Influence of forming method and sintering process on densification and final microstructure of submicrometre alumina ceramics

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Abstract

Conditions of green body preparation and consequently the conditions of sintering are prerequisite for the preparation of dense samples of Al_2O_3 with superior optical and mechanical properties. The goal of this work was to determine the optimum forming conditions for preparation of green body, and to find out the optimal sintering regime facilitating the preparation of ultra-fine grained high purity alumina with maximal density, fine microstructure and small pore size. Axial pressing followed by CIP was found to yield green body with the highest density and narrowest pore size distribution. In the two-stage sintering regime the temperature T_1 has to be higher or equal to 1300°C to obtain closed porosity unstable against shrinkage. The temperature $T_2 \geq$ 1130°C was found to be too high for suppression of grain growth in the final stage of sintering and sintering trajectory was identical with that from standard sintering regime.

Keywords: alumina, green body forming, two-stage sintering

I. Introduction

The uniform packing of particles in green (unfired) bodies is a critical precondition for the preparation of dense, defect-free and pore-free ceramics with fine grained microstructure and desired optical and mechanical properties [1,2]. Refinement of the grain size of polycrystalline alumina below the wavelength of visible light is expected to result in increased optical transparency [3]. In order to achieve such sub-micrometer grain sizes, various sintering, mostly pressure-assisted, techniques are usually applied, with all their disadvantages and limitations.

Chen & Wang reported on a pressureless two-stage sintering process, which was applied with success for densification of a nano-meter sized yttria powder without the final stage grain growth. They postulated that in certain interval of temperatures, called "kinetic window", densification is already in operation, while the grain boundary motion is not yet activated [4]. In this sintering regime a powder compact is sintered at a higher temperature T_1 until the residual porosity becomes unstable against further shrinkage. Then the sintering temperature is lowered to the value T_2 at which densification proceeds further, but no grain growth occurs. However, the application of the two-stage sintering for alumina is questionable, as some works suggest that the activation energy of densification in alumina is in fact higher than the activation energy of grain growth [5]. Our previous work suggests that under a suitable two-stage sintering regime a refinement of microstructure can be observed in comparison to polycrystalline alumina sintered in a standard way. Despite observed microstructure refinement the grain growth was not suppressed entirely, and the sintered specimens still contained about 1 % of residual porosity concentrated in less dense regions. These were created in the course of green body forming by uniaxial pressing [6].

The ultimate goal of our work is to map the two-stage sintering process of submicrometre alumina more thoroughly, and to identify unambiguously the temperature interval of "kinetic window", where the residual porosity in alumina ceramics prepared from a submicrometre powder can be eliminated without the final stage grain growth.

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This paper specifically deals with the influence of pressure conditions (axial pressing and cold isostatic pressing - CIP) on microstructure of green bodies (and sintered samples) shaped from variously treated sub-micrometre-sized alumina powder (Taimicron TM DAR) and on their densification. Further step was to find out optimal sintering regime facilitating the preparation of ultra-fine grained high purity alumina with maximum density, the finest microstructure and the lowest pore size.

II. Experimental

An ultra-fine grained high purity (99.995 %) alumina powder (Taimicron TM DAR) with the primary particle size of 150 nm was used for the experiments (denoted as powder *S*). The powder was then either milling activated (denoted as powder *SM*), or granulated (denoted as powder *TG*) in order to evaluate the influence of the powder state on green body forming and sintering. Powder characteristics are shown in Table 1.

For the optimisation of compacting pressure three different pressures 50, 100 and 150 MPa were applied in axial loading, and 50 MPa axial loading followed by cold isostatic pressing, CIP, at 250 MPa. Green density of pressed samples was measured by Archimedean method in mercury. Pore size distribution of green bodies was measured by mercury intrusion porosimetry. The pressed samples were sintered for 10 minutes at 1350°C and then the density of sintered samples was measured by Archimedean method in distilled water. The relative density of specimens (ρ_{rel}) was related to the theoretical density of alumina 3.98 g·cm^{-3}. To find out the relation between sintering temperature and relative densities the sample *S*-CIP was subjected to 5 various sintering regimes including heating at 10°C/min to a maximum temperature (1250, 1275, 1300, 1325 and 1350°C respectively) without dwell time, and subsequent cooling to room temperature. Based on the results of preliminary sintering experiments (relative density and the mean grain size determined by linear intercept method (minimum of 200 intercepts) from SEM micrographs of polished and thermally etched (1125°C for 8 hours) cross sections of the specimens three different temperatures T_1 = 1300, 1325 and 1350°C were selected, which facilitated elimination of the residual porosity to less than 15 %. These were then used for further experiments in the second stage, with special focus on 1300°C, which yielded specimens with the smallest mean grain size. Three different temperatures T_2 (1130, 1150 and 1170°C) at four different dwell times (2, 4, 8 and 24 hours) were applied and mean grain size was determined by linear intercept method from fracture surfaces.

