

Nitrogen pressure effects on non-isothermal alumina sintering

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Abstract

The densification of a fine grained pure alumina powder was studied during gas pressure sintering. Different nitrogen pressures were applied during non-isothermal sintering runs up to final temperatures between 1150 °C and 1650 °C. Densification, porosity and microstructures have been investigated. A fine alumina powder presents a densification delay during nitrogen pressure sintering mainly due to the gas pressure effect at the beginning of the sintering. The main results of this work concern the influence of nitrogen pressure on non-densifying mechanisms and microstructural evolution, which only depends on densification rate.

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1. Introduction

Effects of atmosphere on the sintering of alumina powder have been studied. In MgO-doped alumina, Coble¹ investigated the effects of various atmospheres on densification rate and limiting density. This study showed that the theoretical density is attainable under hydrogen or oxygen atmosphere. This is not possible when the atmosphere is air, nitrogen, helium or argon. Paek et al.² investigated sintering of MgO-doped alumina at 1600 °C for various times up to 8 h under 1 atm of N₂ or O₂. They reported the same densification rate during the intermediate stage of sintering and a densification increase during longer time experiments for materials sintered under O₂ compared to specimens sintered under N₂. This was attributed to the difference between gas solubilities in alumina. Whatever the atmosphere composition, up to the point of pore closure in alumina, sintering is not affected by the presence of any gas at atmospheric pressure. As soon as the pore closure occurs, gas is entrapped in pores and shrinkage is possible up to the point

where the pressure inside a pore P_f is $P_f = 2\gamma/R$, where γ is the surface tension and R is the effective radius of curvature at the pore surface. Sintering stops if the gas cannot diffuse away. Since nitrogen is assumed to present low solubility and diffusivity in alumina, sintering is limited by gas entrapped in pores. Kang et al.³ calculated the limiting density of ceramics containing entrapped gases and computed the rate of densification as a function of the initial size of isolated pores and the pressure of sintering atmosphere. A spherical pore of radius r_i in an atmosphere of an insoluble gas at pressure P_i can shrink to r_f until the internal gas pressure approaches P_f . By assuming that pore closure occurs when the density is 93% of the theoretical density, a pore with an initial radius of 3 μm containing an insoluble gas at pressure of 1 MPa (10 atm) can reach a final radius of 2.6 μm, which corresponds to a final density of approximately 96%. Since the pore size decreases with the powder size, the final density increases with finer powder.

In the present work, we studied the nitrogen pressure effect during the sintering of alumina. This paper investigates the evolution of densification and grain growth during gas pressure sintering of alumina under non-isothermal conditions.

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2. Experimental procedure

2.1. Green compacts

A spray-dried pure (99.98%) alumina powder (Baikowski Chimie, France) of 0.2 μm average particle size with 500 ppm of MgO as doping element was used. Green compacts were prepared by uniaxial pressing under 150 MPa in order to form pellets of 13 mm diameter. The green compact density was $52 \pm 1\%$ of the theoretical value (3.987 g/cm^3).

2.2. Sintering run

Densification was performed by gas pressure sintering (GPS) in a graphite resistance heated furnace (KCE FPW 100/150-2200-100-AS). The typical non-isothermal sintering run involves: (1) pressurization with N_2 gas to the desired pressure (between 0.1 and 6 MPa) at ambient temperature, (2) heating to the selected temperature (between 1150 °C and 1650 °C) at a rate of 5 °C/min, (3) depressurization of the system in 2 min as soon as the final temperature is reached and (4) cooling to room temperature at a rate of about 40 °C/min.

It must be underlined that samples are neither encapsulated nor introduced in an alumina powder bed. Green compacts are put in the furnace and they are only under hydrostatic gas pressure, without any external mechanical force.

2.3. Characterizations

Final relative density, and open and closed porosities were measured by using the water-immersion method. The pore size distribution of gas pressure sintered materials was obtained using a mercury intrusion porosimeter (Porosimeter 2000, Carlo Erba Strumentazione, Italy) and the specific surface area of specimens was evaluated by the Brunauer-Emmett-Teller (BET) method (ASAP 2000, Micromeritics, USA). Microstructures were observed by field emission scanning electron microscopy (Model 6500F, JEOL, Japan) on polished surfaces thermally etched 30 min at $T = T_{\text{sintering}} - 50 \text{ }^\circ\text{C}$. Average grain sizes were obtained by the intercept method on micrographs and statistical diameter distributions were determined by use of image analyser software (Analysis).

