# ALUMINA CERAMICS PREPARED BY PRESSURE FILTRATION OF ALUMINA POWDER DISPERSED IN BOEHMITE SOL

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*The alumina ceramics was prepared by pressure filtration of electrostatically stabilized alumina and alumina - boehmite water suspensions and subsequent pressureless sintering of as-prepared compacts. The aggregates formation was avoided by stabilization of initial suspension through the regulation of interparticle forces. Nanoparticle boehmite sol was used as a dispersant for alumina suspension, it acts as a lubricant, and moreover it enhances the handling strength of the green compacts and also its sinterability. The kinetic analysis of sintering confirmed, that the definite boehmite addition (2.7 wt.% in green compact) affects positively the densification. The higher amount of boehmite addition has negative influence; it causes the flocculation of the suspensions and decreases the density of sintered bodies.*

## INTRODUCTION

Actual research of ceramic materials, including alumina ceramics, is in many cases oriented to preparation of fine-grain size ceramics in order to improve their properties [1-5]. Colloidal processing represents one of the ways to prepare ceramics with almost theoretical density, homogenous microstructure and submicron grain size. Careful control of dopant influence (dispersant, binder) on rheology of used suspension is needed to obtain ceramics with such properties. By pressure filtration, used in this work, it is important to avoid aggregates formation in suspension because of enhanced flaw creation during calcination and sintering of prepared compacts [6-8].

Handling strength of green compacts is mainly achieved using polymer binders (e.g. PVA). However, polymer additions often influence negatively the suspension rheology, thereby causing its flocculation (the aggregate or the cluster formation). Polymer additions can also cause microstructural defects formation at burning out furthermore their residues may have adverse effect on sintering process. Therefore, it may be an advantage to use inorganic binder instead of polymers at ceramics preparation, especially when it changes its composition directly to desired product during sintering (alumina in our case).

Such binder, nanoparticle boehmite sol, was used at preparation of porous alumina ceramics [9]. Ananthakumur at al. [10] dispersed commercial alumina powder (Al6SG, BET surface area 8.0-11.0 m$^2$/g, particle size 0.3-0.6 μm) in boehmite sol at various boehmite concentrations. The suspension was flocculated by adjusting *pH* value to ~ 6.2 and then concentrated by centrifugation. The compact were prepared by pressure filtration and sintered 2 hours at 1450°C. The sintered samples achieved ~ 97 % of theoretical density of α-alumina and have average grain size ~ 2 μm. The flocculation of the suspension at *pH* ~ 6.2 showed to be favorable in term of enhanced handling strength of green compacts.

The properties of boehmite sol, gel and as-prepared ceramics was studied in our previous works [11, 12]. This work is aimed at using boehmite sol as a dispersing medium. The effect of boehmite content in sol to reological properties of the suspensions will be examined. The concentration of boehmite in sol will be optimised with a view to maximize the sintered density by minimal grain growth.

## EXPERIMENTAL

Alumina powder (Taimicron TM-DAR, Taimei Chemicals Co., Japan) with average particle size 160 nm and surface area 14.5 m$^2$/g was used in this study. The as-received alumina powder was dispersed in distilled water or in boehmite sol with various boehmite concentrations. All suspensions contain 50 wt.% of α-$Al_2O_3$. The solid loading of the suspension varies in dependence of boehmite content in sol. The *pH* of the suspensions was maintained at 3 using dilute $HNO_3$. Deagglomeration was done in rotary mill using zircon grinding balls. Boehmite sol was prepared by peptizing water boehmite suspension (Condea Pural SB-1, primary particle size ~ 5 nm) with $HNO_3$ ($pH \cong 2.5$) at 60°C. The unpeptized part of the boehmite was eliminated from the sol by centrifugation (9000 rpm, 10 min). Boehmite sols were prepared with various boehmite content - 0, 5, 10 and 15 wt.% (in following text we used markings B0, B5, B10, B15). The suspensions viscosity was measured by rotary viscosimeter Rheotest 2.

Compacts were prepared by pressure filtration of the suspensions. The pressure filtration was performed in special die having 15 mm ID. The suspension was poured into the die and after closing pressure (20, 30, 50 MPa) was applied through a hydraulic press. The water from the suspension was drained through massive perforated metal bottom with polymeric membrane (Millipore, pore size 0.2 μm). The fraction of nanoparticles passed through the membrane was estimated according to TG measurements. The compacts were calcinated 15 min at 600°C at heating rate 2°C/min. Sintering was provided at 1350°C at a heating rate 10°C/min.

