Microstructure evolution during pressureless sintering of bulk oxide ceramics

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Abstract

The author's experience concerning the influence of the choice of different pressureless heating schedules on the final microstructure of oxide ceramic materials is summarized in the paper. Alumina, ceria, strontium titanate, as well as tetragonal (3 mol% Y_2O_3) and cubic (8 mol% Y_2O_3) zirconia were cold isostatically pressed or injection moulded and pressureless sintered with different heating schedules – namely with Constant-Rate of Heating with different dwell temperatures (CRH), with Rate-Controlled Sintering (RCS) and with Two-Step Sintering (TSS). It was examined whether some of these three sintering schedules, with the same final density achieved, can lead to a decrease of the grain size of sintered ceramics. The results showed that only TSS (and only for selected materials) brought significant decrease of the grain size.

Keywords*: alumina, zirconia, ceria, strontium titanate, constant-rate of heating, rate-controlled sintering, two-step sintering*

I. Introduction

The most frequent goal in the sintering of advanced ceramic materials is to obtain a material with high relative density and homogeneous microstructure consisting of small grains. In the case of conventional pressureless sintering, no general opinion can yet be found in literature as to whether the final grain size of an individual body of defined final density can also be influenced by the choice of sintering regimes. Based on theoretical models of sintering, it has been suggested that the final density definitely determines the grain size of the sintered bodies [1–5]. On the other hand, there are also reports that have demonstrated that refined microstructures can be obtained by correct choose of the sintering cycle. This paper describes author's experience concerning the influence of the choice of three different pressureless heating schedules on the final microstructure of oxide ceramic materials.

Constant-Rate of Heating (CRH in the following text) is the most frequently used heating profile in the sintering technology. It consists of heating the sample at a constant heating rate up to the sintering temperature, at which a dwell time can be inserted [6]. The aim of the first part of this paper was to examine whether sintering of zirconia ceramics for a shorter period at a higher temperature results in a different final grain size than sintering for a longer period at a lower temperature while the same final density is obtained.

In the 1970s, so-called Rate-Controlled Sintering method (RCS) was developed at the North Carolina State University [7–10]. With this method, the shrinkage rate is being reduced in the open-porosity phase, which should lead to sintered bodies with a more homogeneous structure and smaller grains than in the case of CRH method. In the second part of the paper, the method of RCS and the method of CRH with optimized holding time were used, and the microstructures of the zirconia, alumina and ceria bodies obtained by the two methods were compared.

The method of Two-Step Sintering (TSS) was first published by Chen and Wang [11] and presently this method is widely used for sintering of different kind of ceramic materials [12–17]. In this method the sample is heated to a higher temperature to achieve a density higher than 75% of theoretical sample density (where

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the supercritical pores are removed from the sintered body), then quickly cooled down and held at a lower temperature until its full densification (without additional grain growth). The third part of the paper shows the results of TSS of ceramic materials with tetragonal (ZrO_2 + 3 mol% Y_2O_3), hexagonal (Al_2O_3) and cubic ($SrTiO_3$, ZrO_2 + 8 mol% Y_2O_3) structure and compares them with CRH experiments.

II. Experimental

Materials

Commercially available powders with particle size (established by BET method) ranging from 50 to 370 nm were used. Details of the used powders are given in Table 1.

Preparation of ceramic green bodies

The above ceramic powder materials were shaped into disks (dia 30 mm, height 5 mm) via cold isostatic pressing (CIP - Autoclave Engineering, Inc., USA) and cylinders (dia 5.9 mm, height 60 mm) via injection moulding (IM - Allrounder injection press, Germany). Green bodies were pre-sintered at 800°C/1h and then cut and ground into prisms.

Sintering by CRH

Tetragonal zirconia ceramics (Z3Y shaped by CIP and Z3YS shaped by IM) were used for CRH experiments (see Table 1). The specimens were first sintered in a high-temperature dilatometer (L70/1700, Linseis, Germany) with vertical specimen orientation. The temperature was increased at a rate of 10°C/min up to a temperature of 800°C and then at a rate of 5˚C/min up to the final sintering temperature, at which the isothermal holding time followed. For each type of specimen, three different sintering temperatures were chosen such that final relative densities of 98% of theoretical sample density (t.d. in the following text) and higher were obtained. For the Z3Y-CIP specimens these temperatures were 1400°C, 1450°C and 1500°C while for the Z3YS-IM specimens they were 1450°C, 1500°C and 1530°C. Densification curves $\rho_{rel}(t,T)$ were calculated from dilatometer shrinkage data [18] and further used to establish concrete firing schedules leading to identical densities of specimens sintered at different temperatures and holding times. Firing in these schedules was then performed in a standard resistance (superkanthal) furnace (K 1700/1, Heraeus, Germany).