3. Results

3.1. Nitrogen pressure effects on the densification of alumina

Fig. 1 represents the relative density of samples sintered under different nitrogen pressures. Two behaviours are distinguishable: the evolution of the relative density of materials sintered under atmospheric pressure is different from the

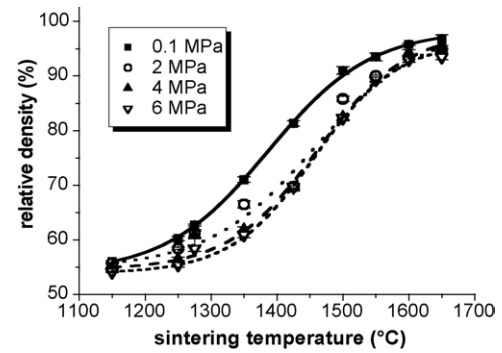


Fig. 1. Relative density of materials sintered under different nitrogen pressures versus sintering temperature.

evolution of the relative density of samples sintered under different nitrogen pressures. It may be noted that the final density of Al_2O_3 specimens sintered under 2, 4 or 6 MPa is almost the same.

At 1425 °C, compared to result obtained under atmospheric pressure, the relative density is reduced from 81% to 70% during a gas pressure sintering. Moreover, this difference in relative densities is significantly reduced at 1650 °C. Thus, the final density is 96.6% theoretical density under atmospheric pressure, whereas it is: 94.8%, 94.6% and 94.5%, respectively under nitrogen pressure of 2, 4 and 6 MPa. The results show that pressure effects on densification are more important during initial and intermediate stages of sintering than at the final stage of sintering. The densification delay is reduced for high sintering temperatures.

3.2. Effects on porosity

Fig. 2 shows closed porosity for samples sintered under different nitrogen pressures. After the beginning of pore closure, which occurs at 1425 °C for pressureless sintered materials and at 1500 °C for materials sintered under nitrogen pressure, all the curves present the same slope for any pressure. This same behaviour suggests that pore closure takes place with the same rate during pressureless sintering than during sintering under higher nitrogen pressures. The

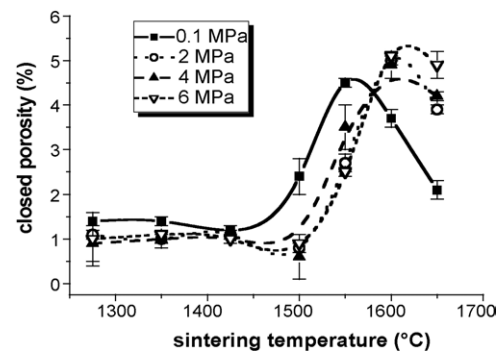


Fig. 2. Closed porosity of materials sintered under different nitrogen pressures versus sintering temperature.

