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Article

Water-Assisted Cold Sintering of Alumina Ceramics in SPS Conditions

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Abstract: A developing energy-saving approach of cold sintering in a pure aqueous medium was applied to the preparation of α -Al₂O₃ ceramics and performed on spark plasma sintering equipment. The initial γ -Al(OH)₃ and γ -AlOOH powders and the cold-sintered ceramics were studied by X-ray diffraction analysis, infrared spectroscopy, thermal analysis, and scanning electron microscopy to reveal the chemical and structural transformations they experienced during the cold sintering. At 450°C and 70 MPa, initial γ -AlOOH transformed into a fragile α -Al₂O₃ material. Porous α -Al₂O₃ ceramics with about 60% porosity was obtained after cold sintering of γ -Al(OH)₃ in the same conditions combined with subsequent annealing at 1250°C for 3 h. The role of water molecules in the studied processes was considered as the enhancement of structural mobility in the cold-sintered material due to its reversible hydroxylation similar to earlier investigated supercritical water action on the precursors during α -Al₂O₃ formation. Further improvement of the cold sintering setup and regimens would open prospects in α -Al₂O₃ ceramics manufacturing by an ecologically benign route.

Keywords: cold sintering; alumina ceramics; spark plasma sintering; vapor; porous ceramics; post-annealing; microstructure

1. Introduction

Dense as well as porous alumina ceramics are well-known technical material with quite a few applications in the industry of corrosion- and wear-resistant components, catalysis, filtration, thermal insulation, sound absorption, tissue engineering, etc. These materials are highly appreciated due to their thermal and chemical stability, excellent mechanical strength and low thermal expansion. Green bodies for dense ceramics are usually shaped by dry and isostatic pressing. To create the desired porosity in alumina ceramics, different approaches have been employed [1] such as partial sintering [2,3], sacrificial templating [4–6], replica technique [7,8], direct foaming [9,10] combined with different types of shaping techniques (pressing, casting, additive manufacturing, etc.).

A significant technological difficulty of alumina ceramics is rather high energy consumption on the stage of its sintering. Commonly, in conventional ceramics sintering, the temperatures of 50 - 75 % of the material's melting point are applied. In the case of alumina, it exceeds 1400 °C [11], while the leucosapphire by Verneuil, Bagdasarov, Stepanov, Bridgen, or Kyropoulos methods is produced at temperatures above the alumina melting point (2072 °C). In recent decades, a few innovative sintering approaches have been introduced combining high heating rates and pressure application, for example, hot pressing [12], hot isostatic pressing [13], microwave sintering [14], field assisted sintering technology (FAST) [15], spark plasma sintering (SPS) [16]. The development of these techniques was aimed to lower the energy consumption and the environmental impact of the ceramics

production. For example, the fabrication of dense [17,18] or porous [19] alumina ceramics by SPS still require high temperatures of 1400-1500 °C with an exception to those prepared from nanopowders [20]. But due to the pulse current, rapid well-controllable heating and simultaneous mechanical pressing, this technique allows significant shortening of the sintering duration to tens of minutes thus reducing the energy budget. In terms of lowering the sintering temperature, the cold sintering process (CSP) seems the most promising among the emerging sintering approaches [21,22]. Commonly, CSP includes uniaxial pressing of the oxide powders at 50 - 500 MPa in the presence of a liquid (acid or alkaline aqueous solutions) on heating below 350 °C [11]. Mainly, the studies of CSP are focused on the preparation of zinc oxide [23–30] as well as ferro- and piezoelectric ceramics (BaTiO_3 [31–34], $(\text{K},\text{Na})\text{NbO}_3$ [35–38] and $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ [39–41]). Alumina ceramics remains an attractive but a “difficult” object for this processing technique. For the moment, only several studies described the manufacturing of Al_2O_3 - NaCl [42,43] and Al_2O_3 - hydroxyapatite [44] composites by the cold sintering. Hérisson de Beauvoir et al. [45] performed the efforts of Al_2O_3 ceramics fabrication with the use of CSP. In this work, starting $\text{Al}(\text{OH})_3 \cdot x\text{H}_2\text{O}$ was treated under CSP conditions at 150 - 400 °C and 500 MPa for 30 - 180 min. to obtain dense semi-transparent samples containing amorphous alumina and boehmite $\gamma\text{-AlOOH}$. After the heating at 500 °C, the samples transformed into $\gamma\text{-Al}_2\text{O}_3$ completely. Kang et al. [46] successfully prepared ~ 98 % dense $\alpha\text{-Al}_2\text{O}_3$ ceramics by CSP of a mixture of α - and $\gamma\text{-Al}_2\text{O}_3$ powders at 300 °C and 300 MPa for 60 min. in glacial acetic acid medium with the second sintering in air above 1250 °C. These results demonstrated the capability of CPS method to fabricate comparatively dense alumina and related ceramic materials. Besides, Suleiman et al. [43] the use of NaCl as a pore-forming agent as well as a sintering aid at the stage of post-annealing in air at 1200-1500 °C.

There are several works reporting ceramics preparation by a hybrid CSP/SPS approach. First of all, this approach allowed sintering with densification above 90 % of so called “thermodynamically fragile materials” such as MnSO_4 , $\text{Na}_2\text{Cu}(\text{CO}_3)_2$, $\text{K}_2\text{Cu}(\text{CO}_3)_2$, $\text{NH}_4\text{FeP}_2\text{O}_7$ [47]. The sintering was featured using hydrated starting powders, which performed higher thermal stability in SPS than in air conditions and were successfully consolidated below 400 °C. The FAST/SPS technique considerably contributed to the development of ZnO cold sintering processing as it elucidated the role of the trapped water in the material densification on high heating rates [24,25,48]. Later, ZnO ceramics with density up to 99 % of theoretical were derived by the CSP/SPS or FAST/SPS/CSP technique at only 250-300 °C and 50-150 MPa for only 5 min. exposure with the additions of water [49,50], acetic acid [51] or zinc acetate and water [52]. Despite the obvious potential, the number of ceramic compositions produced by the mentioned approach remains quite modest and apply only to dense ceramics. Current work is aimed to expand the range of these compositions by preparation of α -alumina ceramics using CSP-SPS conditions. Compared to most of the works mentioned above and devoted to CSP of alumina ceramics, here, we would avoid the use of any auxiliary substances except to pure water. Besides, the initial materials would be chosen in hydroxylated forms (hydrargillite $\gamma\text{-Al}(\text{OH})_3$ and boehmite $\gamma\text{-AlOOH}$). These ideas originated from the earlier results on the synthesis of $\alpha\text{-Al}_2\text{O}_3$ from the same precursors in supercritical water [53]. According to the mentioned results, the interaction of the precursors with supercritical water led to the appearance of solid-state mobility in their structures which favored $\alpha\text{-Al}_2\text{O}_3$ formation at only 400 °C. Supposedly, the combined effect of mechanical pressure and aqueous medium in CSP-SPS would contribute to α -alumina ceramics formation. Also, the results of this work would expand understanding of the role of water in the CSP of ceramic materials including Al_2O_3 .

