

In situ measurement of light scattering in porous ceramics during sintering

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Presented at the 15th European Conference on Thermophysical Properties, Würzburg, Germany, 5–9 September 1999

Abstract. Measuring the pore size distribution in ceramics via preparation of polished sections and image analysis is a tedious task and other measuring methods for that purpose should be investigated. The measurement of light transmission gives a sensitive tool for the detection of changes in pore size distribution.

Light transmission measurements are performed in situ during sintering of alumina samples at temperatures up to 1923 K. They are compared to shrinkage measurements by dilatometry. The temperature dependence of light transmission and the influence of absorption in alumina is discussed. Very pure alumina samples show no influence of absorption on the transmission at high temperatures. In less pure samples, however, increasing absorption with increasing temperature may strongly influence the transmission. The scattering and absorption coefficients could be calculated separately by numerical methods.

1 Introduction

The sintering process makes an essential contribution to the creation of certain material properties of ceramics. The firing process gives rise to an important part of the production costs for sintered ceramics. These costs can be considerably reduced by lower sintering temperatures and shorter sintering times. For that reason the optimisation of the sintering process is very important for any application (Thuemmler 1989). The sintering process is influenced by many parameters, for example the heating rates, the holding times, and the furnace atmospheres. The great number of parameters makes the optimisation of the sintering process by the trial-and-error method difficult. In particular, complete sintering processes and the subsequent analysis of the material properties are expensive and time-consuming. Often many sintering experiments must be made to obtain a certain material property.

In situ measurements provide the possibility to observe the sintering process during the change of material and can help to optimise the firing process efficiently. Many in situ measurement methods are already in use. An overview of different methods is given by Raether et al (1997).

Up to now, microstructural changes of the sample during the sintering process have been detected by means of the sample shrinkage which is measured by a dilatometer. In the final sintering stage, when the density is close to the theoretical density, the sensitivity of the dilatometer decreases strongly.

Finally, the total pore volume stays almost constant but there are changes in the pore size distribution. The total pore number decreases and the average pore size increases. The dilatometer cannot detect these changes in porosity but the light-scattering measurement is a sensitive tool for this task.

Some measurements of the light transmission at high temperatures are presented. A comparison of light transmission and sample shrinkage measurements is given. Furthermore, the results of the temperature-dependent measurements are discussed.

2 Sample preparation

In the experiments the alumina powder A16SG was used (A16SG Alcoa, Bad Homburg, Germany, $d_{50} = 0.4 \mu\text{m}$, where 50% of particles are smaller than d_{50} ; purity 99.8%). The alumina powder was filled into cylindrical silicone vessels. No additives were used. The vessels were then cold isostatically pressed at a pressure of 250 MPa. The cylindrical green compacts had a diameter of about 12 mm and a length of about 30 mm. The average green densities were about 56% of the theoretical possible density which is supposed to be 3.985 g cm^{-3} . For the light-scattering experiments the green compacts were cut into disks of typically 1.5 mm thickness by dry sawing.

3 Experimental setup

The sintering and light-scattering experiments were made by the thermo-optical measuring device called TOM (Hofmann et al 1997; Raether et al 1998). Figure 1 shows a schematic overview of that device. The thermal diffusivity, the sample shrinkage, and the light transmission can be measured simultaneously by that device.