Sintering by RCS

RCS experiments were performed with REY, CE and Z3YS samples (see Table 1) prepared by injection moulding. Sintering by the RCS method was performed strictly following the three-stage model [9], where up to 75% t.d. the rate of densification was 0.4% t.d./min, then to 85% t.d. it was 0.13% t.d./min and after that the rate of sintering fell linearly with time (proportionality constant $-3.3 \cdot 10^{-4}$% t.d./min^2). These experiments were performed in high-temperature dilatometer (L70/1700, Linseis, Germany) equipped by special RCS software.

Sintering by TSS

The Two-Step Sintering of isostatically pressed TAI, REY, Z3Y and Z8YS ceramics was performed in a superkanthal resistance furnace (K 1700/1, Heraeus, Germany) in air atmosphere. According to the data from the literature [11] temperatures higher than those guaranteeing a relative density of 75% t.d. were chosen for the first sintering step. Several combinations of temperatures of the first sintering step (T_1) and the second sintering step (T_2) were tested for each material. The dwell times at the T_2 were between 0 and 20 hours. Sintering proceeded at a heating rate of 10°C/min up to a temperature of 800°C, and at 5°C/min up to a temperature of the first sintering step. The temperature decrease from the first to the second sintering step proceeded at a rate of 60°C/min.

Study of microstructure of sintered samples

The final relative densities of samples were determined on the basis of Archimedes' principle with distilled water (EN 623-2). The samples were ground and polished and then thermally etched to expose the grain boundaries. Etching temperatures was 50°C below the sintering temperature, etching time was 5 minutes. The microstructure of samples was studied using scanning electron microscopy (Philips XL30, the Netherlands). The grain size was estimated by the linear intercept method (EN 623-3). For each sample, at

Table 1 Specification of ceramic powders used

Powder	Producer	Grade	Abbr.	D [nm]	Sintering method
Al_2O_3	Taimei Chemicals, Japan	Taimicron TM-DAR	TAI	100	TSS
Al_2O_3	Malakoff Industries, USA	ReynoldsRC-HP DBM	REY	240	RCS, TSS
CeO_2	Guangzhou Zhuijang Ref., China		CE	370	RCS
$SrTiO_3$	Sigma-Aldrich, Germany	467634	ST	50	TSS
ZrO_2 (+3 mol% Y_2O_3)	Tosoh Corporation, Japan	TZ-3YB	Z3Y	60	CRH, TSS
ZrO_2 (+3 mol% Y_2O_3)	Tosoh Corporation, Japan	TZ-3YS	Z3YS	140	CRH, RCS
ZrO_2 (+8 mol% Y_2O_3)	Tosoh Corporation, Japan	TZ-8YSB	Z8YS	140	TSS

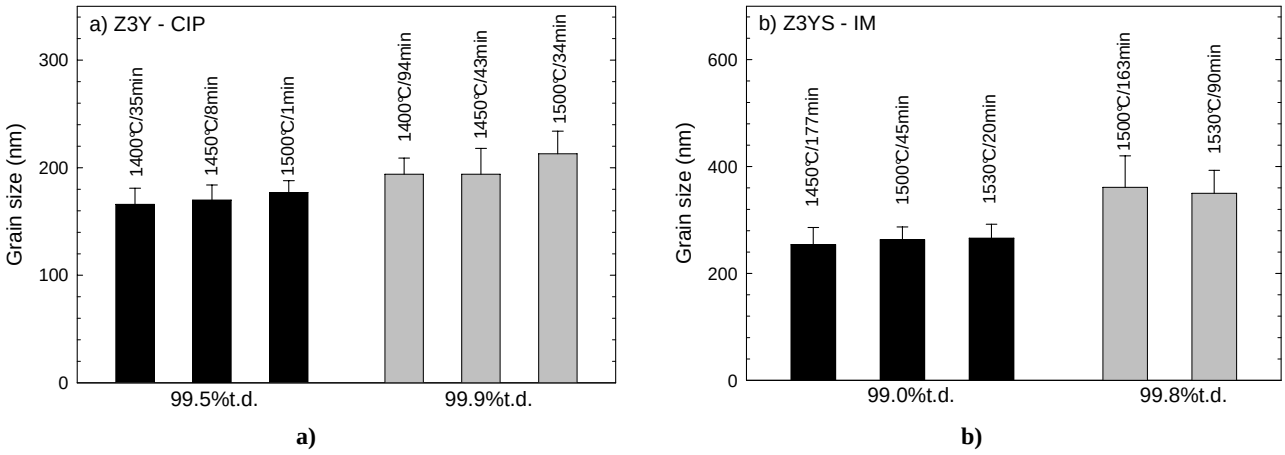

Figure 1. Mean grain size of specimens sintered with different CRH temperature modes a) Z3Y – CIP, b) Z3YS – IM

least three photographs of the microstructure were taken; in each microphotograph a minimum of five line segments were assessed.

