Deagglomeration of a nanocrystalline transition alumina performed using different techniques was first demonstrated to be active in the achievement of a better powder compaction ability under uniaxial pressing and consequently in the development of a highly dense and homogeneous microstructure during pressureless sintering. A major effect, however, was associated to the heating rate chosen during the densification cycle. In fact, the influence of different heating rates (10°C/min or 1°C/min) on phase and microstructural evolution during sintering was investigated in depth on the above best green bodies. A low-rate thermal cycle leads to a significant reduction of the $\alpha$-$\text{Al}_2\text{O}_3$ crystallization temperature and promotes a more effective particle rearrangement during phase transformation. As a consequence, in the low-rate treated material, it was possible to avoid the development of a vermicular structure as usually expected during the densification of a transition alumina and to yield a more homogenously fired microstructure.

Introduction

Recent studies on nanostructured ceramics have highlighted the difficulty in producing fully dense materials without relevant grain growth, particularly in the case of transition nanocrystalline aluminas, currently synthesized by a variety of methods, due to the crystallization of the $\alpha$ phase during sintering. In fact, this transformation from some metastable phases (i.e., $\gamma$ and $\theta$ phase) occurs by a nucleation and growth mechanism. It is accompanied by a volume reduction of about 10.2% because of the higher density of the $\alpha$ phase and by a change in grain morphology.

A vermicular morphology of transformed $\alpha$-$\text{Al}_2\text{O}_3$ is produced at a high temperature (about 1150–1200°C) by a finger growth of $\alpha$-grains into the $\theta$-$\text{Al}_2\text{O}_3$ matrix,
entrap a network of large, elongated pores. As a consequence, the final stages of transition alumina sintering require a very high temperature to achieve full densification, thus leading to a significant grain growth.

Therefore, to lower the sintering temperature, the development of a vermicular structure must be prevented and some strategies have already been proposed in the literature to reduce the crystallization temperature and enhance the densification, such as the application of high compaction pressure, high-energy milling of primary particles, or a combination of high-temperature sintering with hot forging.

Moreover, a variety of seeding procedures have been successfully used to impact the transformation kinetics and to lower the α-phase nucleation temperature.

Finally, the production of homogeneous, defect-free green bodies via optimized and strictly controlled forming processes has been shown to be effective in promoting phase transformation and thus lowering the sintering temperature.

In this work, a commercial, transition nanoalumina powder was uniaxially pressed before and after dispersion in pure water and then pressureless sintered to determine the effect of the dispersion step on the compaction behavior and related green density as well as on the final microstructure. On the dispersed samples, the crucial role of the heating rate in the phase transformation and microstructural evolution during sintering was also pointed out.

Experimental Procedure

A commercial, nanocrystalline transition alumina powder (NanoTek®, supplied by Nanophase Technology, Romeoville, IL), prepared by Physical vapor synthesis (PVS), was used as the starting material. The powder is characterized by an average particle size of 47 nm, a specific surface area of 35 m²/g, and a true density of 3.49 g/cm³, as declared by the supplier. The other physico-chemical properties of this powder have already been listed in a previous paper.

The thermal behavior of the as-received powder was recorded by simultaneous DSC-TG analysis (Netzsch STA 409, Selb, Germany) performed up to 1400°C in static air at a heating rate of 10°C/min. In particular, DSC analysis allows to detect the transition due to the phase transformation from θ-Al₂O₃ to α-Al₂O₃, as explained better in a previous paper. The phase identification was carried out by X-ray diffraction (XRD, Philips PW 1710, Eindhoven, The Netherlands) in the range 5–70° 2θ, with a step size of 0.05° 2θ and an acquisition time per step of 5 s.

NanoTek® alumina slurries (solid content of 33 wt%) were prepared by dispersion in pure distilled water without any dispersant and degglomerated under magnetic stirring for several hours (up to 120 h) or even by ball milling using α-alumina spheres (2 mm in diameter). Ball milling was performed using a powder to sphere weight ratio of 1:10 for 2.5 h at an angular velocity of 130 rpm, selected on the basis of literature data.

The particle size distribution of the slurries as a function of the dispersion time was followed by granulometric analyses (laser particle size analyzer Fritsch model Analysette 22 Compact, Idar-Oberstein, Germany), before a drying step in an oven at 105°C.

Green bars were then prepared by uniaxial pressing at 300 MPa; their density was calculated starting from weight and geometrical measurements; and their sintering behavior was investigated by dilatometric analysis (Netzsch 402E) performed under continuous heating at 10°C/min up to 1500°C with a soaking step of 3 h at the maximum temperature and cooling down to room temperature (RT) at 20°C/min.