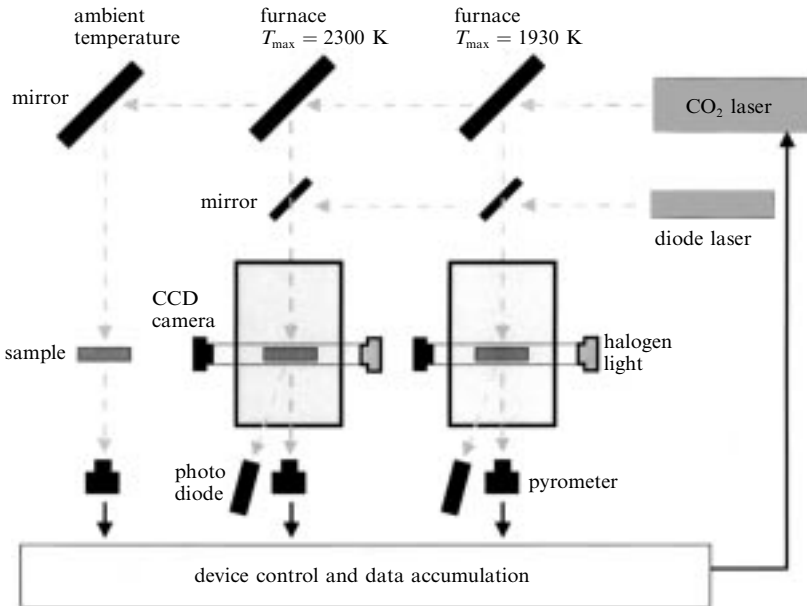


Figure 1. Schematic overview of the thermo-optical measuring device (TOM).

The thermo-optical measuring device consists of three measuring sites: a furnace measuring site for inert and oxidising atmosphere with a maximum temperature of 1930 K, a second furnace measuring site for inert and reducing atmosphere with a maximum temperature of 2300 K, and a measuring site for the measurement of thermal diffusivity at room temperature. The thermal diffusivity is measured according to the laser-flash principle (Parker 1961). An optical dilatometer is used for the measurement of the sample shrinkage.

The light transmission is measured as is shown in figure 2. The sample is illuminated by the radiation of a diode laser with a wavelength of 800 nm and a power of about 80 mW. A chopper modulates the laser frequency. The diffuse scattered radiation at the rear side of the sample is measured by a photodiode at an angle of 15°. By means of a

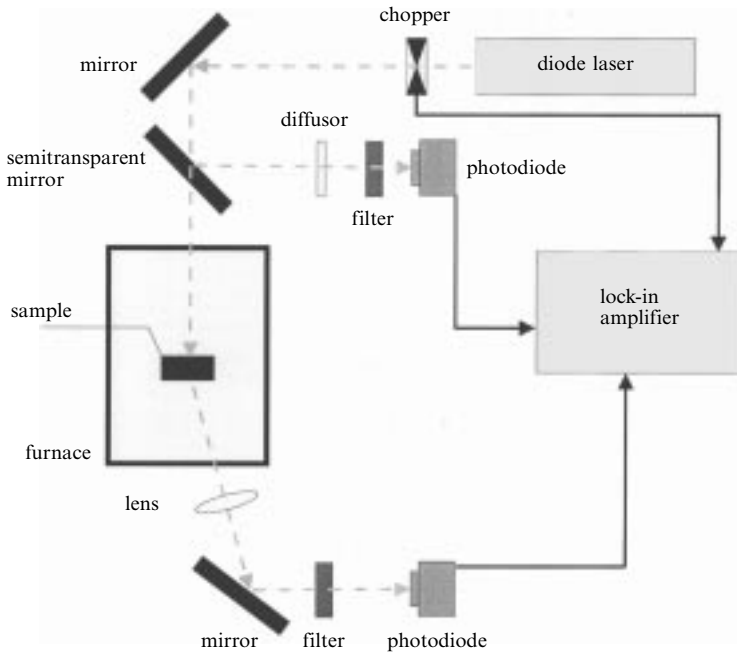


Figure 2. Schematic overview of the light transmission measuring system.

lock-in amplifier (SR 830) the background radiation of the furnace is eliminated. A second photodiode is used to correct for variations in laser power.