2. Materials and Methods

Commercial hydrargillite $\gamma\text{-Al}(\text{OH})_3$ powder (Pikalevo Alumina Refinery LLC, Pikalevo, Russia) with a purity of > 99.6 wt.% and boehmite powder $\gamma\text{-AlOOH}$ were used as starting materials for ceramics processing. $\gamma\text{-AlOOH}$ was synthesized from $\gamma\text{-Al}(\text{OH})_3$ by its treatment in supercritical water as follows. The initial $\gamma\text{-Al}(\text{OH})_3$ powder was placed into a stainless steel container inside a laboratory stainless steel autoclave. The required amount of distilled water was poured into the autoclave outside the container with $\gamma\text{-Al}(\text{OH})_3$. Further, the autoclave was sealed and heated up to 400 °C with

a rate of $200\text{ }^{\circ}\text{C h}^{-1}$. The pressure of supercritical water during the synthesis reached 26.0 MPa. After a 5 h exposure, the autoclave was drastically cooled down to the room temperature, the obtained product was removed from it and dried in air at $70\text{ }^{\circ}\text{C}$ for 10 h.

To provide alumina nucleation [54] during the cold sintering, $\alpha\text{-Al}_2\text{O}_3$ powder (Treibacher Industrie AG, Althofen, Austria) in an amount of 5 wt.% was added to $\gamma\text{-Al(OH)}_3$ as well as to $\gamma\text{-AlOOH}$ by joint sieving through a sieve with 300 μm cell. Densification of the prepared mixtures was carried out with use of SPS machine H-HP D 25 (FCT Systeme, GmbH, Rauenstein, Germany) with a conventional graphite mold of 20 mm in diameter. During the SPS experiments, the mold containing initial powder mixture and 5 wt.% of distilled water was exposed to a pressure of 70 MPa and heated up to $450\text{ }^{\circ}\text{C}$ with a rate of $300\text{ }^{\circ}\text{C min}^{-1}$. After reaching $450\text{ }^{\circ}\text{C}$, the mold was kept at this temperature for 20 min and then cooled to the room temperature without an applied pressure. The surfaces of the prepared ceramic samples were mechanically cleared from graphlex residues. The samples prepared from $\gamma\text{-Al(OH)}_3$ powder were further annealed at $1250\text{ }^{\circ}\text{C}$ for 3 h in air with the heating rate of $250\text{ }^{\circ}\text{C h}^{-1}$ following the previously reported data [46]. The labeling of the obtained ceramic samples was collected in Table 1.

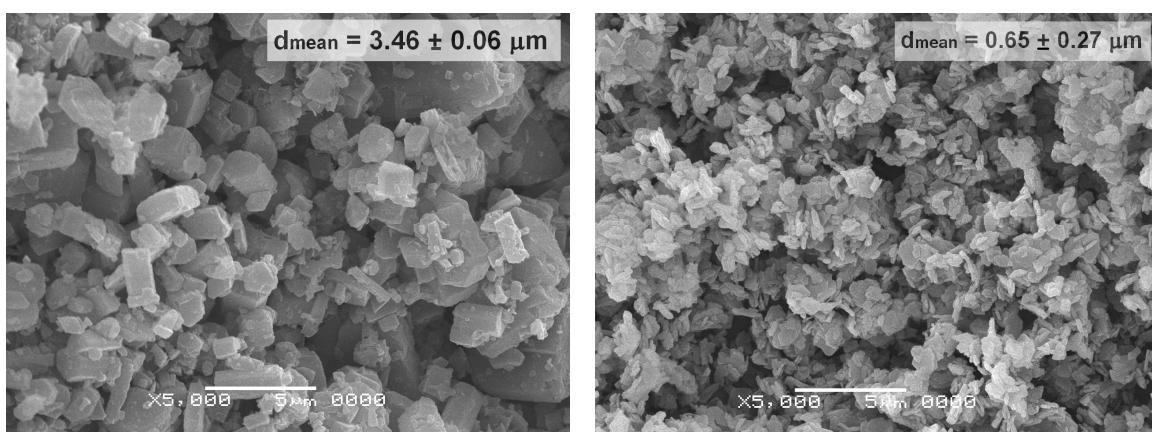
Table 1. Samples prepared by CSP-SPS and the following annealing in air.

Initial powder	Samples after CSP-SPS	Samples after annealing in air
$\gamma\text{-Al(OH)}_3$ (HA-P)	HA-CS	HA-CS-A
$\gamma\text{-AlOOH}$ (BO-P)	BO-CS	-

Phase contents of the starting powders and the prepared ceramics after their thorough grinding were studied by the means of Rigaku D/Max-2500 (Rigaku Corporation, Tokyo, Japan) X-ray diffractometer in a range of $10\text{ }^{\circ} < 2\theta < 70\text{ }^{\circ}$ with a step of 0.02 ° . The phases were identified by comparing the obtained patterns with the data from PDF-2 database [55]. JSM-6380 LA (JEOL Ltd, Tokyo, Japan) scanning electron microscope was used to observe the morphology of the powders and the fractured surfaces of the ceramics. Particle and grain sizes were estimated by linear segment measurements in the SEM images using ImageJ software [56]. Thermal analysis was performed at combined TG-DSC analyzer STA 449C Jupiter with a mass-spectrometer QMS 403 C Aeolos (Netzsch GmbH, Selb, Germany). The ceramic sample was heated with a rate of $10\text{ }^{\circ}\text{min}^{-1}$ in the range of 40-1000 or 40-1200 $^{\circ}\text{C}$ in a flow of air. Infrared spectra were studied by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) in a range of 400-4000 cm^{-1} with the use of IR Fourier spectrometer EQUINOX 55/S (Bruker CO., Billerica, MA, USA). Apparent density of the ceramic samples was determined by Archimedes method using kerosene as a saturating liquid.