As-received NanoTek® samples were also pressed and sintered as a reference.

The sintered density was measured by the Archimedes method in distilled water. A density value was also calculated by exploiting green density, final weight measurements, and shrinkage data.

The fired microstructures were characterized by SEM (Hitachi S2300, Tokyo, Japan) performed on fractured, untreated surfaces.

On a selected material, various sintering cycles were tested by varying the maximum sintering temperature in the range 1450–1500°C, the soaking time at the maximum temperature from 1 to 3 h as well as the heating rate from 10°C/min to 1°C/min.

The phase composition as well as the microstructural evolution as a function of temperature at each investigated heating rate were studied on samples obtained by interrupting the densification runs when a select linear shrinkage or temperature was reached.

The samples, rapidly cooled to RT (at 20°C/min), were then characterized via XRD and SEM.
Results and Discussions

NanoTek® powder is a mixture of transition aluminas, \(\delta\)-Al\(_2\)O\(_3\) and \(\gamma\)-Al\(_2\)O\(_3\), as declared by the supplier.\(^{24}\) However, also the \(\delta^*\)-Al\(_2\)O\(_3\) phase was detected by XRD performed on the as-received material, probably as a consequence of the industrial synthesis procedure.\(^{26}\) The DSC-TG curves of the powder are reported in Fig. 1. The exothermal signal could be attributed to the crystallization of the \(\alpha\)-Al\(_2\)O\(_3\) from the transition phases, as stated by the literature.\(^{21,27}\)

In the starting powder, the agglomerate sizes corresponding to 10%, 50%, and 90% of the cumulative volume distribution are about 1.7, 5.5, and 10.4 \(\mu\)m, respectively.

The cumulative size distributions by volume of the samples dispersed under the already detailed conditions are shown in Fig. 2 and compared with the as-received material, showing a reduction of the above agglomerate sizes by about one order of magnitude.

To reach a similar agglomerate size distribution, 120 h of magnetic stirring were required, whereas just 2.5 h were needed for the ball-milled suspensions.

Pollution of the ball-milled powders due to the alumina milling media was not detectable by XRD (Fig. 3). In the inset of Fig. 3, a detail of the pattern referred to the range 40–46° 2\(\theta\) (step size of 0.02° 2\(\theta\), time per step of 4 s) is reported, in which the mean \(\alpha\)-alumina crystallographic peak (113) should be present (in the position indicated by an arrow).

The green densities of the uniaxially pressed bars are presented in Table I. A relevant green density improvement (of about 13–18%) was obtained using dispersed powders; ball milling has been shown to be the more effective process.

The sintering behaviors up to 1500°C for 3 h of both dispersed samples are compared with that of the as-received material in Fig. 4.

![Fig. 1. TG (dotted line) and DSC (solid line) curves of the as-received NanoTek® powder.](image1.png)

![Fig. 2. Cumulative size distribution by volume of the as-received NanoTek® (solid line without symbols) and of the magnetically stirred (squares) or ball-milled (triangles) powder dispersions.](image2.png)

![Fig. 3. X-ray diffraction pattern of NanoTek® powder after 2.5 h of ball milling.](image3.png)
All the samples presented almost the same onset temperature of about 1070 °C. In addition, a two-step linear shrinkage was recorded for all the samples, as commonly observed for transition aluminas. In agreement with previous studies, the first step from the onset shrinkage temperature to about 1200 °C is associated with rearrangement phenomena of the transition alumina particles and their transformation to the α phase, whereas the latter from about 1200 °C to 1500 °C is mainly associated with α-alumina densification by sintering.

From the derivative of the densification curves, the temperature associated with the maximum transformation rate during the first step was almost the same (about 1120 °C) for all the samples. A certain disagreement between this temperature and the value determined by DSC can be reasonably attributed to the nature of the samples, powders for DSC, and pressed powders for dilatometry. In fact, when thermal data were collected on pressed samples, the detected transformation temperature strongly approached the dilatometric value of this work.

In addition, the above statements strongly support the hypothesis that alumina pollution from the milling media, if present, was so limited in the milled sample as not to induce any observable modification of onset shrinkage as well as transformation temperature.

In any case, some differences can be pointed out if the as-received and dispersed samples are compared; during the first step, the magnetically stirred material recovered a slightly higher linear shrinkage. During the second step, both the dispersed samples—in particular, the ball-milled one—shrank considerably more than the as-received powder.