4 Results and discussion

4.1 Light transmission at room temperature

The light transmission of the samples depends on the scattering and absorption coefficients and the amount of surface reflections. These parameters furthermore are influenced by the wavelength of the scattered radiation, the number and the size of the pores, the index of refraction of the sample material, and temperature. From the spectral variation of the extinction coefficient one can determine the size of pores (Peelen and Metseelaar 1974; Chen and Dunn 1993). In contrast to the directional–directional transmission (here the intensity of the directly measured radiation decreases exponentially) the scattered radiation of the directional–hemispherical transmission can easily be measured for samples with a higher optical thickness. Provided that the absorption of the sample is negligible, the transmitted diffuse radiation approximately decreases inversely with the effective optical thickness. From the variation of the effective extinction coefficient with wavelength—which also takes into account forward scattering—the pore size distributions can be determined by fitting theoretical light-scattering models (Mie theory and solutions of the equation of radiative transfer) to the experimental data.

At the Bavarian Centre for Applied Energy Research, the directional–hemispherical transmittance and reflectance of partially sintered alumina samples were measured at room temperature in the wavelength range from 700 nm up to 2500 nm. A three-flux solution of the radiative transfer equations (Burger et al 1997) was used to describe the transmittance and reflectance and to compare it with experimental results. The three-flux solution gives the relationship between the directional–hemispherical transmittance and reflectance on the one hand and the absorption and scattering coefficient on the other. A detailed description of the results is given by Manara et al (1999). The three-flux solution was also used to analyse the light transmission at high temperatures as a function of scattering and absorption coefficients.

4.2 Light transmission measurements at high temperatures

At the Fraunhofer Institut für Silicatforschung various measurements of diffuse light transmission were performed at high temperatures. During all sintering processes the heating rate was set to 10 K min^{-1} until the maximum temperature was reached. First, an example of the isothermal measurements is shown and discussed. The sample thickness and the light transmission were measured at a temperature of 1823 K. The sample density was calculated by means of the sample thickness, which was measured by the optical dilatometer, and the final sample density. Figure 3 shows the sample density and the diffuse light transmission during the holding time. At a holding time above 500 min the density of the sample increases less than 1% but the diffuse light transmission increases more than 20%. That means that the total pore volume is almost constant but the pore size distribution shifts to larger pore sizes. The final density was 3.938 g cm^{-3} (98.8% td, where td refers to the theoretical density). The optical properties of alumina at high temperatures were investigated by several groups (Sova et al 1992; Shigapov 1998). It was shown that the spectral absorption coefficient of alumina (synthetic sapphire) rises strongly with increasing temperature, but it has no significant influence on the transmission for wavelengths below 4000 nm (Oppenheim 1962). In the present study, various alumina samples show a dependence of the light transmission on the measuring temperature. The results for two alumina samples of different purity are shown in figure 4. The 99.8% pure alumina sample shows a strong decrease in the transmission at temperatures above 1273 K. Because the microstructure did not change it is supposed that the absorption of the sample increases with higher temperatures. The sample of 99.99% pure alumina (TM-DAR, Boehringer Ingelheim Chemicals, Tokyo, Japan, $d_{50} = 0.2 \mu\text{m}$) does not show such behaviour. Up to a temperature of 1923 K, that

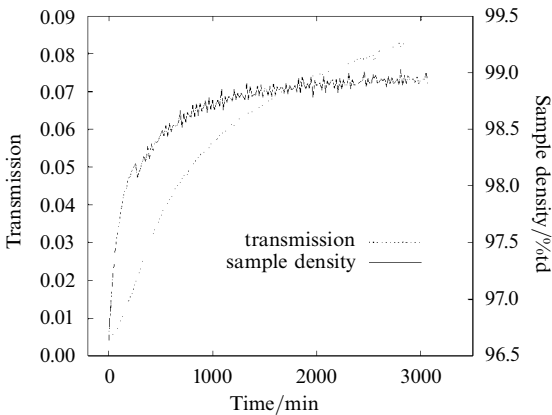


Figure 3. Sample density and light transmission during sintering of an alumina sample at 1823 K.