3. Results

The initial $\gamma\text{-Al(OH)}_3$ powder consisted of mostly prismatic particles with the mean size of $3.46 \pm 0.06\text{ }\mu\text{m}$. The starting $\gamma\text{-AlOOH}$ powder contained finer particles of about $0.65\text{ }\mu\text{m}$ in average which possessed plate-like shape (Figure 1).



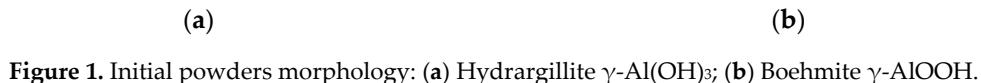


Figure 1. Initial powders morphology: (a) Hydrargillite γ -Al(OH)₃; (b) Boehmrite γ -AlOOH.

Figure 2 showed the results of XRD analysis of ceramic samples obtained from hydrargillite powder by the CSP (sample HA-CS) as well as by further annealing in air at 1250 °C (sample HA-CS-A). The cold sintering led to phase transformation of γ -Al(OH)₃ into boehmite (PDF2 #00-074-1895) and γ -Al₂O₃ (PDF2 #00-029-0063). The presence of α -Al₂O₃ in this sample was attributed to the alumina powder initially added to hydrargillite in the amount of 5 wt.%. To promote transformation of the bulk into α -alumina, the sample was treated at high temperature. After the annealing of these cold sintered ceramics, α -Al₂O₃ (PDF2 #00-010-0173) became the main phase in the sample along with the traces of β -Al₂O₃ (PDF2 #00-010-0414). The least is known as layer-structured oxide with a composition x Na₂O·11Al₂O₃ where x is from the range of 1.0 - 1.6 [57]. Its formation could be explained by probable presence of Na₂O admixture in γ -Al(OH)₃ powder initially used in the experiment.

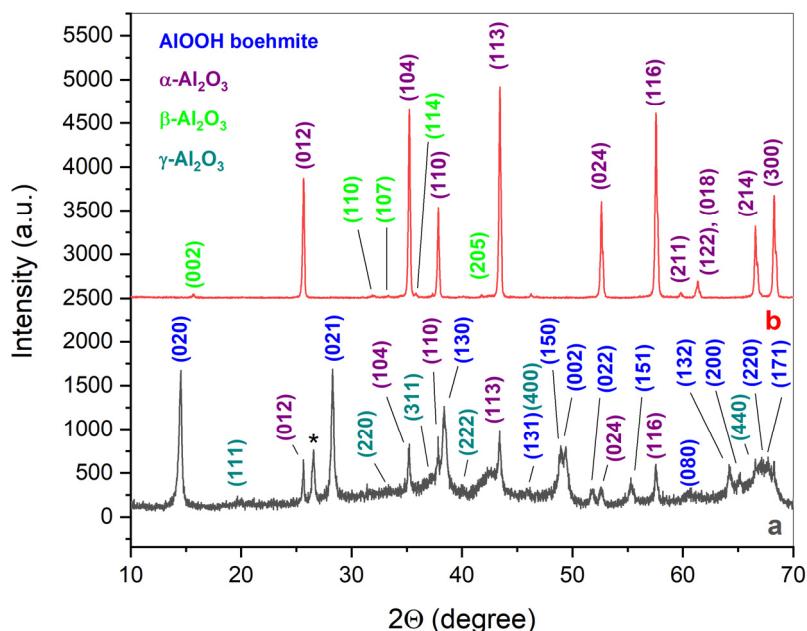


Figure 2. XRD patterns of ceramic samples prepared from the mixture of 95 wt.% γ -Al(OH)₃ and 5 wt.% α -Al₂O₃: (a) as-sintered *via* CSP-SPS; (b) annealed at 1250 °C for 3 h in air after CSP-SPS. Miller indices are colored as the phases mentioned in the left upper angle of the figure, correspondingly. Asterisk indicated carbon contamination (PDF2 #00-026-1076).

After the treatment of hydrargillite powder in supercritical water at 400 °C and 26 MPa during 5 h, boehmite (PDF2 #00-074-1895) with a minor phase of α -Al₂O₃ (PDF2 #00-010-0173) was obtained (Figure 3a). Boehmite formation in these conditions was expected from the previously reported data [58]. Cold sintering of this powder mixed with additional 5 wt.% of α -alumina led to its full transformation into α -Al₂O₃ as it was performed by XRD (Figure 3b).

