In-Situ Sintering Studies on Nano-Alumina

Lia A. Stanciu[*] , F. Raether[**] and J.R. Groza[*]

[*]Chemical Engineering&Materials Science Department, University of California at Davis, One Shields Avenue, Davis, CA 95616

[**]Fraunhofer Institute for Silicate Research, 2 Neunerplaz, Wuerzburg, Germany

ABSTRACT

The optimization of the sintering process becomes nowadays a very important step towards obtaining improved quality ceramics for applications into many industrial areas. Recently, a thermooptical measuring device (TOM) has been developed to in-situ monitor the thermal diffusivity, shrinkage and light scattering of materials during sintering.

In present work the TOM method has been used to identify the temperature boundary between different stages of sintering of nano-alumina and to measure the diameter of the sintering necks formed during the incipient stages of the consolidation process.

The initial nanopowders have been characterized for particle size by the TEM method. The nano-crystalline powders were sintered into the TOM device in a temperature range between room temperature and 1300°C, with a heating rate of 12°C/min.

Interrupted sintering experiments were performed by TOM and Microwave Sintering followed by microstructural observations.

Keywords: sintering, nanopowders, laser-flash.

1. INTRODUCTION

The mechanisms of densification during the thermal treatment processes was for a long time more a question of trial and error and based more on intuition than on scientific research. Although much progress has been realized in the field, the exact mechanisms of sintering have not yet been completely explained.

In-situ characterization of the sintering process can offer more insight into the mechanisms that govern it. The conventional optical dilatometry has played the main role into the characterization of the sintering process and microsctructure evaluation for a long time. Nowadays, alternative in-situ characterization techniques became available, one of which has been developed at Fraunhofer Institute for Silicate Research in Würzburg, Germany [1, 2]. It allows the simultaneous evaluation of the thermal diffusivity by the laser flash method [3], and of the sintering shrinkage via an optical dilatometer.

In the initial stages of sintering of micron sized alumina, it has been shown [4, 5] that the thermal diffusivity increases two times. The shrinkage is very small and almost not detectable at this stage. The increase in thermal diffusivity has been shown to take place due to the microstructural changes that occur in the sintering body by formation of the sintering necks. This finding shows that the thermal diffusivity measurements are an useful tool to investigate the first sintering stage, when the optical dilatometry cannot be used.

When we consider the heat transfer during the thermal treatment as taking place through the solid phase only, the thermal resistance R* (constriction resistance), is approximately equal to:

$$R^*_{int} = f_s^*(r_c) = 0.506/r_c + 0.044 \quad (1)$$

If we imagine the sample as being constructed of basic cells of a simple cubic lattice of spheres, in the first stage of sintering, the thermal conductivity of the lattice is given by:

$$k_{cub} = k_0 \frac{1}{2R^*(r_c,...)} \quad (2)$$

where:

k_0 is the theoretical thermal conductivity of alumina.

The formula can also be written, in absence of gas and contact layers as:

$$k_{cub} = k_0 \frac{1}{2 f_s^* r_c} \quad (3)$$

In the above formulas, the r_c is the radius of the sintering neck and is used to describe the sintering state of a lattice of monodisperse spheres. By taking the material constants for alumina from literature, one can calculate by the above formulas, from a measured thermal conductivity, the sintering neck radius of the powder of interest.

Present work reports the results of investigations on nano α-Al_2O_3 powders sintering behavior during conventional and microwave sintering.

2. EXPERIMENTAL

The initial α-Al_2O_3 powders were characterized by bright field TEM and Electron Diffraction, by using a Philips CM-12 Transmission Electron Microscope, operating at 100 kV. The XRD pattern for the initial nanopowder has been recorded with a Philips Vertikal-Goniometer PW 1050 Diffractometer. The phase identification has been performed by searching the JCPDS database.
The green nano-alumina samples have been prepared in cylindrical silicon molds, by cold isostatically pressing for 3 minutes at a pressure of 250 MPa with no additives. The cylindrical green bodies have been then cut into 1.5 mm high, 12 mm diameter discs. The resulted samples have been in-situ measured for thermal diffusivity and sintering shrinkage using the Thermooptical Measurements device (TOM), with a heating rate of 12°C/min from room temperature up to 1300°C. The thermal diffusivity was measured by a laser-flash method and the non-contact measurements of the shrinkage have been performed by an optical dilatometer. The TOM device uses a resistance heated $MoSi_2$ furnace using synthetic air at a flow of 1l/min. Details of the TOM device are given elsewhere [2]. The sintering process has been interrupted at 400, 800, 1100 and 1300°C and the fracture surface has been viewed for particle size by SEM. The same samples have been sintered by microwave sintering at the same temperatures, with a heating rate of 50°C/min, followed by microstructural observations. The microstructural investigation by SEM have been performed by using a Hitachi S800 Scanning Field Emission Electron Microscope, operating at 25kV.

3. EXPERIMENTAL RESULTS

The particle size of the α-alumina powder we used for this work was of 10nm, as determined by TEM and the corresponding Diffraction Pattern indicates an α phase (Figure 1).
The results of the XRD experiment are shown in Figure 2.