III. Results and Discussion

With the selected powder a set of experiments was carried out, which resulted in determination of the minimum temperature, where a stage of closed porosity will be achieved, with the mean diameter of pores facilitating their closure in the second stage of sintering. For this, a preparation of sufficiently dense green body with narrow pore size distribution is vital. The highest green density was achieved for the granulated powder pressed isostatically; only small differences were found for the as received and milling activated powders *S* and *SM* (Fig. 1). Mercury porosimetry showed significant decrease of the overall pore volume, shift of the mean pore size, and more narrow distribution of pore sizes in CIP-ed specimens (Fig. 2) especially for the powders *S* and *SM*. This was caused by two complementary effects – isostatic nature of the applied pressure and higher applied pressure. The broad pore size distribution in the case of the powder *TG* is the consequence of two types of porosity: the pores inside individual granules (smaller), and those among them (larger). The untreat-

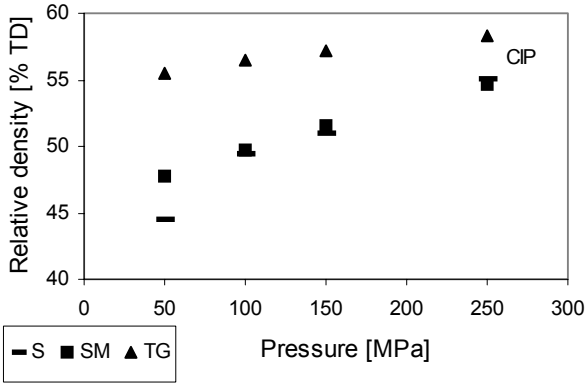


Figure 1. Relative densities of green bodies after different powder treatment and after different applied pressure

Table 1. Powder characteristics

Powder	Primary particle size [nm]	Specific surface area [m^2/g]	Density [g/cm^3]	Dopants	Binder
S		17.6	3.95 *	-	-
SM	~150	18.1	3.95 #	-	-
TG		14.5	3.95 #	500 ppm	Acrylate

* Pressureless sintering in air at 1300 °C, 1 hour.
# Pressureless sintering in air at 1350 °C, 1 hour.

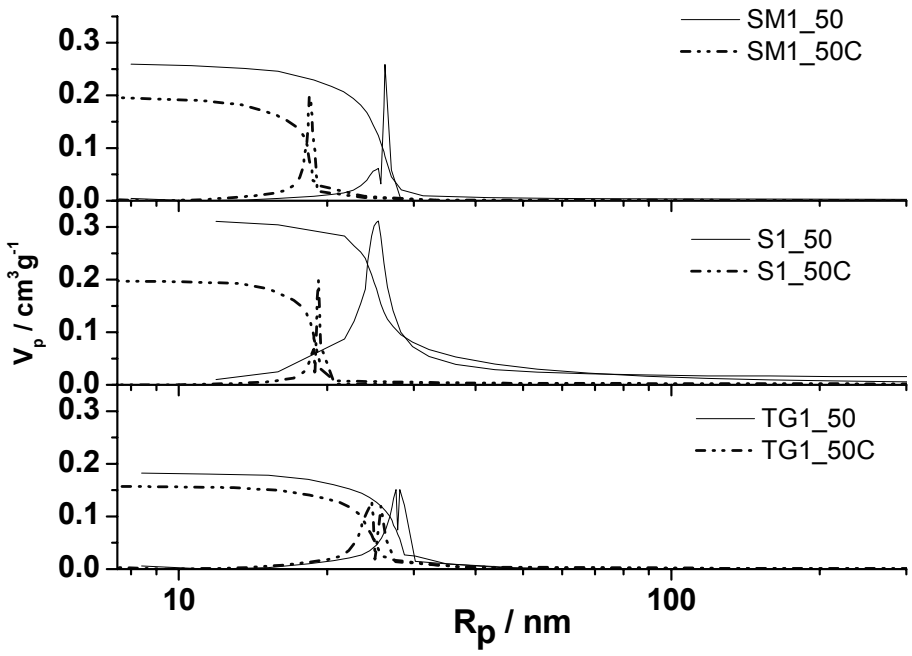


Figure 2. Radius of pore necks of green bodies before and after CIP

ed *S* powder after CIP yielded green bodies with lowest pore radius and with sufficiently narrow pores size distribution for sintering experiments. This was confirmed by preliminary sintering test where the *S*-CIP green bodies achieved sufficiently high green density to justify their use in two-stage sintering experiments (Fig. 3). The sintering at various temperatures without isothermal dwell indicate that the temperature as low as 1300°C is sufficient for elimination of the residual porosity to about 15 % (Table 2). Determination of the grain size by linear intercept method moreover revealed the finest mean grain size of 270 nm for the specimen sintered at 1300°C without isothermal dwell (Table 2).