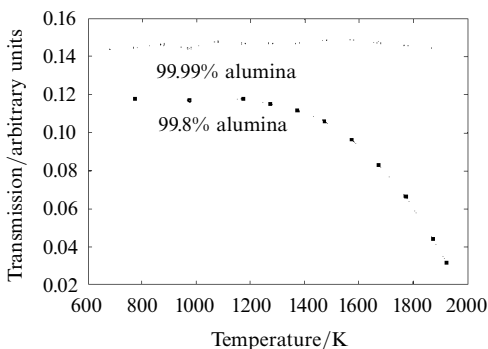


Figure 4. Light transmission of different pure sintered alumina samples.

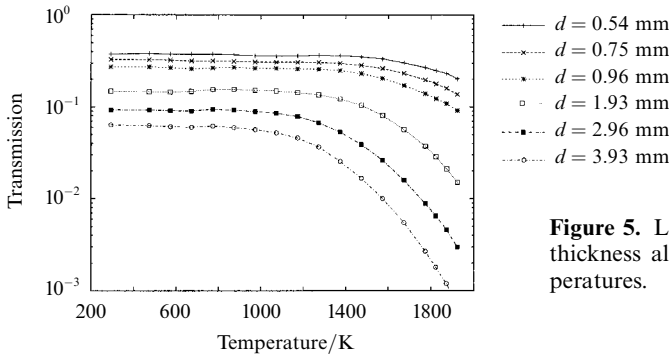


Figure 5. Light transmission of different thickness alumina samples at different temperatures.

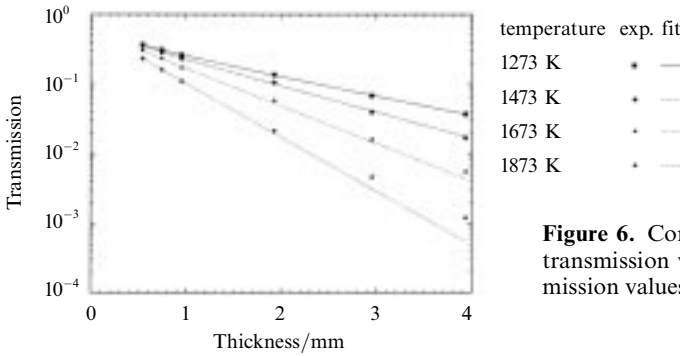


Figure 6. Comparison of the calculated transmission values with the measured transmission values at different temperatures.

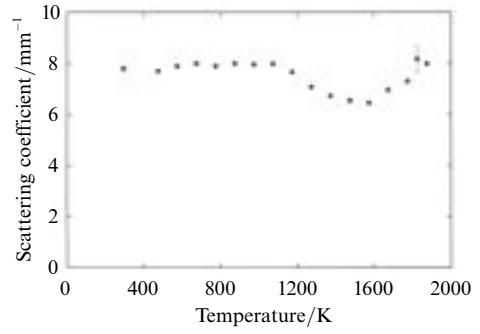
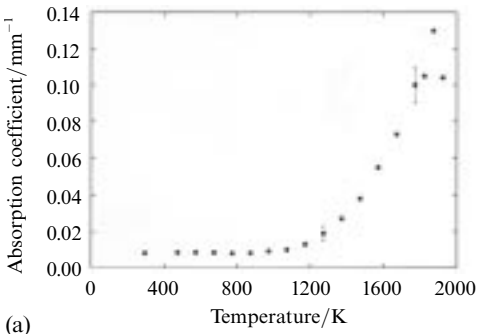


Figure 7. Results of the three-flux calculations for 99.8% pure sintered alumina: (a) absorption coefficients and (b) scattering coefficients.

sample has no significant change in the diffuse light transmission. From this result it follows that the absorption of highly pure alumina is negligible. Impurities in the sample material cause the absorption effect at high temperatures.

For a quantitative study of the temperature-dependent absorption, an alumina sample (purity 99.8%) was sintered at a temperature of 1923 K for 24 h to a final density of 3.907 g cm^{-3} (98% td). Disks of different thicknesses were cut from this sample with a diamond saw and the light transmission was measured for different temperatures (figure 5).

