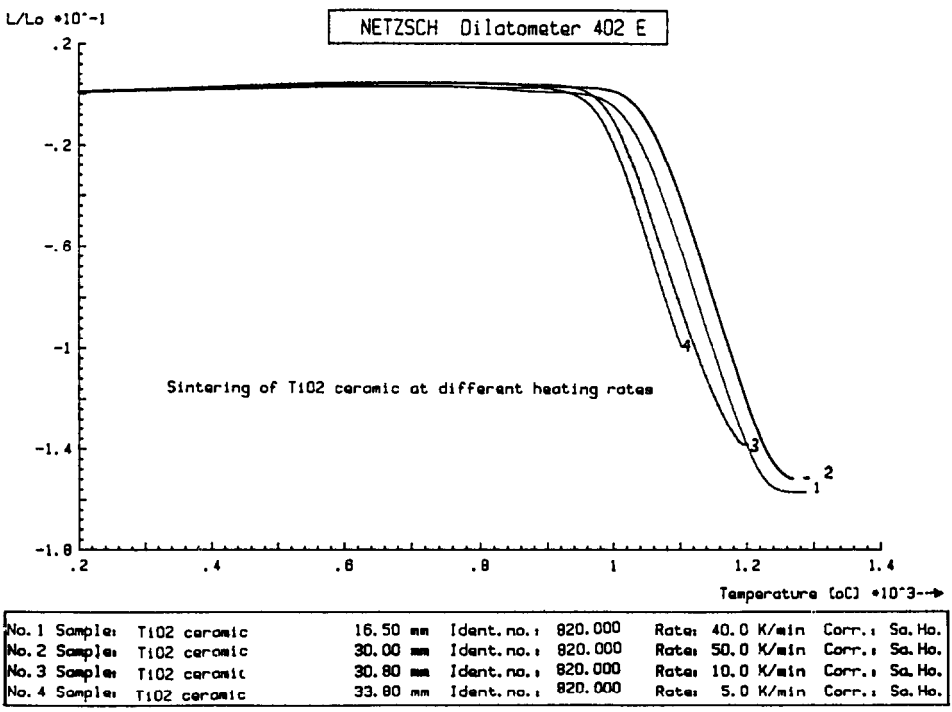

Fig. 3. Sintering curves for TiO_2 ceramic (heating rate 5–50 K min^{-1}).

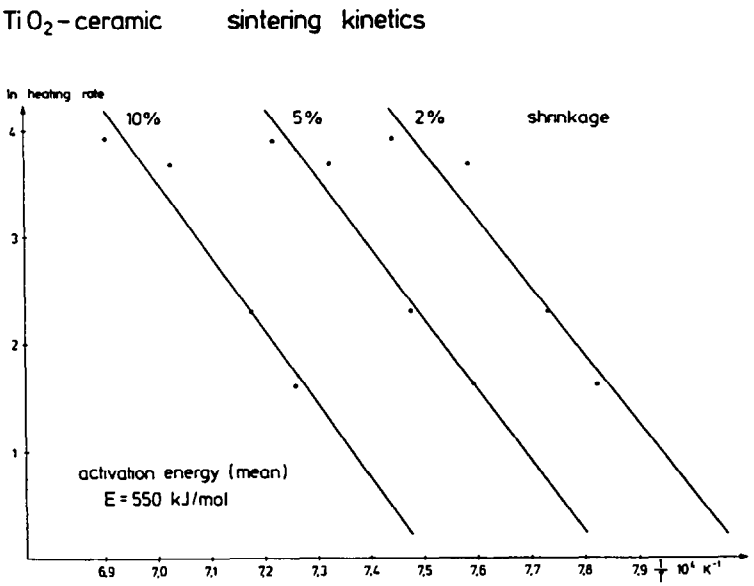

Fig. 4. Natural logarithm of heating rate against $1/T$ for TiO_2 ceramic at different stages of shrinkage for the sintering process.

In a similar study three samples of lead zirconate titanate (PZT), a piezo-electric material of considerable importance to electronics technology, were measured in the same high temperature dilatometer. All samples were unfired with a PVA (polyvinyl acetate)-based binder prepared by extrusion. Samples 1 and 2 are the same material but different batches, sample 3 is sample 2 after 3 h grinding. The samples were heated at 500 K h^{-1} in a dynamic air atmosphere (50 ml min^{-1}). The atmosphere was lead-enriched by the presence of lead zirconate ($PbZrO_3$) in the sample holder. The sample thermocouple (Pt/Pt–10%Rh) was protected from attack by an aluminium oxide protective cap. The results are listed in Table 2, together with a comparison computer printout of the measurements (Fig. 5). Comparison shows that sample 1 is probably not fully reacted and the effect at 700°C can be attributed to further formation of titanate [2].