In addition, the total linear shrinkage was considerably higher for the dispersed materials as compared with the as-received powder, and once again the ball-milled material presented the highest value (94.8%). The fired densities are presented in Table I and expressed as percentage of the theoretical value (3.987 g/cm³). The calculated values are in good agreement with those measured by the Archimedes method.

Figure 5 presents the curves of linear shrinkage versus soaking time at 1500 °C for all the samples: a

<table>
<thead>
<tr>
<th>Table I. Green Density (g/cm³), Final density (% theoretical value) and Total Linear Shrinkage (ΔL/L₀)₁₀ for the As-Received and Dispersed Samples</th>
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<tbody>
<tr>
<td>Green density</td>
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<tr>
<td>(g/cm³)</td>
</tr>
<tr>
<td>---------------------------------------------------------------</td>
</tr>
<tr>
<td>As-received</td>
</tr>
<tr>
<td>Magnetically stirred</td>
</tr>
<tr>
<td>Ball milled</td>
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</table>

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**Fig. 4.** Dilatometric curves up to 1500 °C for 3 h of as-received NanoTek® (solid line without symbols) and of magnetically stirred (squares) or ball-milled (triangles) samples.

**Fig. 5.** Linear shrinkage versus soaking time at 1500 °C for as-received NanoTek® (solid line without symbols) and for magnetically stirred (squares) or ball-milled (triangles) samples.
continuous shrinkage as a function of time was recorded for the as-received material. On the contrary, the magnetically stirred and the ball-milled samples almost completely recovered their linear shrinkage after 1 h at 1500 °C. This feature was exploited in the subsequent test to optimize the sintering cycle.

Figure 6 shows the SEM images of the fired materials. The vermicular microstructure of the sample processed from the as-received NanoTek® powder (Fig. 6a) is made of fine-grained alumina particles (about 300 nm in size) entrapping a diffuse residual porosity. The microstructure of the magnetically stirred material (Fig. 6b) is less porous, but, in spite of its better densification, the ultrafine primary particle size was still partially retained, yielding round-shaped alumina grains having a mean size of about 450 nm.

Highly dense microstructures were finally observed in ball-milled materials (Fig. 6c); the densification was, however, accompanied by a significant grain growth. Microstructures consist of well-facetted alumina grains about 2 μm in size, with a limited residual porosity mostly located in intragranular positions.

From the above results, the ball-milled powder was selected and exploited for further investigation, during which various sintering parameters were modified to achieve high densification without inducing relevant grain growth.

During the first attempt, sintering was performed by heating up to 1500 °C (heating and cooling rate of 10 °C/min), with 1 h of soaking at the maximum temperature, as stated on the basis of the previous test (see Fig. 5). In spite of the reduced soaking time, a high final density (94.3%) was obtained again. The related fired microstructure, presented in Fig. 7a, is highly homogeneous and fully dense. A slight refinement of the alumina grains was observed for comparison with the sample fired at 1500 °C for 3 h (see Fig. 6c).

Another sintering cycle was carried out up to 1450 °C, followed by an isothermal step for 3 h at the maximum temperature. In this case, a slight decrease of the final density (93% of the theoretical value) as well as a grain size refinement (about 1.5 μm; Fig. 7b) were obtained.

Because the lowering of the maximum sintering temperature did not allow to obtain an ultrafine, fully dense microstructure, it was decided to investigate the role of the heating rate during sintering by performing dilatometric measurements at a lower heating rate (1 °C/min). This parameter was changed only in the

Fig. 6. SEM micrographs of the as-received NanoTek® (a), of the magnetically stirred sample (b), and of the ball-milled material (c), sintered up to 1500 °C for 3 h.
temperature range of 700–1500°C, in which the main phenomena involved in thermal treatments occur. The dilatometric and derivative curves performed at 1°C/min (dashed line) and 10°C/min (solid line) up to 1500°C for 3 h are compared in Fig. 8.

The heating rate strongly affects the sintering behavior: the curve of the low-rate heated material is clearly displaced to lower temperatures.

In fact, the onset shrinkage temperature is about 1070°C and 1010°C for the samples heated at 10 and 1°C/min, respectively. In addition, the low-rate treated sample was characterized by a first densification step in the range 1010–1090°C and a second in the range 1090–1500°C. The inflection points, identified by the derivative curves, are related to the maximum transformation rate temperature and they are located at about 1120°C and 1060°C for the fast- and low-rate-fired materials, respectively. The derivative curve of the low-rate-sintered material (dashed line) also shows a second, slight inflection point, located at about 1410°C, associated with the maximum sintering rate of the α-phase, not detected on the other curve.