As shown in figure 6, the light transmission varies with temperature and with sample thickness. At a fixed temperature, the experimental data have been fitted by a least-squares fit with the three-flux model described in section 4.1 with the absorption and scattering coefficients as parameters (compare figure 6). The resulting absorption and scattering coefficients are shown in figure 7. The fitting routine used was the Levenberg–Marquardt method. As a result one obtains the absorption and scattering coefficient

with the standard error and the correlation coefficient. The standard errors are shown in figure 7 for some values.

In general the correlation coefficient can be between -1 and 1 . If the correlation coefficient is 0 , the absorption coefficient and the scattering coefficient cannot be assumed to be interdependent. If the correlation coefficient is 1 , the absorption coefficient and the scattering coefficient are interdependent, which means that the absorption coefficient increases with increasing scattering coefficient and vice versa. For a correlation coefficient of -1 , the absorption coefficient decreases with increasing scattering coefficient, and vice versa.

In our case the correlation coefficient becomes -0.95 for temperatures above 1000 K, which makes it difficult to determine the absorption and the scattering coefficient reliably.

The absorption coefficient strongly increases at temperatures above 1273 K. For temperatures above 1773 K, the absorption coefficient is uncertain because of the low transmittance at high temperatures. The increase is attributed to the thermal population of electronic impurity levels which can absorb near-infrared radiation. The scattering coefficient—determined by the fitting procedure—is nearly constant in the whole temperature range (figure 7). This would have been expected from the invariance of microstructure to temperature and demonstrates the validity of the model used.

5 Conclusions

The results show that it is possible to measure the diffuse light transmission during the sintering process. The light transmission measurement is more sensitive in the final sintering stage than the sample shrinkage measurement by a dilatometer (compare figure 3). So the light transmission measurement can be used to find an appropriate stopping criterion for the sintering process. For a correct interpretation of the in-situ measuring data, the contribution of absorption to the diffuse light transmission has to be known. It was shown that the absorption coefficient in light-scattering samples can be determined by high-temperature measurements with samples of different thickness and by a fit with a three-flux model of radiative transfer.

Acknowledgements. This work was supported by the German Science Foundation (DFG), Bonn.

References

- Burger T, Kuhn J, Caps R, Fricke J, 1997 *Appl. Spectrosc.* **51** 309–319
 Chen W W, Dunn B J, 1993 *Am. Ceram. Soc.* **76** 2086–2092
 Hofmann R, Hahn O, Raether F, Mueller G, 1997, in *Proceedings Stuttgarter Werkstoffwoche '96, Symposium 6* Eds G Ziegler, H Cherdron, W Hermel, J Hirsch, H Kolaska (Frankfurt: DGM-Informationsgesellschaft) pp 665–670
 Manara J, Caps R, Raether F, Fricke J, 1999 *Opt. Commun.* **168** 237–250
 Oppenheim U P, 1962 *J. Opt. Soc. Am.* **52** 1078–1079
 Parker W J, 1961 *J. Appl. Phys.* **32** 1679–1684
 Peelen J G J, Metseclar R, 1974 *J. Appl. Phys.* **45** 216–220
 Raether F, Boese H, Leitner G, Jaenicke-Roessler K, 1997, in *Proceedings Stuttgarter Werkstoffwoche '96* Eds G Ziegler, H Cherdron, W Hermel, J Hirsch, H Kolaska (Frankfurt: DGM-Informationsgesellschaft) pp 655–663
 Raether F, Zimmer J, Springer R, 1998, in *Proceedings CIMTEC '98, Florenz, Italia* (Florence: Techna Srl) pp 711–720
 Shigapov A B, 1998 *High Temp.* **36** 35–39
 Sova M R, Linevsky M J, Thomas M E, Mark F F, 1992 *Johns Hopkins APL Tech. Dig.* **13** 368–378
 Thuemmler F, 1989, in *Pulvermetallurgie in Wissenschaft und Praxis* volume 5, Ed. H Kolaska (Freiburg: Verlag Schmid) pp 261–294