TABLE 2

Sintering measurement on PZT ceramic with organic binder

Sample PZT ceramic	Start of shrinkage (°C)	Total shrinkage (%)
No. 1	1096	21.1
No. 2	1091	21.2
No. 3	1071	17.4

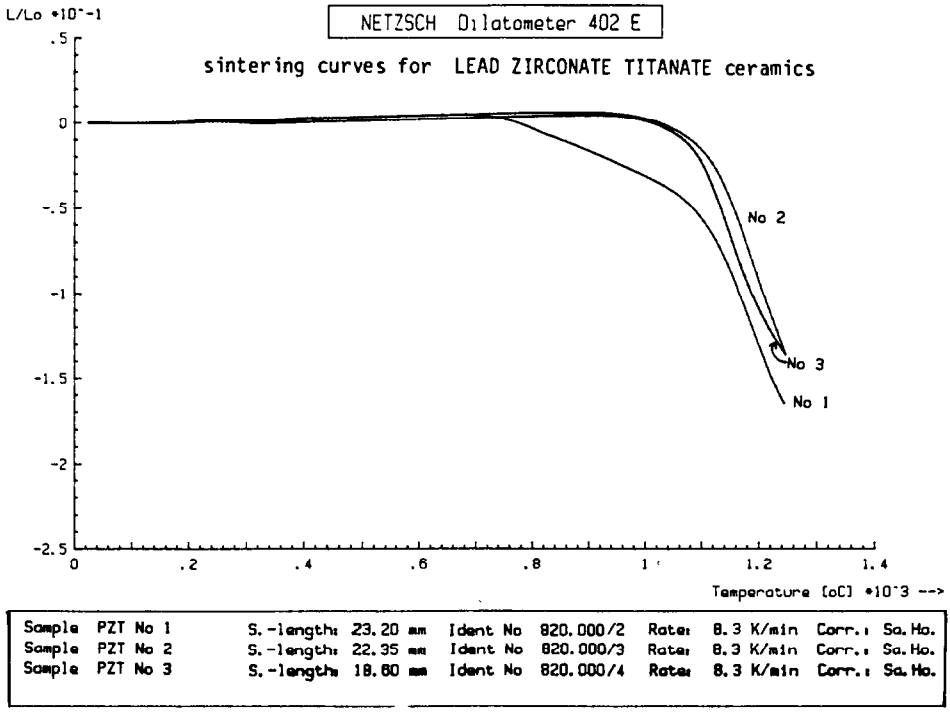

Fig. 5. Sintering curves for three different PZT ceramic samples.