These results are in good agreement with previous investigations, in which the direct influence of the heating rate on the first transformation/densification step of transition aluminas and on the subsequent sintering was clearly stated. Legros et al.28 reported that the enhanced densification that occurred when a low heating rate is applied is associated with a more effective particle rearrangement involved during the phase transformation of transition aluminas and related change in density. In the present study, however, the difference in linear shrinkage was only observed during the heating step of the second densification stage, from about 1135°C to 1500°C (Fig. 8). In fact, during this step, the low-rate-fired material presents an enhanced densification but a negligible shrinkage during the isothermal step. Therefore, the fast-fired material was able to recover the delayed densification during the isothermal soak, reaching a final density very close to that of the low-fired sample.

To follow the microstructural and phase evolution as a function of temperature and heating rate, new
sintering cycles performed at 1° and 10°/C/min were interrupted at fixed temperatures corresponding to selected linear shrinkages.

Namely, the runs at 10°/C/min were carried out up to 1000°C, 1085°C, 1118°C, 1135°C, 1300°C, 1400°C, and 1500°C (points A, B, C, D, E, F, and G, respectively, as shown in Fig. 9) while the runs at 1°C/min were interrupted at 1000°C, 1060°C, 1085°C, 1135°C, 1300°C, 1400°C, and 1500°C (points A', B', C', D', E', F', and G', respectively, in the same figure).

These points were chosen in order to have a couple of samples comparable in terms of both reached temperature and shrinkage: see for instance the four samples E, E', F, and F', in which a comparison can be performed between E and E' or F and F' treated up to the same temperature, but, at the same time, E' and F can be also compared because they showed a similar shrinkage. In other cases, however, the characteristic temperatures of each material were chosen for interrupting the run: see for instance 1118° and 1060°C for samples C and C', respectively, corresponding to the inflection points of the first densification step for the fast-rate- and low-rate-heated materials, respectively.

The samples rapidly cooled at RT and were then subjected to XRD analysis. In Fig. 10, the XRD patterns of the samples fired at 10°/C/min (a) up to 1000°C, 1085°C, and 1135°C and at 1°C/min (b) up to 1000°C and 1085°C have been reported. Strongly different crystallization paths were detected as a function of the heating rate. After calcination at 1000°C, the material heated at 10°C/min was just a mixture of transition aluminas while the low-rate-fired sample also contained traces of α-Al2O3 (pattern I in Figs. 10a and b). The latter yielded a well-crystallized α phase after calcination at 1085°C while in the fast-heated sample only traces of α phase appeared at the same temperature (pattern II). Finally, after calcination at 1135°C, only pure α-Al2O3 was detected in this material (pattern III).

The phase composition as well as the recovered shrinkage of the low-rate-fired material calcined at
1000°C (point A' in Fig. 9) are quite similar to those of the sample fast heated at 1085°C (point B). The fast- and low-rate-heated materials after calcination at 1135°C (point D) and 1085°C (point B'), respectively, behaved similarly.

To strengthen these data, the XRD patterns of the samples calcined at 1°C/min at 1060°C (point C) and at 10°C/min at 1118°C (point C) have been compared in Fig. 11, because they also attained similar shrinkage. Once again, a comparable phase composition, made of a mixture of transition and α aluminas, was presented by both materials. The 10°C/min heated material just presented a slightly higher intensity of α-Al2O3 peaks.

The microstructural development of the low- and fast-fired samples was followed by SEM observations. At treatment temperatures <1135°C due to the very low grain size and the high amount of residual porosity, it is not easy to point out a significant difference in microstructure between the two differently heated materials, in spite of their different phase evolution, clearly stated by the above-discussed XRD data.

At 1135°C, samples D and D' start to differ in microstructure (Fig. 12) even if they have reached the same linear shrinkage.

The fast-rate-heated material D (Fig. 12a) presents a heterogeneous microstructure, consisting of agglomerates of ultrafine alumina particles of about 150–200 nm, entrapping large porous areas. On the contrary, in sample D' (Fig. 12b), a highly compact and homogenous structure, made of well-packed particles, was observed, and probably due to this better packing, more significant grain growth occurred (about 400 nm as mean size).