III. Results and discussion

Sintering with constant rate of heating and different dwell temperatures and times

Via controlled sintering of cold isostatically pressed (Z3Y) and injection moulded (Z3YS) zirconia powders the same final specimen densities were obtained by different sintering schedules (a longer holding time at a lower temperature or a shorter holding time at a higher temperature during CRH experiments).

In case of zirconia Z3Y powder shaped by CIP the density of cca 99.5% t.d. was reached by sintering at three different sintering temperatures and times (1400°C/ 35 min, 1450°C/ 8 min, and 1500°C/ 1 min). As can be seen in Fig. 1a, the grain size of all three samples was almost identical – 170 nm. Higher final density (99.9% t.d.) was achieved after sintering at the same sintering temperatures but for longer times (1400°C/ 94 min, 1450°C/ 43 min, and 1500°C/ 34 min). Also in this case the grain size of all three samples was nearly the same – 200 nm.

Similar results were obtained with Z3YS powder (with larger particles than Z3Y) shaped by injection moulding. Due to different particle size and different shaping technology, the microstructure of the green body was expected to be different from the Z3Y sample. This led to slightly lower final densities of Z3YS samples – a density of 99.0% t.d. was reached after sintering at 1450°C/ 177 min, 1500°C/ 45min and 1530°C/ 20 min and the final density of 99.8% t.d. after sintering at 1500°C/ 163 min and 1530°C/ 90 min. Again, at the same final density also the grain size was the same (260 nm at 99.0% t.d or 350 nm at 99.8% t.d.), irrespective of the sintering schedule (see Fig. 1b).

While examining the microstructure of sintered specimens, it was proved statistically that the choice of CRH sintering schedule did not have any effect on the grain size of sintered material, which means that for a given specimen (characterized by the microstructure of ceramic green body, i.e. by the distribution of particle and pore sizes) the grain size was a function of specimen density irrespective of the CRH temperature mode with which this density had been obtained [6].

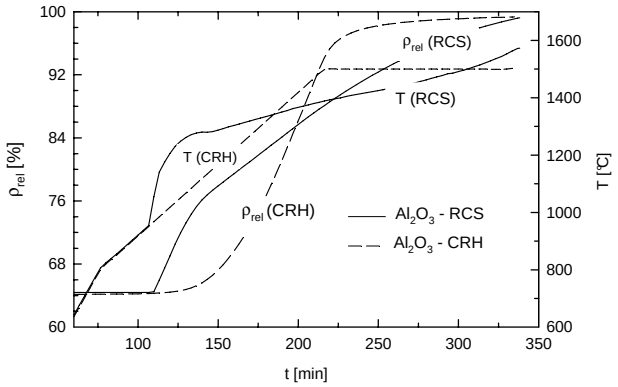

Figure 2. The dependence of relative alumina (REY) density and temperature on time during RCS and CRH sintering

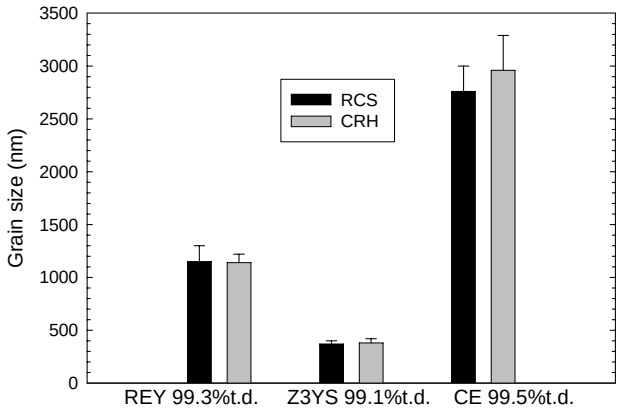

Figure 3. Mean grain size of REY, Z3YS and CE ceramics sintered by means of RCS and CRH methods

Rate-Controlled Sintering

Alumina (REY), tetragonal zirconia (Z3YS) and ceria (CE) samples prepared by injection moulding were used for sintering by means of RCS method. The microstructures obtained by RCS were compared with that obtained by optimized CRH sintering of these samples. The typical course of the RCS is demonstrated for alumina ceramics in Fig. 2. In the RCS method the sample densification rate in the open porosity phase ($\rho_{rel} < 90\%$) was lower than in the CRH method. This should prevent separation of pores from grain boundaries, and thus also influence the microstructure development towards higher homogeneity and smaller grain size [7–9].