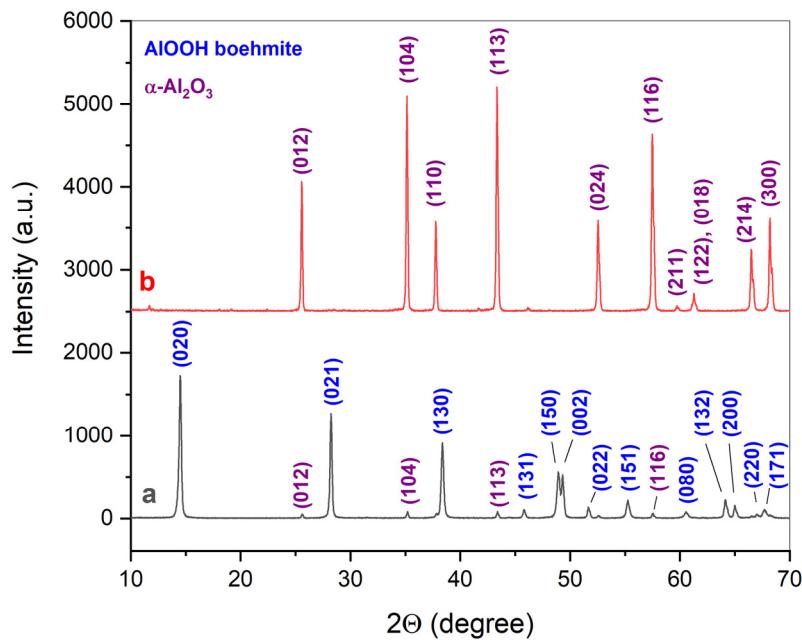


Figure 3. XRD patterns of the samples: **(a)** The synthesized γ -AlOOH: **(b)** Ceramics as-sintered *via* CSP-SPS from the mixture of 95 wt.% γ -AlOOH and 5 wt.% $\alpha\text{-Al}_2\text{O}_3$ powders. Miller indices are colored as the phases mentioned in the left upper angle of the figure.

Thermal analysis of the initial hydrargillite powder HA-P (Figure 4a) showed its rather typical behavior in the case of coarse particles, with a shift of the effects on DSC curve towards higher temperatures compared to earlier data [59]. Endo-effects observed at 245.2 and 324.6 °C corresponded to the gradual formation of boehmite from $\gamma\text{-Al(OH)}_3$ as well as formation of transient Al_2O_3 phase from this newly formed γ -AlOOH. The mentioned processes were accompanied by the most significant weight loss at TG curve (over 25 wt.%). Next, endothermic peak at 522.8 °C displayed termination of the transition from boehmite to $\gamma\text{-Al}_2\text{O}_3$ [60,61] with the corresponding losses of about 6 wt.%. The chosen heating rate of 10 °C min⁻¹ appeared fast enough to hide the effect of further γ - to δ -alumina transition at DSC curve [60]. However, there was a visible exothermic peak at 1080.2 °C, which could accompany either δ - to $\theta\text{-Al}_2\text{O}_3$ or θ - to $\alpha\text{-Al}_2\text{O}_3$ transformation. Following the literature, this temperature was fairly low for α -alumina formation [62], however, θ - to $\alpha\text{-Al}_2\text{O}_3$ transformation was also reported to occur from 1050 °C [60]. Besides, the lowering of the transition temperature could be associated with the initial presence of $\alpha\text{-Al}_2\text{O}_3$ in the studied sample.

Thermal behavior of the ceramic sample obtained from the mixture of 95 wt.% $\gamma\text{-Al(OH)}_3$ and 5 wt.% $\alpha\text{-Al}_2\text{O}_3$ (HA-CS) was performed in Figure 4b. It demonstrated a considerable content of physisorbed water (above 3 wt.%) and chemisorbed water (about 1 wt.%) gradually emitted up to 300 °C. This process was followed by boehmite decomposition to $\gamma\text{-Al}_2\text{O}_3$ with endo-effects at 400.7 and 526.2 °C. Previously, boehmite was reported to lose hydroxyl groups during its thermal decomposition in two stages [63]. First, weakly bonded OH-groups were eliminated while boehmite structure was preserved. Then, strongly bonded hydroxyl groups left boehmite during its transformation into alumina. Worth noting that less defective boehmite possessed lower amount of the weakly bonded hydroxyls and showed higher transformation temperature. In the mass-spectrum, water emission occurred together with the processes of its release mentioned above (Figure 4b).

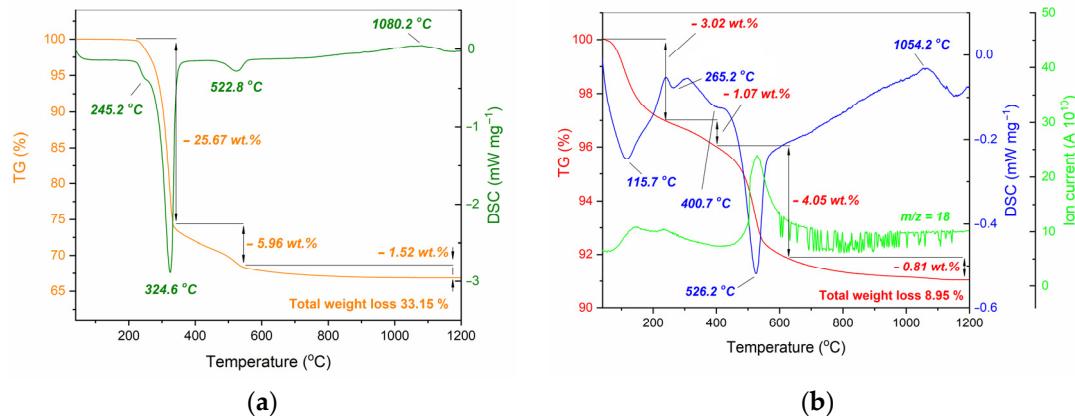


Figure 4. Thermal analysis for the samples: (a) The initial γ -Al(OH)₃ powder; (b) Sample as-sintered by CSP-SPS from the mixture of 95 wt.% γ -Al(OH)₃ and 5 wt.% α -Al₂O₃ powders (m/z - ion mass to charge ratio corresponding to H₂O⁺).

Temperature of the weight losses and the heat effects recorded for boehmite powder BO-P synthesized in supercritical water (Figure 5a) corresponded well to those observed in ceramics HA-CS and related to γ -AlOOH transformation into γ -Al₂O₃ (Figure 4b). Again, boehmite decomposition occurred in two steps with endo-effects at 396.2 and 533.8 °C. A slight shift of the second endo-effect to higher temperature compared to the sample HA-CS was associated to less defective structure of γ -AlOOH obtained by the synthesis in supercritical water [63]. The conditions of boehmite powder synthesis in an aqueous medium and its duration favored both hydroxylation and dehydroxylation in its structure which led to the defect elimination. Exothermic peak at 916.2 °C was likely to accompany a transition between Al₂O₃ modifications. The observed total weight loss of about 17 wt.% corresponded well to calculated value for boehmite transformation into alumina considering the adsorbed water. TG and DSC curves of the ceramic sample BO-CS showed the adsorbed water ejections with endo-effects at 99.1 and 248.5 °C. Besides, an exo-effect at 956.0 °C pointed to the presence of residual Al₂O₃ transient phases along with the main phase of α -alumina. The shape of these curves resembled those registered for a commercial α -alumina powder (Figure A1). However, the release of water at about 250 - 265 °C inherent for the prepared ceramics (HA-CS and BO-CS) appeared as a footprint of the cold sintering process they experienced.

