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ScienceDirect
Journal of the European Ceramic Society 27 (2007) 701–705
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In situ measurement of dimensional changes and temperature fields during sintering with a novel thermooptical measuring device

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Available online 6 June 2006

Abstract

With a novel thermooptical measuring device (TOM) dimensional changes are investigated during sintering of components and samples up to 50 mm in size. Sintering shrinkage is measured without contact using an optical method. This optical method additionally enables the monitoring of warpage, cracking and caking phenomena which often occur in developing new sintering processes. Creep, caused by uniaxial loading of the samples, can also be measured in the axial and transverse direction. Simultaneously, thermal diffusivity and heat transfer coefficients are measured by the laser-flash technique. Material properties are obtained by an inverse simulation of the temperature distribution in the sample.

Keywords: Firing; Sintering; Porosity; Creep; Thermal conductivity

1. Introduction

The performance of ceramic products is largely affected by the sintering process. For example, sintering conditions constitute the porosity, grain size, phase composition and homogeneity of sintered materials. During sintering a multitude of process parameters are used to control the change of microstructure. The time–temperature cycle and the furnace atmosphere are most important. Whereas at the beginning of scientific investigations on sintering, temperature was held constant, it is now well known that the entire time–temperature cycle, including different heating and cooling stages and sometimes several holding temperatures, has to be carefully matched to the demands of the specific component. Furnace atmosphere may be changed during the process as well.

Optimisation of these process parameters by trial and error is laborious and inefficient and due to the large number of parameters and their large interaction methods of experimental design also often fails. Therefore, one of the most important strategic goals of sintering research is the development of measuring methods, which allow an insight into the furnace and a better control of process parameters. Those in situ measuring methods may be applied directly in the production furnace for production control or in a laboratory furnace for the development of new sintering processes. In the latter case, the transferability of the conditions determined in the laboratory furnace to the production furnace is a precondition for a successful development. This requires well defined temperatures and atmospheres in the laboratory furnace which can be varied in the same range as in the respective industrial furnace. It also needs samples sizes in the laboratory furnace, which are large enough to avoid artificial scaling effects. For example, with samples in the millimetre range as they are used in many conventional laboratory systems for thermal analysis, gas phase reactions at the sample surface often change sintering behaviour completely. In addition interactions of the in situ measurements with the sintering process have to be eliminated.

At Fraunhofer ISC a novel type of non-contact in situ measuring methods has been developed which is applied in closed furnaces with variable atmospheres using samples in the range of some centimetres. The paper presents different applications of these thermooptical measuring methods (TOM).

2. Experimental setup

Fig. 1 shows the setup of the thermooptical measuring device, which allows a simultaneous in situ measurement of shrinkage, warpage, creep and heat transfer during sintering. A resistance heated hood-type laboratory furnace in a water cooled and vacuum tight stainless steel box was used. The inner diameter of the heating zone was 170 mm and the height 280 mm. Only small

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doi:10.1016/j.jeurceramsoc.2006.04.043

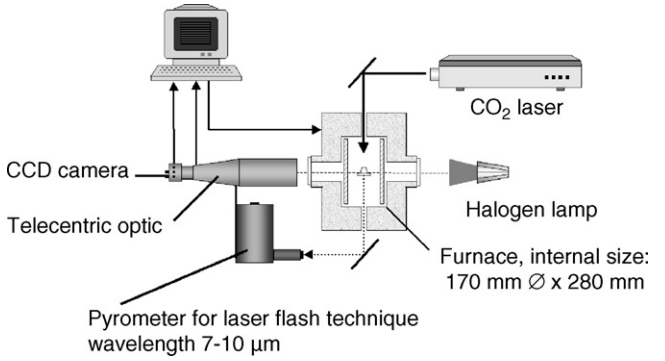

Fig. 1. Setup of the thermooptical measuring device.