A prerequisite for successful densification during the second, low-temperature step of sintering is that the pores become subcritical and unstable against shrinkage. This stage is, according to the original paper of Chen and Wang [4], achieved in nanosized yttria when the relative density exceeds 70 %TD. They conclude that the relative density of 75 %TD after the first step is sufficient for complete densification of yttria by low-temperature heat treatment in the kinetic window [4]. However, our experience has shown that 75 %TD is not sufficient in case of the used alumina powder, and the stage near to the closed porosity, which in case of alumina corresponds to about 90 %TD, must be achieved before the second, low temperature sintering step is applied [6]. The sintering trajectories (relative density – grain size dependences) of the specimens after the two-stage sintering are summarised in Fig. 4 and Table 3 and compared with the specimens sintered in a standard way, i.e. by a routine pressureless sintering with maximum temperature between 1100 and 1350°C and dwell time between 0 and 60 min. The microstructures of specimens sintered at the T_1=1130°C and afterwards at T_2=1300°C for 2 h and those sintered at T_1=1130°C and afterwards at T_2=1300°C for 24 h are shown in the Fig. 5. After the second step in all cases the mean grain size of our samples, as well as the

Table 2. Average grain size of samples after first step of two stage sintering

Powder	Temperature [°C]	Grain size [nm]	Relative density [%TD]
S	1300	270 ± 70	84.7
	1325	390 ± 120	90.7
	1350	450 ± 140	95.0

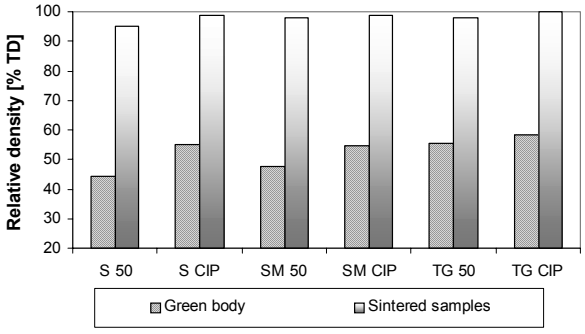


Figure 3. Comparison of the relative density before and after sintering (pressureless in air at 1350°C for 1 hour)

Table 3. The mean grain size after the second step of two-stage sintering process

Samples	T_1 [°C]	T_2 [°C]	Dwell time [hours]	Grain size [nm]		Relative density [g/cm³]
				after T_1 [nm]	after T_2 [nm]	
1	1300	1130	2	270 ± 70	360 ± 120	87.8
2	1300	1130	4	270 ± 70	410 ± 140	90.4
3	1300	1130	8	270 ± 70	470 ± 150	92.3
4	1300	1130	24	270 ± 70	520 ± 180	95.4
5	1300	1150	2	270 ± 70	380 ± 110	89.5
6	1300	1150	4	270 ± 70	450 ± 140	91.9
7	1300	1150	8	270 ± 70	520 ± 180	94.1
8	1300	1150	24	270 ± 70	580 ± 190	95.9
9	1300	1170	2	270 ± 70	400 ± 140	91.0
10	1300	1170	4	270 ± 70	460 ± 160	93.8
11	1300	1170	8	270 ± 70	500± 190	96.2
12	1300	1170	24	270 ± 70	750 ± 260	98.5
13	1350	1170	4	450 ± 140	620± 190	97.3
14	1350	1170	8	450 ± 140	710 ± 240	98.5
15	1350	1170	24	450 ± 140	970 ± 250	99.0

relative density increased with increasing isothermal dwell at T_2. Interestingly, at all temperatures the sintering trajectories fell into a single line identicalwith the sintering trajectory of specimens sintered with the use of a standard one-stage regime. The only exception is the specimen, which achieved the relative density of 99 %TD at the 720 nm mean grain size after 24 h dwell at T_2=1170°C. The mean grain size of a standard way sintered specimen with comparable relative density (99.2 %TD) was 960 nm.