The microstructural evolution observed in this study is similar to that stated in a previous paper, in which, using materials having green densities of 2.16 g/cm³ (which is close to the values in the present paper), the difference was a consequence of the green-forming process. However, in this case, an easier and more effective particle rearrangement during transformation phenomena seems to be promoted by applying a lower heating rate, independent of the green packing efficiency, which is the same for both materials. In any case, the microstructural differences are comparable, as underlined by the insets in Fig. 12, which simulate the expected microstructures from differently packed greens, but that may also be successfully associated with the samples developed in this study.
The discrepancy in particle rearrangement assumes a crucial role in the following sintering step leading to a more and more diverging microstructural development. The loosely packed material D develops a vermicular structure as observed at 1300°C (sample E, Fig. 13a), whereas the low-rate-heated material E' is still made of almost equiaxial grains homogeneously packed just grown in size, entrapping very small pores (Fig. 13b). This trend is also confirmed at higher temperatures, stated as an example, in Fig. 14, in which the microstructures of samples F (a) and F' (b) sintered at 1400°C are compared.

Considering the low-rate treatment, it should be pointed out that the main phenomena related to the transition phase were almost complete at 1085°C (B'). In fact, at this temperature, almost pure α-Al₂O₃, as shown by XRD analysis (see Fig. 11, curve II), was present, showing a homogeneously packed microstructure made of particles of about 200 nm. Thus, during firing up to 1135°C (D') grain growth occurred, yielding the microstructure already reported in Fig. 12b.

These observations are also supported by the density measurements (Table II).

Therefore, this study has allowed to elucidate well the influence of the heating rate during phase transformation and conventional sintering of effectively dispersed, transition alumina nanopowders.

These results represent well-grounded basic knowledge for further investigations, in which less conventional sintering routes, such as master-rate-controlled, and two-step sintering could also be exploited. These papers have demonstrated the effectiveness of newly designed thermal cycles in the control of grain growth in well-densified materials. Most studies are, however,
Table II. Densities of Materials (% of the Theoretical Value) Fired in the Range 1300–1500 °C (in Parentheses, Sample Designation)

<table>
<thead>
<tr>
<th>Sintering temperature (°C)</th>
<th>Final density (% Theoretical value) heating rate of 1 °C/min</th>
<th>Final density (% Theoretical value) heating rate of 10 °C/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1300</td>
<td>75.1 (E)</td>
<td>72.6 (E)</td>
</tr>
<tr>
<td>1400</td>
<td>84.1 (F)</td>
<td>78.4 (F)</td>
</tr>
<tr>
<td>1500</td>
<td>93.1 (G)</td>
<td>86.4 (G)</td>
</tr>
</tbody>
</table>

devoted to compositions that do not undergo phase transition during the thermal treatment, such as α-alumina-, ytria-, ZrO2- and α-alumina-based composites.29,32 In fact, if reference is made to transition aluminas, the above innovative densification routes have not been applied systematically, and only a few data are present in the literature (see for instance Bowen et al.34). In this work,34 a transition nano-alumina was subjected to a two-step sintering cycle, following the approach suggested by Chen and Wang.32 A very fine, fired microstructure (about 600 nm as mean grain size) was obtained and compared with a conventionally sintered one, in which a heterogeneous microstructure characterized by a mean grain size of more than 1 μm was attained. However, a detectable pollution by ZrO2 milling media was observed in the submicronic material.

The materials obtained in the present work were able to attain an intermediate state, such as a homogeneous and unpolluted microstructure, but constituted of grains about 1.5 μm in size, just by exploiting basic process parameters like dispersion and control of the heating rate.

Therefore, an enhanced refinement of the microstructures could be pursued by two-step sintering procedures, even approaching the different solutions for thermal cycles proposed in the literature, for instance that followed by Chen and Wang32 and Bowen et al.34 or the new one recently exploited by Gadow and Kern.35

Conclusions

From the above experimental results, the following conclusions can be drawn:

- The dispersion in a liquid medium before dry uniaxial pressing is effective in improving green density and sinterability with respect to the as-received, nanocrystalline transition alumina powder. Ball-milled samples behaved better than magnetically stirred materials.
- Under fixed dispersion conditions, the heating rate was shown to play a major role during the two-step shrinkage path of the transition alumina, associated with a different phase evolution in the first step and a different microstructural development in the second one.
- The longer duration of the heating step in the temperature range of 1000–1135 °C for the low-rate-heated sample promoted a more effective particle rearrangement during phase transformation from transition to α-alumina. Consequently, a homogeneous and well-packed microstructure developed during densification in the high-temperature regime.
- On the contrary, a faster heating rate did not allow such improvement of the packing density and homogenization of the microstructure during phase transformation, inducing the appearance of a vermicular structure and therefore leading to a lower sinterability.

References