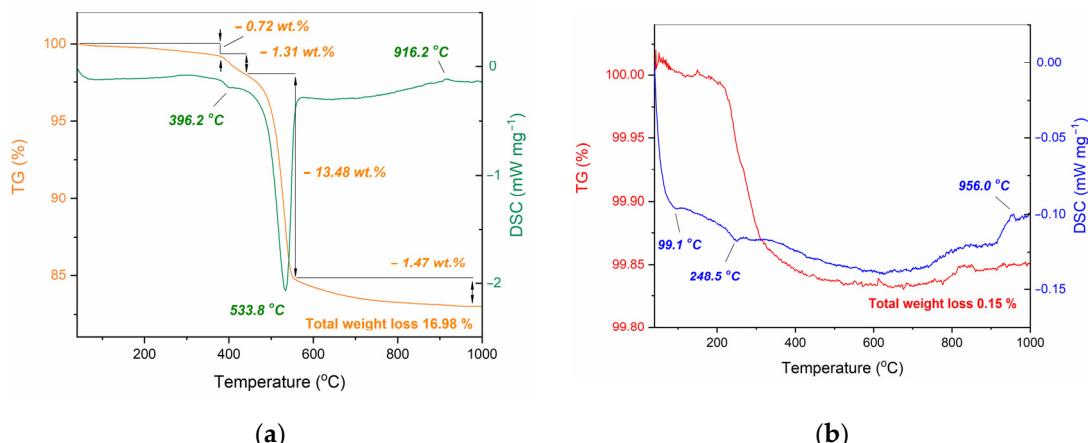


Figure 5. Thermal analysis for the samples: (a) The initial AlOOH powder; (b) Sample as-sintered by CSP-SPS from the mixture of 95 wt.% AlOOH and 5 wt.% α -Al₂O₃ powders.

Most of the bands performed by the sample HA-CS in its IR spectrum (Figure 6a) conformed the data earlier reported for boehmite [64–67]. Among the observed bands, those at 1065 and 1155 cm⁻¹ related to symmetric and asymmetric deformation vibrations in hydroxyl groups, while the bands at

3105 and 3296 cm^{-1} corresponded to their valence vibrations. The bending mode of the adsorbed water also manifested at 1638 cm^{-1} . The bands observed in a range of 487-900 cm^{-1} could be assigned to the vibrations in AlO_6 octahedra, though the position of 721 cm^{-1} differed from the literature. In the vicinity to this band, other authors reported the valence vibrations of Al-O in boehmite at 752-770 cm^{-1} [64,66]. The observed shift to the lower wavenumber might be caused by the structural transformations of boehmite to γ -alumina as it was shown above by XRD. Al-O stretching vibrations in α -alumina located at 447-457 cm^{-1} and 488 cm^{-1} [68,69] mostly coincided with boehmite bands in HA-CS spectrum. Thermal treatment of HA-CS sample led to noticeable changes in IR absorption bands (Figure 6b). AlO_6 valence vibrations in the sample HA-CS-A appeared as a shoulder at 507 cm^{-1} as well as a broad band between 630 and 840 cm^{-1} . While the least corresponded well to the literature and the data obtained for commercial α -alumina powder, 507 cm^{-1} band was likely to contain unresolved bands located at 487 and 559 cm^{-1} (Figure A2). This shifted band location reflected uncompleted structural transformations in HA-CS-A during its annealing. Also, the bands at 1037, 1634, 3320, and 3478 cm^{-1} assigned to the re-adsorbed water bending preserved in the spectrum of the heated ceramics. The absorption at 2541 cm^{-1} could be attributed to the presence of β - Al_2O_3 band [70].

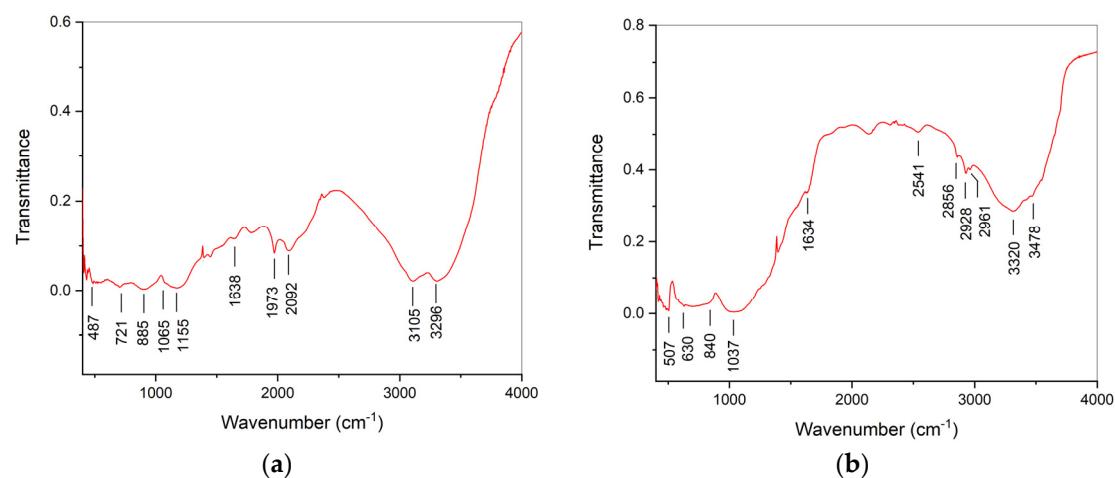


Figure 6. Infrared spectra for the ceramic samples prepared from the mixture of γ - $\text{Al}(\text{OH})_3$ and 5 wt.% α - Al_2O_3 powders: (a) The sample after CSP-SPS (HA-CS); (b) The sample after CSP-SPS followed by annealing in air at 1250 $^{\circ}\text{C}$ (HA-CS-A).