It therefore appears that in all reported cases the T_2 (1130, 1150 and 1170°C) was too high to facilitate efficient suppression of the grain growth. Further experiments at lower T_2 are therefore required to verify, or reject definitely the applicability of the two-stage sintering for densification of alumina without the final stage

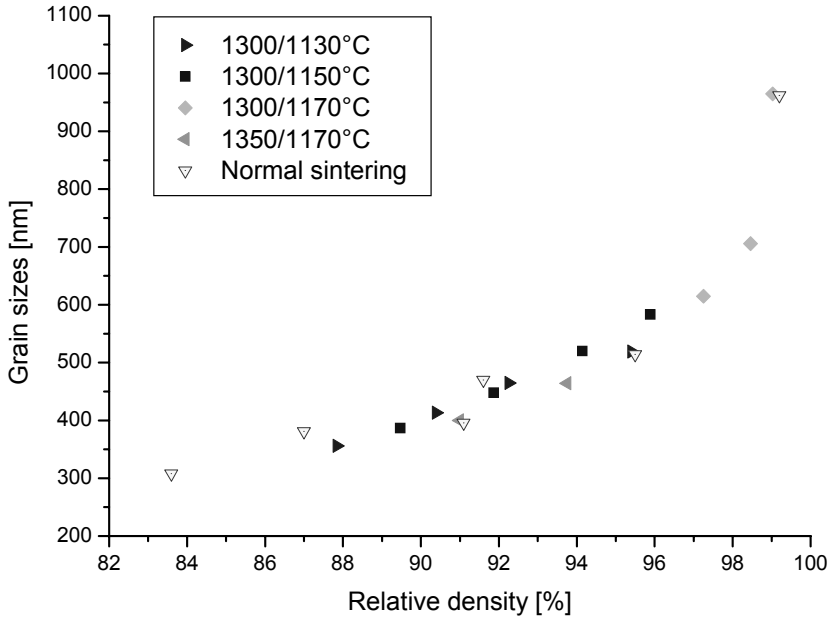
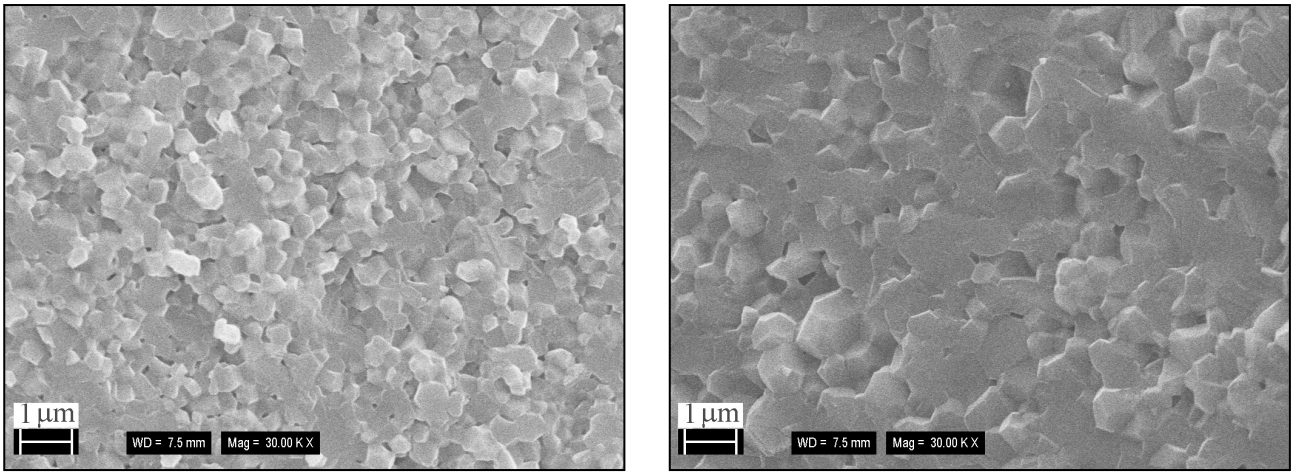


Figure 4. Sintering trajectories of polycrystalline alumina sintered in a standard way and by two-stage sintering



a) b)

Figure 5. Microstructures of samples sintered at T_1=1130°C, and then at T_2=1300°C/2 h (a), and T_1=1130°C, T_2=1300°C/24 h (b)

grain growth. Moreover, further investigations involving the two-stage sintering experiments with green bodies prepared by wet forming methods (pressure filtration) are under way to evaluate further the influence of green microstructure on the sintering trajectory**.**

Conclusions

Axial pressing of as-received ultra-fine alumina powder followed by CIP was selected as an optimum green body forming method. CIP reduces the porosity of green bodies significantly narrows the pore size distributions and shifts the mean values of pore necks diameters to lower values in comparison to axially pressed pellets. This is reflected also in better densification of CIP-ed specimens. The sintering at temperatures ≥ 1300°C without dwell eliminates the residual porosity to an extent, which gives a chance for complete densification without final stage grain growth during the second, low temperature sintering step. Temperature T_2 ≥ 1130°C results in further densification of alumina compacts, but the grain growth is not suppressed. Further experiments at lower temperatures T_2 are required to verify, or reject, the applicability of two-stage sintering for suppression of the final stage grain growth in polycrystalline alumina.

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