openings were used for the in situ measurements to achieve a homogeneous temperature distribution within the heating zone: the diameter of the horizontal openings was 50 mm and that of the vertical openings was 20 mm (compare Fig. 1). The variation of temperature within the heating zone was less than 1 °C/cm at 1000 °C. To realise a wide variety of atmospheres, different materials were used for resistance heating and thermal insulation of the furnace: $MoSi_2$ heaters and alumina fibre insulation for heating in oxidising atmosphere up to 1800 °C, graphite heaters and graphite fibre insulation for heating in reducing atmospheres up to 2200 °C and tungsten heaters and a tungsten radiation shielding for heating in vacuum up to 1800 °C or in inert atmospheres up to 2000 °C. Heaters and the respective insulations were mounted in compact modules which were replaced when the furnace atmosphere was changed. Gas flow was controlled by a mixing unit for four different gases, which was controlled by a PC. Up to 20% of water vapour could be added to the furnace atmosphere. This was achieved by using a special vaporiser and by heating the supplies and the cooling water of the furnace to avoid condensation of water. With the water vapour the furnace atmosphere of gas fired kilns was simulated. Composition of the exhaust gas was controlled by electrochemical sensors. Temperature was calibrated by observing the melting of pure materials with the optical dimensional measuring system described below with an accuracy of ±2 °C.

Shrinkage and warpage were measured using an optical dimension measuring system. Therefore, the contour of the sample was imaged on a CCD camera by a telecentric optics. The sample was illuminated by a halogen lamp at temperatures below approximately 1100 °C. At higher temperatures the thermal radiation of the sample was sufficient for its imaging. Thermal flickering was eliminated by averaging multiple images. The method could be used for arbitrary shapes of the sample provided that the profile was within the horizontal opening of the furnace of 50 mm diameter. Most measurements were done with disk shaped samples of about 10–20 mm height and 20–30 mm diameter. The samples were supported by simple plates (Fig. 2A). The material of the sample support was usually chosen according to the setup of the industrial firing process. A resolution of 2 µm for dimensional measurements was achieved and the reproducibility was very high. Width and height of the sample could be measured at different positions simultaneously and other geometrical parameters, e.g. profile curvature or contact

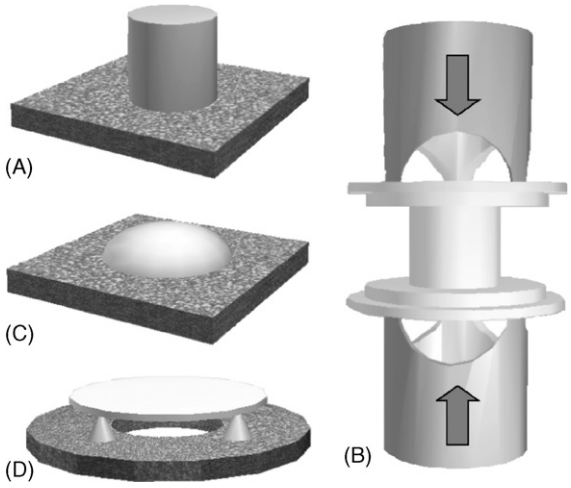

Fig. 2. Different arrangements of samples and supports used for various measurements with TOM: (A) standard dimensional measurement, (B) creep measurement with uniaxial load, (C) wetting experiment with sessile droplet and (D) laser-flash experiment.

angle (compare Fig. 2C), could be measured as well. Details of the method are described elsewhere.[1,2] Thermal expansion was corrected, if desired, by scaling the dimensional measurements with the data of a sintered sample of the same material measured at the respective temperatures. If composition of the samples did not change during sintering, density was determined by measuring the density of the sintered ceramics (by the Archimedes method) and by reversely calculating the density during sintering from the shrinkage. (If weight changes occurred, the sample was suspended from an additional balance and the weight was monitored simultaneously with the shrinkage measurement.[3])

Creep was measured by positioning a disk shaped sample between two vertical punches (Fig. 2B) which were uniaxially compressed by a small motor using a proportional rotary solenoid, which was mounted outside the thermal insulation of the heating zone within the vacuum tight housing of the furnace. Only small forces between 0.5 and 6.6 N were applied to avoid disturbance of the sintering process. The motor was calibrated by a balance. The accuracy of force control was within 0.2 N. The dimensional changes during uniaxial loading were simultaneously measured parallel and perpendicular to the load direction by the optical dimension measurement described in the previous paragraph.