The sample BO-CS demonstrated high resolution of the absorption bands related to the vibration in AlO_6 octahedra (487, 554, 630-822 cm^{-1}) which pointed to low defect concentration in its structure (Figure 7). Pronounced bands located at 1032, 3292 and 3468 cm^{-1} indicated the presence of moisture and hydroxyl groups. The bands at 1977 and 2107 cm^{-1} resembled those from the spectrum of boehmite (Figure 6a) and signified that its traces remained in the ceramics after the CSP-SPS.

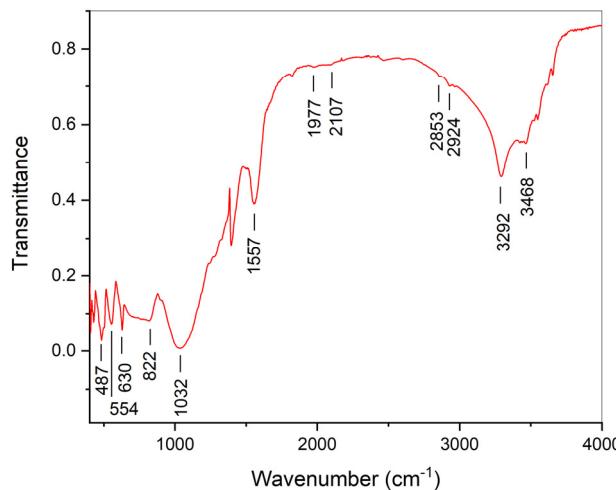


Figure 7. Infrared spectrum of the sample BO-CS prepared by CSP-SPS from the mixture of γ -AlOOH and 5 wt.% α -Al₂O₃ powders.

Cold sintering of HA-P powder was accompanied by a preservation of the initial prismatic shape of hydrargillite crystals in the sample HA-CS (Figure 8a,b). The newly formed prismatic grains in the sample HA-CS demonstrated mostly smooth faces and clear edges. Partial densification occurred due to the destruction of the neighboring particles under the applied pressure, and the porosity after CSP-SPS exceeded 50% (Table 2).

Annealing of the sample HA-CS in air at 1250 °C for 3 h resulted in the formation of vermicular structure in HA-CS-A (Figure 8c,d). This type of microstructure was reported to form in alumina ceramics during γ -modification transition into α -Al₂O₃ on sintering [71–73]. The appearance of vermicular grains led to the increase of open porosity up to 60% due to the development of the grains' surface (Table 2).

Table 2. Integral structural properties of ceramics samples obtained from the mixture of 95 wt.% γ -Al(OH)₃ and 5 wt.% α -Al₂O₃.

Sample	Density after CSP-SPS (g cm ⁻³)	Porosity after CSP-SPS (%)	Density after annealing (g cm ⁻³)	Porosity after annealing (%)
HA-CS 1	1.57	51.9	1.52	60.5
HA-CS 2	1.53	53.3	1.46	60.2
HA-CS 3	1.53	52.9	1.50	60.2

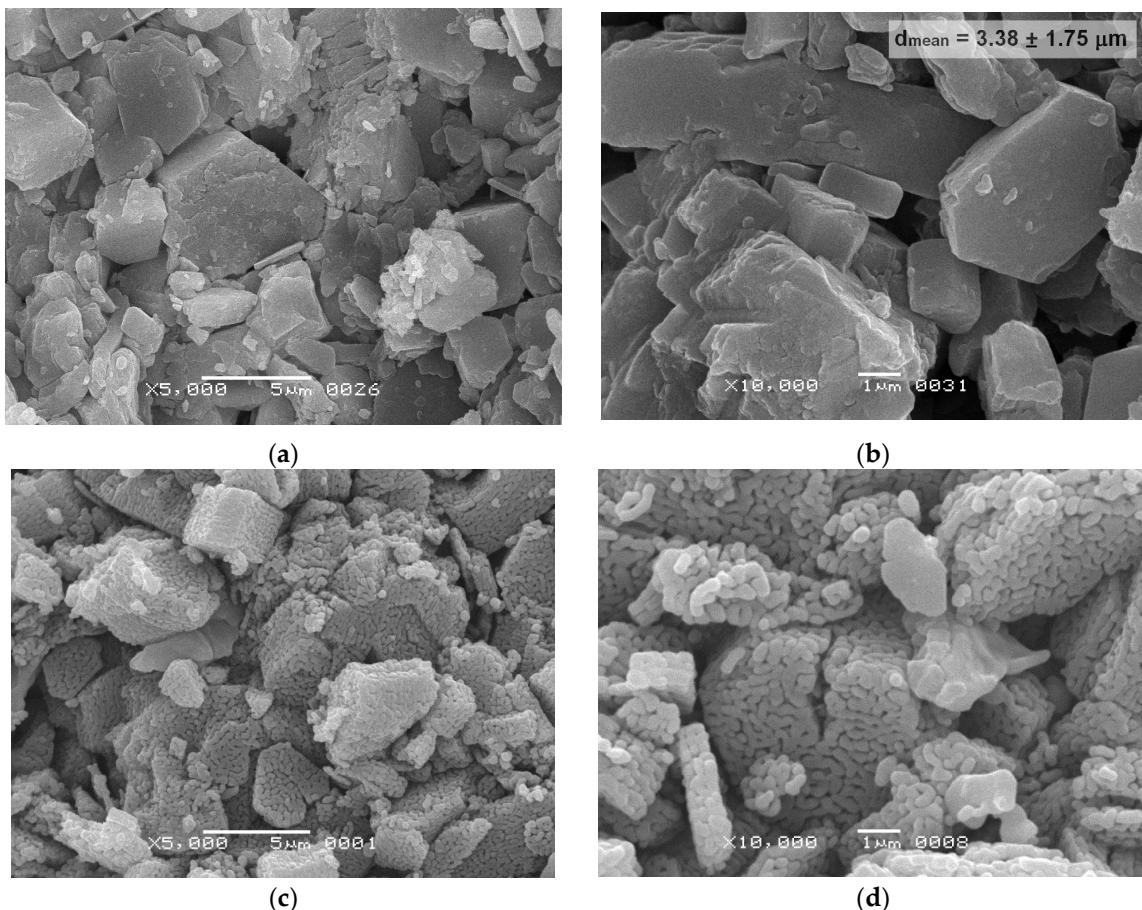


Figure 8. SEM images of ceramics fractured surfaces: (a, b) Sample as sintered by CSP-SPS from the mixture of 95 wt.% γ -Al(OH)₃ and 5 wt.% α -Al₂O₃ powders; (c, d) Sample sintered by CSP-SPS from the mixture of 95 wt.% γ -Al(OH)₃ and 5 wt.% α -Al₂O₃ powders with further annealing at 1250 °C 3 h in air.