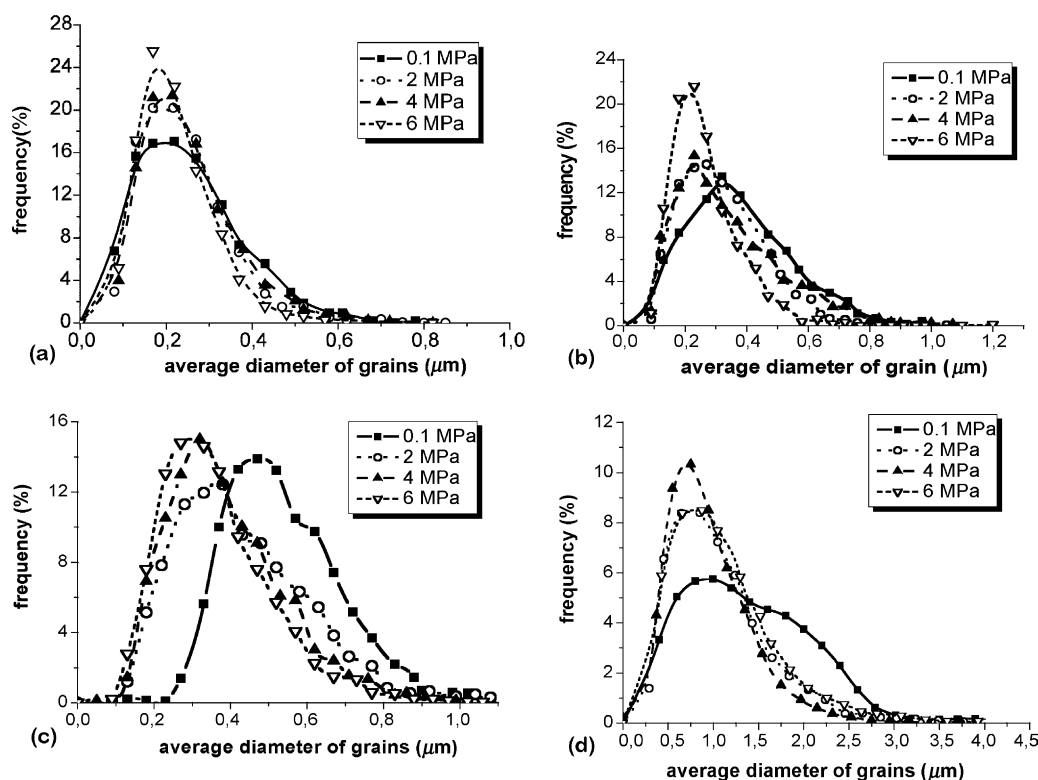


Fig. 3. (a) Average grain diameter distribution for materials sintered at 1350 °C, (b) Average grain diameter distribution for materials sintered at 1425 °C, (c) Average grain diameter distribution for materials sintered at 1500 °C, (d) Average grain diameter distribution for materials sintered at 1650 °C.

temperature corresponding to the maximum of closed porosity rate is shifted from 1550 °C for pressureless sintered materials to 1625 °C for materials sintered under nitrogen pressure. Because of the lack of experimental data on pore resorption, the closed pore elimination cannot be discussed. We can just observe that for materials sintered at 1650 °C, the final closed porosity is 2.1% for pressureless sintered materials and it is: 3.9%, 4.2% and 4.9% respectively under 2, 4 and 6 MPa.

3.3. Effects on microstructure

Statistical average diameter distributions of grains determined by use of micrograph analysis are represented in Fig. 3 and the average grain sizes are summarized in Table 1.

These figures obtained on samples sintered at 1350 °C, 1425 °C, 1500 °C and 1650 °C under different nitrogen pressures show that, for a given temperature, gas pressure has an effect on the average diameter of grains. Fig. 3(a) and

Fig. 3(b), which represent distributions obtained on materials sintered at 1350 °C and 1425 °C, point up a decrease of the width distribution with increasing pressure. Moreover, up to 1425 °C, the results comparison (Table 1) of the different pressures shows that a nitrogen pressure is able to reduce the average grain size between 18% and 30% compared to results obtained for nitrogen atmospheric pressure. At 1500 °C (Fig. 3(c)), microstructures do not present the same average diameter distributions as those observed at below temperatures. Indeed, whatever the pressure applied (2, 4 or 6 MPa), the curves have the same shape compared to the curved obtained for materials sintered under atmospheric pressure and the width distribution is the same for any pressure between 2 MPa and 6 MPa. Pressure only changes the modulus of the average grain size distributions. An increase in the pressure range causes a decrease in the average diameter of grains of about 20–25% (Table 1). For the final stage of sintering, Fig. 3(d) shows a reduction of the average grain diameter of materials sintered under pressure compared to materials pressureless sintered at 1650 °C. This average grain size reduction increases up to nearly 50% when sintering occurs under nitrogen pressure, as observed on Fig. 4(a) and (b). It appears that, for a given temperature, a nitrogen pressure is able to limit grain growth, since the frequency of grains with an average grain size between 1.7 μm and 2.7 μm is less important for gas pressure sintered materials than for pressureless sintered ones.

Table 1
Average diameter of grains (μm) for materials sintered in different temperature and pressure conditions

	1350 °C	1425 °C	1500 °C	1650 °C
0.1 MPa	0.28	0.32	0.44	1.87
2 MPa	0.23	0.23	0.35	0.91
4 MPa	0.21	0.21	0.34	0.77
6 MPa	0.19	0.21	0.32	1.04