Heat flow within the sample was measured using the well known laser-flash technique[4] by heating the front side of the sample by a short laser pulse and by monitoring the temperature at its back side by a pyrometer (compare Fig. 1). To avoid heat flow between sample and sample support, the disk shaped sample was usually held by the edges of three small prismatic ceramic pieces (Fig. 2D). From the rise time of the temperature at the back side and the sample thickness the thermal diffusivity of the sample can be determined.[4] Since sample thickness changes during sintering it was measured simultaneously optically as described above. Many ceramics are semitransparent in the wavelength range of 1–2 µm which is customarily used for the laser pulses and for pyrometry.[5] Therefore, absorbing coat-

ings on the sample surface are usually required to make sure that heat pulses are generated and detected exactly at the surface of the sample. These coatings are problematic during sintering. Therefore, since nearly all ceramics are opaque above 10 μm, a CO_2 laser with a wavelength of 10.6 μm and an edge filter for wavelengths larger than 10.6 μm for the pyrometer were used with the laser-flash measurements. Signal to noise ratio was improved by averaging typically 5–10 temperature curves.

The usual data evaluation of laser-flash measurements requires one dimensional heat flow[4] which is only possible by homogenously heating the entire sample surface and by using thin samples. With large samples and small windows in the furnace this precondition cannot be satisfied and more sophisticated methods of data evaluation are required. An inverse modelling procedure was used to identify the sample properties which fit to the measured temperature curve. For that the transient temperature distribution after the laser pulse within the sample was simulated by a Finite Element program (ANSYS®). The difference between the measured and the simulated temperature curve at the sample back side was determined by chi-squared. Chi-squared was minimised by subsequent FE simulations using a downhill simplex method to vary the material properties. Computing time was reduced using an axially symmetric setup. Differently from customary laser-flash technique, linear heating ramps of the furnace during the measurements were allowed for the simulation to apply the method to technical heating processes. Details will be given elsewhere.[6]

3. Results

Fig. 3 shows the shrinkage of a green sample of SiC (containing a total of 10% of sintering aid: Y_2O_3 and Al_2O_3) during pressureless liquid phase sintering. The sample was heated with a heating rate of 10 °C/min in Ar atmosphere, using the graphite heating module of TOM. It was found that for successful sintering of these SiC-samples a careful control of furnace atmosphere is essential. Small amounts of CO in the range of 800 ppm already led to a reduction of the liquid phase. (Similar gas phase reactions were observed for liquid phase sintering of AlN and are described in more detail in Ref.[7]) Up to 1600 °C the dimensional

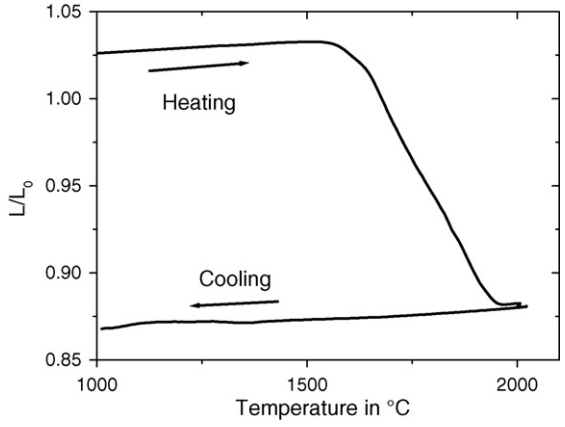

Fig. 3. Shrinkage of liquid phase sintered SiC during heating in Ar atmosphere.