During the CSP-SPS of boehmite powder, a significant grain growth was observed (Figure 9). Compared to the initial γ -AlOOH particles, the mean size of alumina grains increased 4.5 times from 0.65 to 2.94 μm . In Figure 9b, one could observe the formation of dense agglomerates of crystals which morphology was similar to that of neighboring non-agglomerated crystals. Because of this partial agglomeration, a large pore space remained between the crystals of BO-CS sample. It resulted in a poor transport strength of these ceramics.

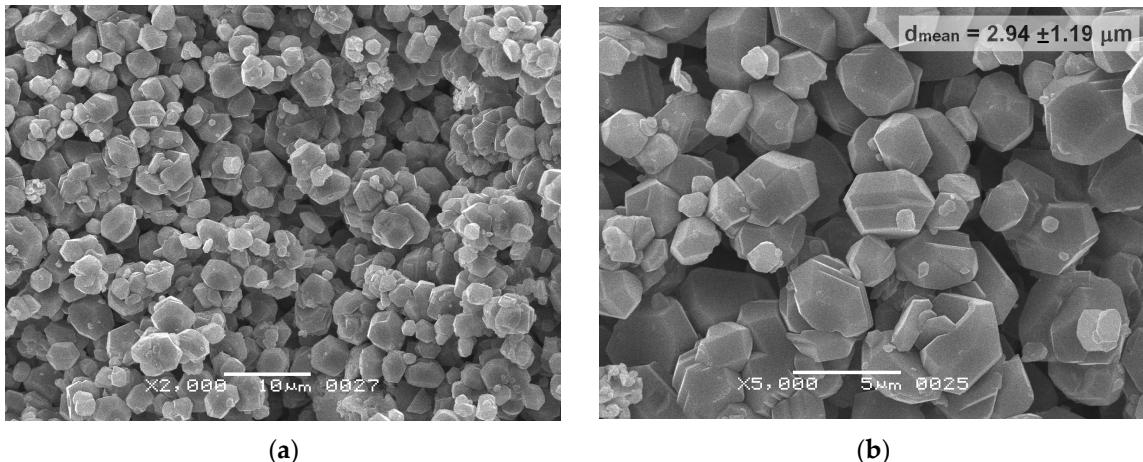


Figure 9. SEM images of ceramics fractured surfaces: (a, b) Sample as sintered by CSP-SPS from the mixture of 95 wt.% AlOOH and 5 wt.% α -Al₂O₃ powders (different magnifications).

4. Discussion

For the cold sintering process, the most recognized mechanism is mass transfer due to dissolution - precipitation [21,74], which implies the following stages: (1) powder compaction under mechanical pressure; (2) rearrangement of particles facilitated by the liquid phase; (3) grain growth and closure of pores due to the dissolution of highly stressed points of contacting particles, followed by deposition on non-contacting surfaces with low stress [21]. However, a few subsequent studies have called this model into question showing more complex mechanisms involved in the CSP [75]. Dissolution and precipitation as purely surface phenomena can only lead to coarsening of particles but not contribute to ceramics densification. Besides, the smallest amount of water sufficient for the CSP couldn't allow dissolution of the solid [49]. Considering the role of adsorbed water and its species incorporated in the oxide structure, densification during the CSP was explained by a decrease in the activation energy of atomic diffusion along grain boundaries due to a high concentration of hydroxide ions and other defects [24,25,49].

In this work, during the cold sintering in SPS machine, hydrargillite and boehmite powders both previously mixed with 5 wt.% of α -Al₂O₃ transformed into ceramic materials in the presence of 5 wt.% of distilled water. Boehmite-based powder exposed to CSP-SPS conditions in the presence of water turned into α -alumina. This result corresponded well to the data on α -alumina processing in supercritical water medium [53], where its formation from boehmite occurred directly and bypassing the transient alumina modifications. The traces of remnant boehmite and the presence of trapped water in the prepared ceramics BO-CS pointed to the relation of the CSP-SPS and the processes known for oxides exposed to supercritical water or subcritical vapor [63,76,77]. In that water media, the solid oxides are believed to undergo dissociative adsorption of water molecules which increased the defect concentration in their structure. Gradually, water dissociative adsorption and oxide hydroxylation came to a quasi-equilibrium with water desorption leading to a decreased activation energy of the solid-state transformations [78].

Cold sintering of the hydrargillite-based powder led to the formation of γ -AlOOH as well as γ -Al₂O₃, which both inherited the morphology of the initial γ -Al(OH)₃ (Figures 1a, 8a,b). These pseudomorphism and presence of γ -Al₂O₃ pointed to a low pressure of water inside the mold caused by its premature evaporation through gaps between the components of the mold. As a result, the

mechanism of phase transitions turned to usual thermal decomposition of boehmite instead of its direct transformation to α -Al₂O₃ in supercritical water. The pressure of the supercritical water during the preparation of HA-CS sample appeared too low for the quasi-reversible hydroxylation of boehmite and promotion of its solid-state mobility. The difference in the decomposition temperatures of γ -AlOOH in the sample HA-CS (526 °C, Figure 4b) compared to the well-crystallized synthesized boehmite (533 °C, Figure 5a) was a consequence of its defective structure.