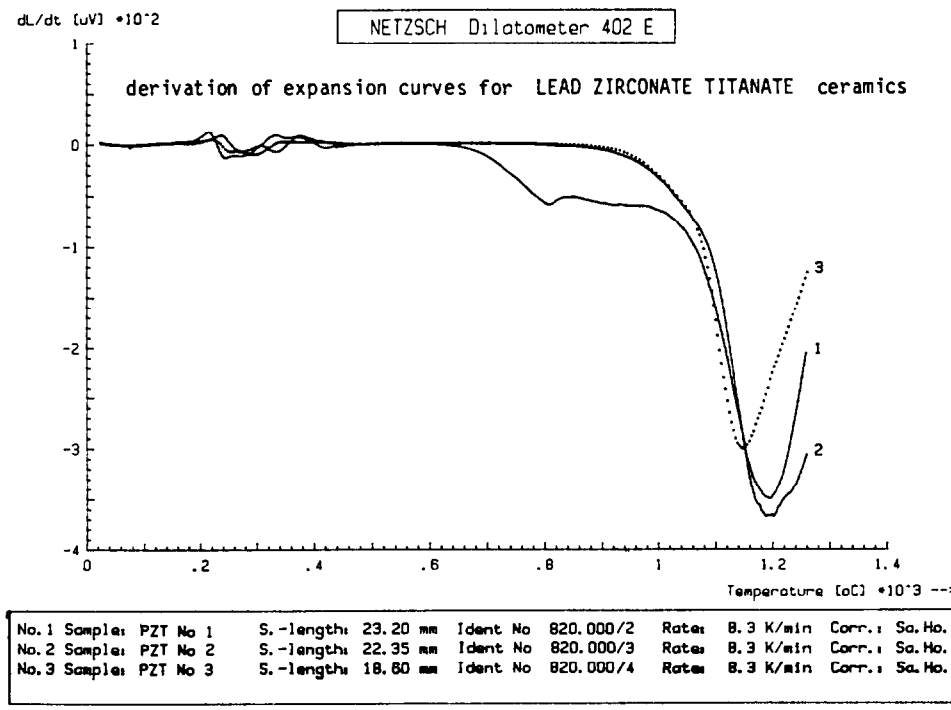

Fig. 6. Derivation of expansion curve for PZT ceramic samples up to the sintering temperature.

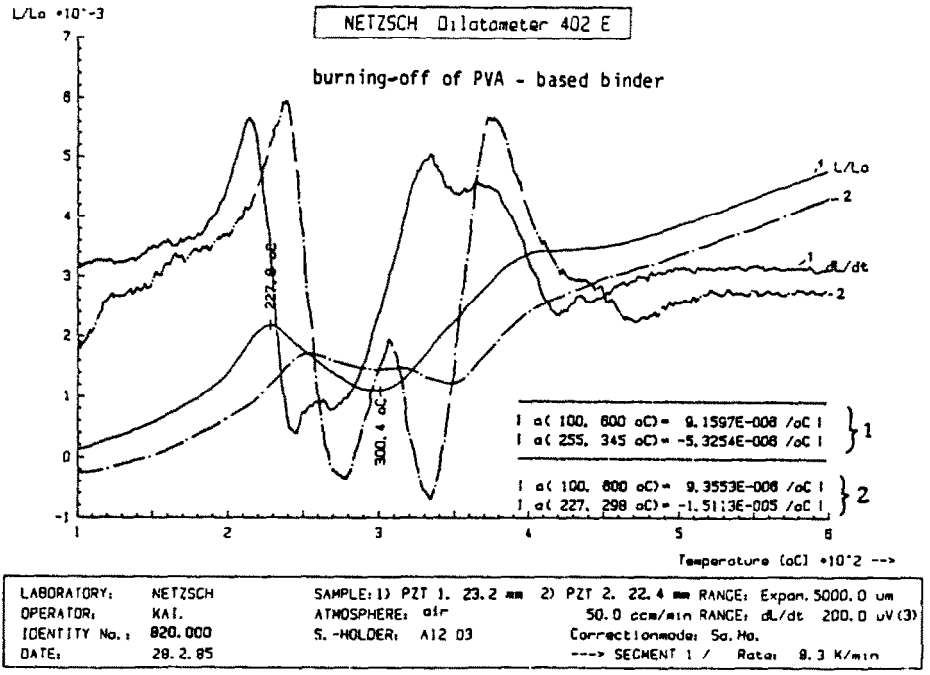

Fig. 7. Section from PZT ceramic expansion curves (and derivation).

Most significant is the clear reduction in sintering temperature caused by grinding the sample, the maximum rate of sintering occurring 50°C earlier in sample 3 compared to sample 2 (Fig. 6). This marked reduction in sintering temperatures on grinding was also clearly illustrated by studies of the monoferrite reaction for the production of barium hexaferrite in a simultaneous thermal analysis system [3]. The sintering temperatures in this case being reduced by as much as 200°C after 25 h grinding of the raw materials $BaCO_3$ and Fe_2O_3 in a ball mill.

Figure 7 shows a section of a typical PZT curve expanded by the computer clearly illustrating the smaller effects from burning-out of binder and mineral structure changes in the same measurement. The influence of binder decomposition in oxidative atmosphere on the expansion curve is different for samples 1 and 2, again showing the difference in the materials of the two batches.

CONCLUSION

This work has clearly shown that dilatometry is ideally suited to study many properties of special ceramic materials, often closely related, such as sintering temperature, shrinkage in firing and mineral reactions. In addition

the influence of the type, structure and preparation of raw materials, plasticizers and binding materials for forming and compressing can be observed.

Computerization of the routine application of dilatometry has opened up new horizons for exact quantitative evaluation due to considerable savings in time and man-power. The facility to study both large effects, e.g. sintering, and smaller changes, e.g. crystal transitions, in one measurement and the kinetic evaluation of the data are of particular significance.

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