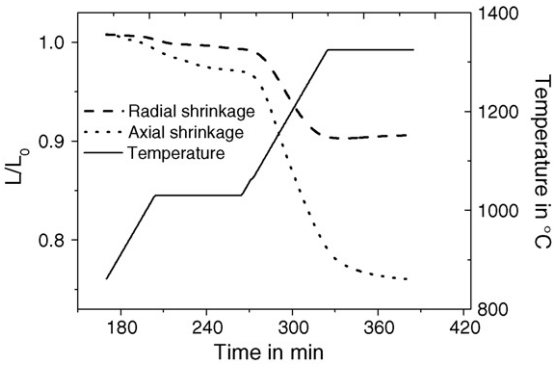

Fig. 4. Anisotropic shrinkage measured during sintering of a porcelain sample under uniaxial compression of 6.6 N.

measurement only reflects thermal expansion of the specimen. At 1600 °C shrinkage sets in without any indication of a rearrangement stage. (A short period of fast shrinkage in the initial sintering stage would have been expected for rearrangement and has been reported for many liquid phase sintered systems.[8]) Shrinkage proceeds steadily and is finished during the heating period at 1950 °C. No additional dimensional changes were observed during the 60 min hold period at 2000 °C.

Fig. 4 shows the radial and axial shrinkages of a green sample of alumina porcelain (C120). This sample was sintered with a constant uniaxial force of 6.6 N corresponding to an initial pressure of 85 kPa. The furnace atmosphere was air with 20% of water vapour. When the external pressure was transferred via rigid ceramic punches, caking of the porcelain at the punches was observed. This led to discontinuous shrinkage and to warpage of the sample. Therefore, the sample was placed between two additional disk shaped green compacts from the same material (compare Fig. 2B). Radial shrinkage was measured from the diameter of the sample at the centre and axial shrinkage was measured from the vertical distance of the two additional disk shaped green compacts. Thereby the effect of uneven shrinkage due to caking was essentially eliminated. With small uniaxial compression of the sample during sintering, shrinkage was superposed by creep that enhanced deformation in the direction parallel to the load and reduced deformation in the perpendicular direction (Fig. 4). (Holding periods at the onset and at the end of shrinkage were introduced to obtain accurate data in temperature regions where creep was very small.) By measuring the deformation at different loads quasi-viscous shear and bulk moduli could be derived according to Ref.[9] which describe the response of the material to stresses during sintering.

Fig. 5 shows the temperature signal of the pyrometer at a furnace temperature of 1300 °C for the same porcelain (C120) during a laser-flash measurement when the sample had a density of 2.59 g/cm^3. The disk shaped green sample (diameter 22.2 mm, thickness 3.0 mm) was heated in air with 20% of water vapour at a heating rate of 1 K/min. A 100 W laser pulse with a spot diameter of 22 mm was applied at time zero for 300 ms. Heat transfer within the sample led to a steep increase of the back side temperature of about 0.7 °C within 4 s. Due to heat radiation between sample and furnace a fast equalisation of temperature occurred

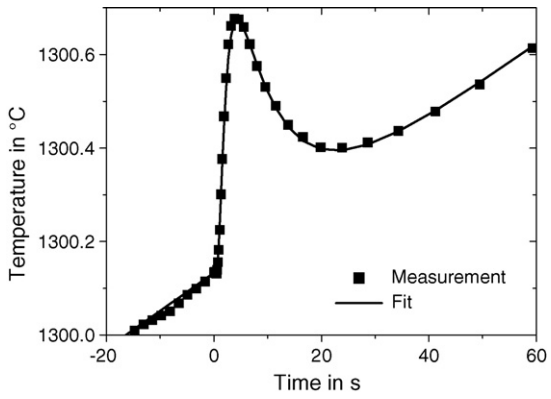

Fig. 5. Measured temperature at the back side of a porcelain sample after heating the front side with a short laser pulse at $t = 0$ and simulated temperature after inverse modelling of the transient temperature distribution.

thereafter within 40 s. The heating rate of the furnace superposed the laser-flash signal. Thermal diffusivity of the sample was determined by inverse modelling of the transient temperature signal by FEM. A perfect agreement between experimental data and simulation was obtained for a thermal diffusivity of 0.55 mm^2/s and a coefficient of heat transfer of 760 $W/(m^2\,°C)$ (Fig. 5).