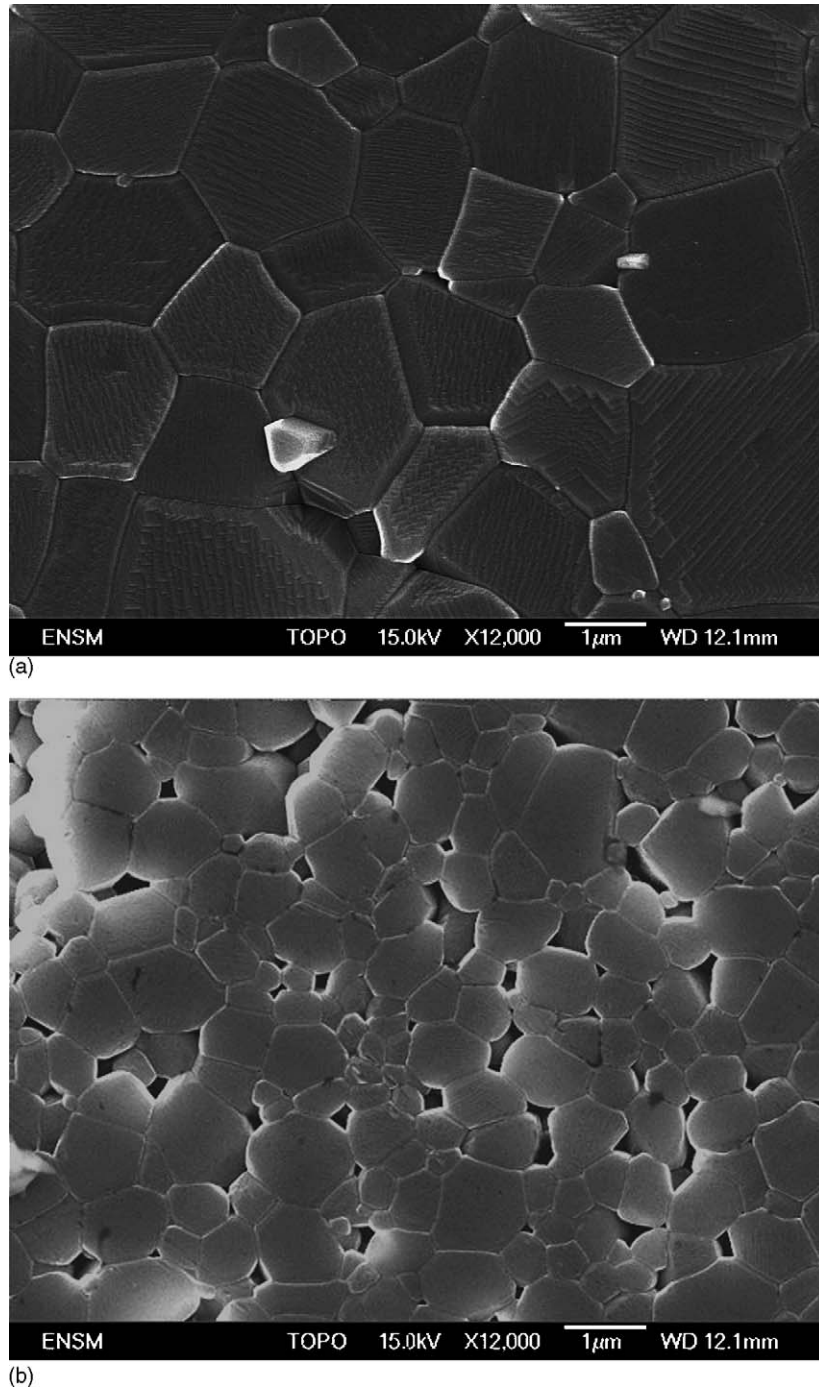


Fig. 4. Microstructure of alumina sample sintered up to 1650 °C (a) under 0.1 MPa (relative density: $d = 96.6 \pm 1.0\%$), (b) under 6 MPa (relative density: $d = 94.5 \pm 0.5\%$).

4. Discussion

Results concerning densification of a fine alumina revealed that the pressure effect during a non-isothermal cycle is mainly observable during initial and intermediate stages of sintering. Thus, other measurements have been performed to characterize and illustrate the nitrogen pressure influence on the microstructure evolution all along a non-isothermal sintering run.

4.1. Initial stage of sintering

In order to observe pressure effects on neck consolidation and growth during the initial and the intermediate stage of sintering, specific surface area measurements have been realized on materials sintered at temperatures in the range of 1150 °C and 1550 °C. Fig. 5 represents the evolution of the specific surface area as a function of the sintering temperature.