In the case of the sample BO-CS, heating up to 450 °C resulted in a complete boehmite transformation into α -Al₂O₃ due to the preservation of supercritical water inside of the mold. As reported in [54], α -Al₂O₃ formation from γ -AlOOH in supercritical water in an autoclave was accompanied by spreading of small boehmite crystals over the surface of larger ones. Because of the mechanical pressure applied during the CSP, α -Al₂O₃ crystals in the sample BO-CS agglomerated (Figure 9a). Earlier, a formation of the similar agglomerates was demonstrated in the cold sintering of ZnO ceramics prior to its densification which occurred due to a coalescence of the crystals [77]. The coalescence of ZnO crystals was accompanied by a forced faceting of the newly formed ones and the elimination of the pore space between them. However, in BO-CS sample, the boundaries preserved between the crystals in the agglomerates while the sizes of these crystals remained close to the non-agglomerated crystals (Figure 9a). Hence, the coalescence of the neighboring crystals was hampered by their crystallographic discrepancy. Probably, the crystals in BO-CS sample possessed a low solid-state mobility for their diffusion re-orientation under the cold sintering conditions. Besides, the ordering of α -Al₂O₃ structure in the sample BO-CS could occur more rapidly than the re-orientation of the crystallographic planes because of the presence of the initially added α -alumina [54]. During the rapid ordering of α -alumina crystals, the major part of the agglomerates was destroyed.

Because of the low pressure of the supercritical water in the mold, boehmite structure in HA-CS sample remained poorly ordered and partially transformed in the pseudomorphic γ -Al₂O₃ during the CSP. Further lowering of the pressure supposedly would lead to the formation of tohdite 5Al₂O₃·H₂O instead of boehmite similarly as it was shown for hydrargillite treatment in an autoclave at different ratios of supercritical water to alumina [79]. Tohdite is known to transform into κ -Al₂O₃ at a temperature above 700 °C [80,81].

High-temperature annealing of the cold-sintered ceramics HA-CS resulted in the formation of α -alumina ceramics with considerable porosity of about 60% (HA-CS-A). The obtained value was comparable to those reported earlier for technical porous alumina ceramics. In recent works, the obtaining of alumina ceramics with porosity of about 54% was reported in a context of indirect selective laser sintering application [82]. Foaming process with the use of natural agents allowed reaching higher porosities of 80-87% [83]. The ceramics prepared in the current work by CSP-SPS was promising for further investigation on its structural and mechanical properties and their tailoring by variation of the sintering conditions.

For the moment, reproducible preparation of α -Al₂O₃ material with the use of CSP-SPS in the presence of water as a transient liquid was limited by the constriction of the mold. A disadvantage of the currently used mold was connected to an insufficient reproducibility of its sealing. Previously, the importance of the mold sealing system and the choice of appropriate materials for it was demonstrated in the cold sintering of ZnO ceramics [84]. The improvement of the mold design would allow preservation of the CSP-SPS conditions for a longer exposure and open prospects in obtaining dense α -alumina ceramics by a novel ecologically pure and energy-saving technique.

5. Conclusions

Current work performed a new processing route for α -Al₂O₃ ceramics which involved cold sintering using SPS equipment in the presence of only distilled water as a transient liquid. The study of phase contents, thermal behavior and microstructure of the cold-sintered ceramics pointed to the vicinity of mechanisms governing this sintering process and the transformations in oxides in vapor and supercritical water. In this case, the decisive role in the sintering belonged to the processes of intense hydroxylation and dehydroxylation of the solid rather than its dissolution. Due to the second annealing in air, the cold-sintered material mostly consisting of boehmite was successfully

transformed into α -Al₂O₃ ceramics with vermicular structure and porosity of about 60%. Further improvement of the cold sintering design and adjustment of its regimens would open prospects for an economical and ecologically benign route to α -alumina ceramics.

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Appendix A

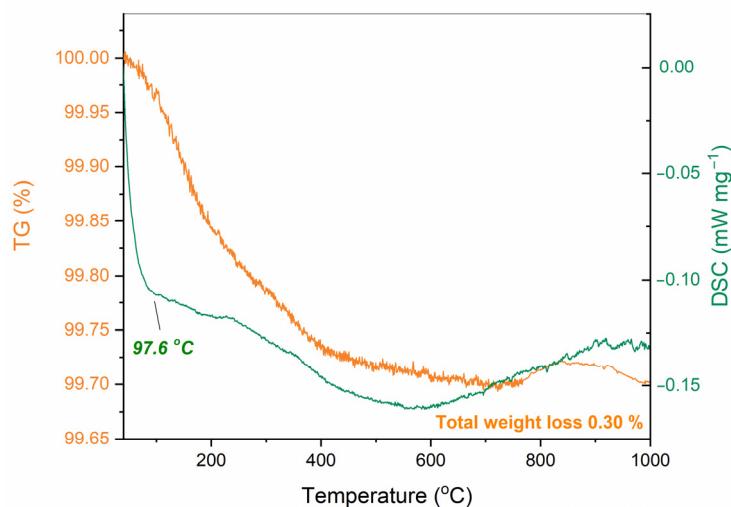


Figure A1. Thermal analysis of a commercial α -Al₂O₃ powder.

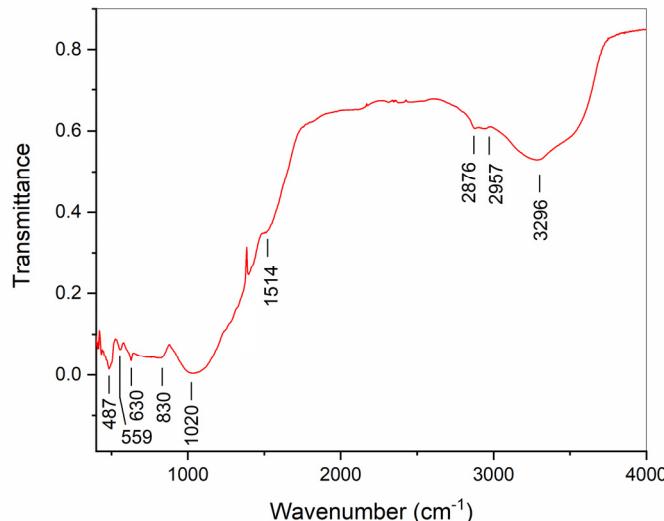


Figure A2. Infrared spectrum of a commercial α -Al₂O₃ powder.

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