The simultaneous measurement of shrinkage and thermal diffusivity allows the construction of sintering maps. This was shown for ZTA green samples (75% alumina with 25% zirconia where the zirconia was partially stabilised by 3 mol% of yttria) which had been produced by tape casting (experimental details are given in Ref.[10]). Fig. 6 shows the fractional density which was calculated from the measured shrinkage of the samples during sintering and the thermal diffusivity. (To eliminate thermophysical effects the thermal diffusivity data were scaled by the thermal diffusivity of a dense ZTA sample measured at the respective temperatures.) It was demonstrated that an increase of thermal diffusivity in the initial sintering stage is caused by the formation of sintering necks.[11] Therefore, the steep increase of thermal diffusivity in Fig. 6 is attributed to neck growth caused by surface diffusion. Other possible diffusion mechanism (volume or grain boundary diffusion) would have been accompanied by shrinkage which would have led to a decrease of the initial slope in Fig. 5. Apparently these mechanisms only become active at higher temperatures. The ratio between neck formation and shrinkage was not affected by heating rate (Fig. 6).

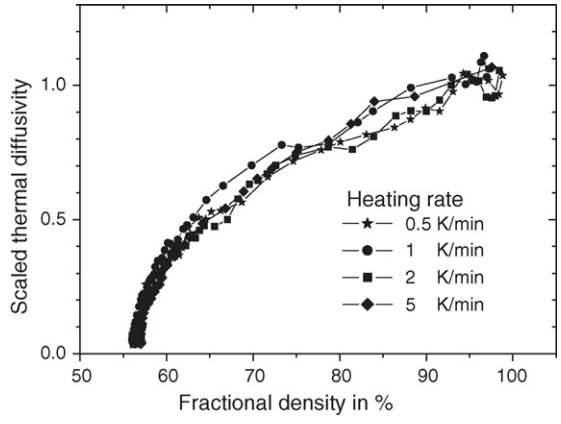

Fig. 6. Scaled thermal diffusivity vs. fractional density during sintering of ZTA green samples at various heating rates.

4. Summary

Examples of in situ measurements by TOM of various ceramics are presented. Using large samples turned out to be especially advantageous, when gas phase reactions or evaporation led to a change of sample composition near the sample surfaces. Also the non-contact measurement provided by TOM was helpful in avoiding artificial interactions—e.g. in measuring weak materials during liquid phase sintering. The problem of caking that often disturbs creep measurements could be solved using a special setup (Fig. 2B) and the non-contact dimensional measurement.

Besides the shrinkage and creep measurements the optical imaging system was also used for the investigation of other phenomena: warping of samples was detected by measuring the curvature of the contour; wetting phenomena were investigated by measuring the contact angle of a sessile droplet (Fig. 2C) and caking or cracking of samples was monitored by sudden changes of the contour. Samples were investigated with a setup similar to the production furnace using identical kiln shelves. Since arbitrary contours can be measured also entire real components were measured. Furnace atmospheres were adapted closely to that of the respective industrial furnaces. Even the atmosphere of gas fired kilns was accurately simulated in the laboratory furnace.

Thus, sintering in the in situ furnace of TOM could be compared to production furnaces and the in situ measurements were used for an optimisation of industrial firing cycles. For example, the measured data from the dimensional and the laser-flash measurements were used as input for the simulation of sintering kinetics, temperature gradients and the resulting thermo-elastic and sintering stresses. Sintering conditions were optimised by varying the time–temperature cycles and by minimising stresses in the components.

Acknowledgements

The authors acknowledge the help of Dr. E. Ruska (CeramTec AG Marktredwitz), Dr. J. Adler (Fraunhofer IKTS Dresden, Germany) and G. Faßbinder (Lapp Insulators Wunsiedel, Germany) for making available the ZTA, SiC and porcelain green samples, respectively.

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