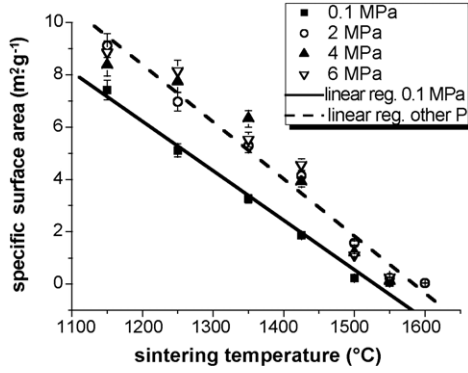


Fig. 5. Specific surface area as function of sintering temperature.

This figure shows a linear decrease of the specific surface area in the range of temperatures considered for any pressure applied. Experimental results obtained on materials sintered under 2 MPa, 4 MPa and 6 MPa belong to the same line, which is different from the line that connects experimental results of materials pressureless sintered. These lines tend to show results of convergence for the highest sintering temperatures.

Using geometrical considerations, it is possible to calculate the neck radius between two spherical grains during neck formation without shrinkage in the earlier stages of sintering (Fig. 6).

The formation of a neck causes the lost of two spherical portions, so the surface change could be written:

$$\Delta S = \frac{\pi^2}{r} x^3 - 2\pi(h^2 + x^2) \quad (1)$$

where r is the grain radius, x the neck radius, α the neck curvature and h one-half of the neck thickness. By assuming that

$$h \approx \alpha = \frac{x^2}{2r} \quad (2)$$

ΔS becomes:

$$\Delta S = -\frac{\pi}{2r^2} x^4 - \frac{\pi^2}{r} x^3 - 2\pi x^2 \quad (3)$$

The coordination number c which represents the number of interparticle contacts per sphere is introduced in the relative surface change and we obtain:

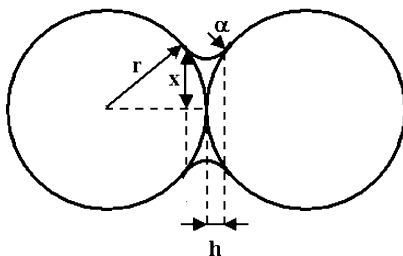


Fig. 6. The geometry of the neck between two spherical grains.

$$\frac{\Delta S}{S_0} = \left(\frac{c}{8}\right) \left(-\frac{1}{2r^4} x^4 + \frac{\pi}{r^3} x^3 - \frac{2}{r^2} x^2\right) \quad (4)$$

Prochazka and Coble⁴ calculated the coordination number as a function of the relative density for a random packing of particles. The value of the coordination number needed in (4) is taken from their study. The neck radius values are determined to the point when the reduction of specific surface is less than 50% in order to consider that the materials are still in the beginning of the sintering. The grain radius values are evaluated by the intercept method on micrographs for materials sintered at 1350 °C and they are taken as equal to 0.1 μm for the green compact and for materials sintered at 1150 °C and 1250 °C.

Fig. 7 represents the neck radius evolution of materials sintered under different temperature and pressure conditions. On the one hand, this figure shows that, for a given temperature, a nitrogen pressure higher than atmospheric pressure is able to reduce the neck radius. On the other hand, the slope of the curve corresponding to materials sintered under 0.1 MPa is different from gas pressure sintered materials one. The temperature of neck formation beginning is evaluated by a linear extrapolation of experimental values. It shows that this phenomenon occurs at 990 °C for pressureless sintered materials and at 1060 °C for materials sintered under different nitrogen pressures. For a given temperature increase, the corresponding neck radius increase is reduced under pressure compared to the one obtained under atmospheric pressure. At the end of the initial stage of sintering, the neck radii are smaller for materials sintered under pressure. This finer neck microstructure is maintained up to higher temperature than for pressureless sintered materials.

4.2. Intermediate and final stages of sintering

In order to understand the influence of a gas pressure sintering on a fine alumina, the evolution of pore closure rate versus the relative density is plotted in Fig. 8. The points represented on this graph are obtained by differentiation of the curves on the Fig. 2. We can distinguish three domains.

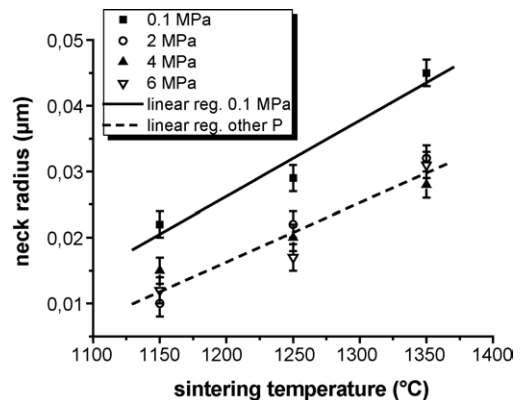


Fig. 7. Neck radius as a function of sintering temperature.