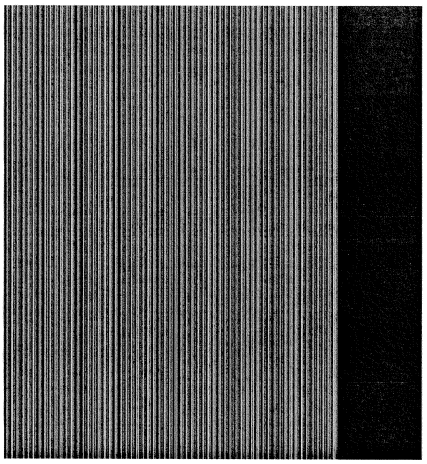

Figure 1. TEM bright field image and diffraction pattern of the initial alumina powder

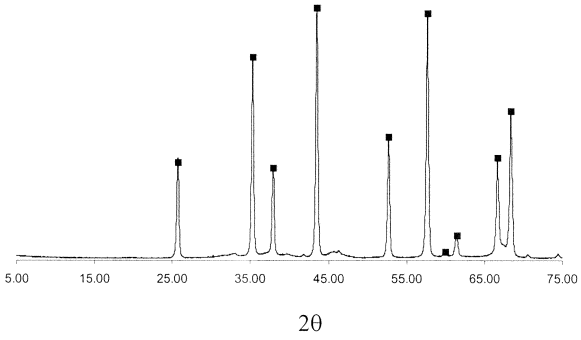

Figure 2. XRD spectra of alumina nanopowders. The symbol (■) indicates an alpha alumina phase.

The results show that besides α-Al_2O_3, which is the dominant phase in the powder, there are still transition aluminas present in small amounts. These may influence the evolution of thermal diffusivity and densification, due to additional phase transformation from transition aluminas to α-alumina.

The results of the TOM experiments are shown in Figure 3. The thermal diffusivity increases between 250 and 1500°C. The first sintering necks started to form at around 250°C, which is not a significantly lower value than the results reported in literature for conventional alumina powders. The onset of shrinkage started around 900°C and two peaks of the sample diameter are visible at about 900 and 1100°C. The fact may be ascribed to the phase transformations between the additional phases that were identified in small amounts in the initial powder.

Representative SEM pictures for conventional and microwave sintered samples are shown in Figures 4 and 5, respectively. The mean particle size was smaller for microwave sintered sample, as a result of the higher heating rate used, the grain size being in the range 100-125nm for both samples, with no large difference between the resulted microstructures of the two samples.

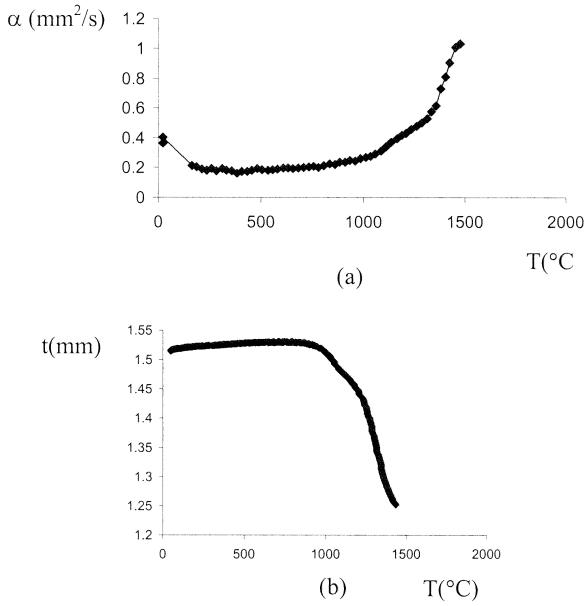

Figure 3. Thermal diffusivity (a) and sample thickness (b) variation with temperature

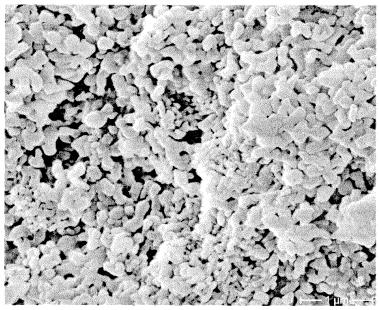

Figure 4. SEM picture of nano-alumina sample, conventional sintered at 1300°C

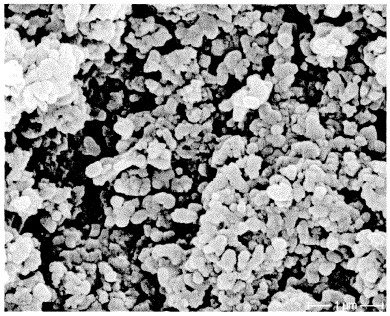

Figure 5. SEM picture of nano-alumina sample, microwave sintered at 1300°C

4. CONCLUSION

The sintering behavior of nanosized α-Al_2O_3 has been investigated by thermal diffusivity measurements, conventional sintering, and microwave sintering. The sintering neck diameter in the first stage of sintering can be evaluated from thermal diffusivity measurements.

Submicron grain sized sintered bodies of α-alumina, with grain sizes not exceeding 200nm, can be obtained by microwave and conventional sintering, when nanoalumina powders are used, with grain sizes in the lower range when high heating rates are used.

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