It is evident from Fig. 2 that the same final density of alumina (REY) ceramics (99.3% t.d.) was obtained by RCS and CRH sintering schedules. Due to proper optimization of CRH cycles the same final densities after RCS and CRH cycles were reached also for zirconia (Z3YS) ceramics (99.1% t.d.) and ceria (CE) ceramics (99.5% t.d.). It can be seen from Fig. 3 that the grain size of samples sintered by RCS and CRH was nearly the same for alumina (1150 nm) and zirconia (370 nm), or within the standard deviation of grain size evaluation for ceria ceramics (2760 nm after RCS, or 2960 nm after CRH).

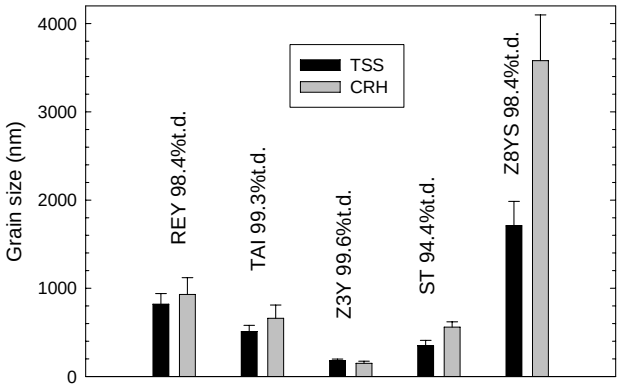

Figure 4. Mean grain size of REY, TAI, Z3Y, ST and Z8YS ceramics sintered by means of TSS and CRH methods

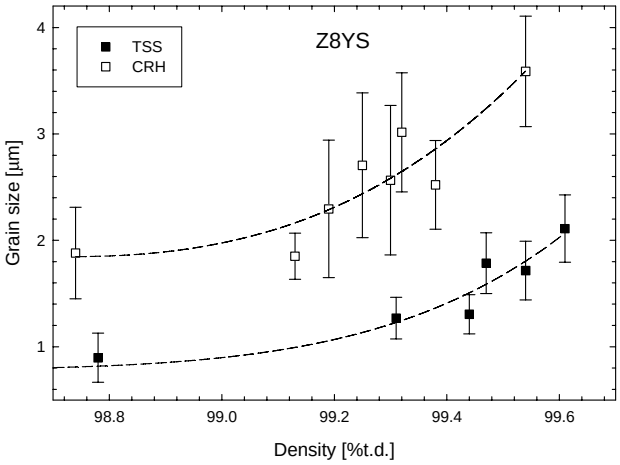

Figure 5. Dependence of grain size on sintered density of cubic zirconia samples (Z8YS) sintered by TSS and SSS methods

By sintering samples prepared from three different materials, it was possible to prove that RCS method did not lead to microstructures with a smaller mean size of grains than in the case of the optimized sintering cycle with CRH.

Two-Step Sintering

The method of Two-Step Sintering was applied to isostatically pressed tetragonal zirconia (Z3Y), hexagonal alumina (REY, TAI) cubic zirconia (Z8YS) and strontium titanate (ST) ceramics. Details on temperatures of the first and second sintering steps as well as dwell times at the second sintering step are given elsewhere [19,20].

As it can be seen from Fig. 4 the TSS method was applied with great benefit to cubic zirconia ceramics (Z8YS, see Fig 5) and also to cubic strontium titanate ceramics (ST). The effect of the TSS method on refining the microstructure of tetragonal zirconia (Z3Y) and hexagonal alumina ceramics (REY, TAI) was only within the standard deviation of grain size evaluation.

At the moment we do not have any explanation of this phenomenon. Further experiments are necessary to clarify if it is caused by differences in values of activation energy of sintering and grain growth or by crystal structure or by some other effect .

IV. Conclusions

The influence of the choice of pressureless heating schedule on the final microstructure of various oxide ceramic materials is summarized in the paper. It was found that the method of Two-Step Sintering was effective in refining the microstructure of cubic zirconia ceramics and cubic strontium titanate ceramics. On the other hand, the positive influence of Two-Step Sintering method on decreasing of grain size of tetragonal zirconia and hexagonal alumina ceramics was not statistically proved. Similarly, an optimization of the dwell temperature and time during Constant-Rate of Heating as well as Rate-Controlled Sintering of tetragonal zirconia, alumina and ceria ceramics did not lead to any remarkable decrease in their grain size.

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