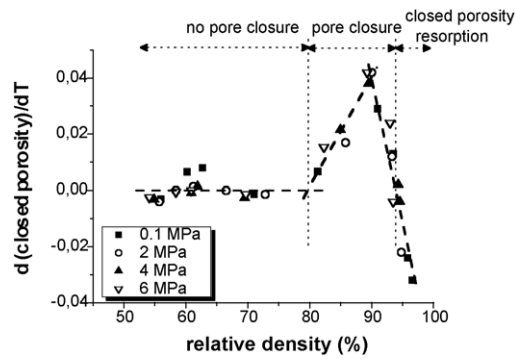


Fig. 8. Pore closure rate as a function of the relative density.

For a relative density between 50% and 80%, the pore closure does not occur whatever applied pressure. As soon as the densification reaches a value between 80% and 93%, the closed porosity rate increases and shows an inflection point close to a relative density of 90%, whatever the nitrogen pressure applied. This most important point underlines that the pore closure is independent of the nitrogen pressure applied. Taking into account the low number of experimental results, we cannot conclude anything concerning the closed porosity resorption which takes place for higher densities.

Anyway, this figure versus the relative density gives more information than a representation as a function of the temperature. It indicates that the pore closure occurs at the same rate for a given relative density whatever the pressure applied. It's known that the grain boundary diffusion is the main densification mechanism during the intermediate stage of sintering⁵. Under pressure, the neck growth delay implies a shifting to higher temperatures for the beginning of the intermediate stage of sintering. But as soon as the grain boundaries number is sufficient, the mechanism of grain boundary diffusion is activated and then, the presence of nitrogen under pressure doesn't influence this mechanism.

4.3. Pressure effects on the microstructure evolution—representation as a function of the relative density

At a given temperature of sintering, we observed that the materials are not in the same state of densification if the sintering run is performed under atmospheric pressure or not. Thus, in order to compare gas pressure effect on the materials microstructures, average grain sizes are neither represented as a function of the sintering temperature nor as a function of the applied nitrogen pressure, but versus relative density as it has already been proposed by Kanters et al.⁶

Fig. 9 represents average grain diameter of alumina specimens sintered under different nitrogen pressures versus corresponding final relative densities. On the one hand, this figure shows that grain growth does not occur up to 80% relative density. On the other hand, an abrupt increase in grain growth rate is observable over 85% relative density for any

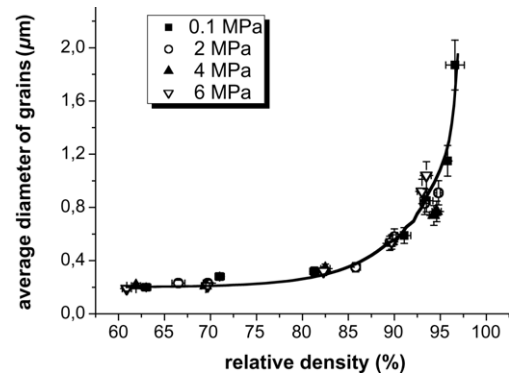


Fig. 9. Average grain size as a function of the relative density.

pressure. The most important result is the same exponential grain growth rate observed during this study. Indeed, for any value of the applied pressure, experimental points belong to the same exponential law. This representation, average grain size versus relative density, indicates that a given relative density is linked to a grain size whatever applied pressure (between 0.1 MPa and 6 MPa).

This phenomenon is also observable during the initial stage of sintering. Indeed, on Fig. 7, the slope corresponding to materials sintered under pressure (between 2 MPa and 6 MPa) is lower than the pressureless sintered materials one. Thus, materials sintered under pressure need higher sintering temperature than pressureless sintered ones to reach this given relative density corresponding to a given microstructure.

5. Conclusions

On the one hand, this study on the nitrogen pressure effects on non-isothermal sintering of a fine grained alumina pointed up a densification delay due to the lower neck consolidation rate under pressure.

On the other hand, this study underlined that, up to a relative density of 93%, the activation of densification mechanisms are not affected by the presence of nitrogen under pressure. During the densifying stage, the densification takes place with the same rate as soon as a required microstructure is reached, which occurs at higher temperature under pressure. Indeed, the representation of pore closure rate and of the average grain size as a function of the corresponding relative density did not show any difference for any pressure applied.

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