The density of sintered samples was measured by the Archimedes method. With respect to the aim of the work, the values of density are present in percentage of $\alpha$-$Al_2O_3$ theoretical density (3.987 $g/cm^3$). The standard deviation of repeated measurements was 0.005 $g/cm^3$, i.e. 0.1 %. The density of calcinated compacts was determined from dimensional measurements.

Netzsch 402E dilatometer was used to obtain the shrinkage data at constant heating rates. Three different heating rates, i.e. 2°C/min, 5°C/min, 10°C/min were used to increase the temperature from 25°C to 1250°C. The shrinkage, temperature and time were recorded. The measured data were used for kinetic analysis of sintering. The microstructure of fracture surfaces was observed by SEM (Tesla BS 300). The average grain size was calculated according linear intercept method [13].

## RESULTS

### Rheology behaviour of alumina-boehmite water suspensions in dependence on boehmite content in sol

The viscosity - shear rate dependence of B0 and B5 is approximately equal (figure 1); the viscosity does not depend on shear rate (Newtonian behaviour). However, the viscosity of B10 is much higher and shows shear rate dependent behaviour. The viscosity of B10 decreased with increasing shear rate, which corresponds to pseudoplastic behaviour. This finding is documented also in figure 2, which shows the shear stress - shear rate dependences. Whereas Newtonian behavior is characteristic for well dispersed (not concentrated) systems, the decrease of the viscosity with increasing shear rate corresponds to suspensions formed by weakly attractive network of particles or by isolated clusters [14]. Therefore, the change in rheological behaviour of suspension at higher boehmite content in sol (B10) is likely a result of its changed suspension state (from dispersed to flocculated). This change could not be attributed to higher solid content in B10 because the viscosity - shear rate dependence of the suspension with 55 wt.% $\alpha$-$Al_2O_3$ (which corresponds to the same volume of solid phase as in B10) was in principle the same (figure 1).

### The influence of applied pressure on calcined density

The calcined density of the samples prepared by pressure filtration of alumina - water suspension B0 was not pressure sensitive (table 1). This result is in accordance with published works [3, 15]. By contrast the calcined density of compacts prepared from the other suspensions (B5, B10, B15) increased with enhanced pressure. To prepare the high dense compact, only the highest pressure of 50 MPa was used in the further part of the work (also in case of alumina - water suspension).

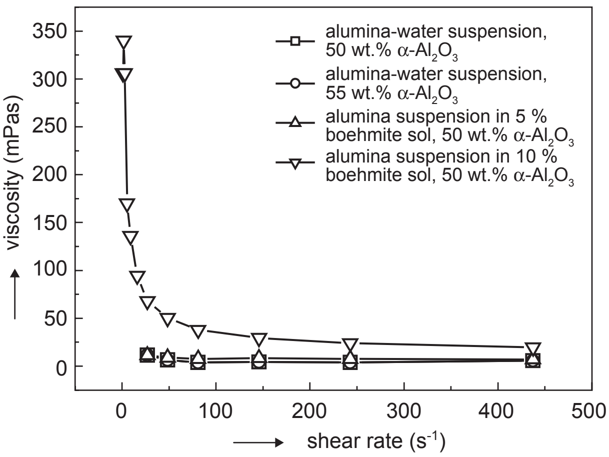


Figure 1. The vicosity - shear rate dependences for various alumina - water (B0) and alumina - boehmite water suspensions (B5 and B10), respectively.

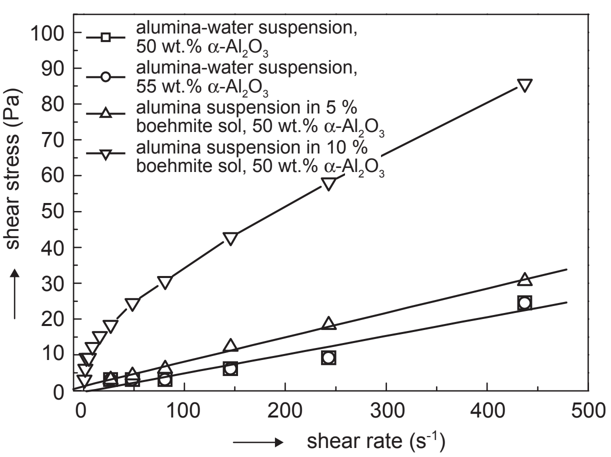


Figure 2. The shear stress- shear rate dependences for various alumina - water and alumina - boehmite water suspensions, respectively.

The presented relative densities were calculated from the theoretical density of $\alpha$-$Al_2O_3$ ($\rho$ = 3.987 g/cm$^3$) and $\gamma$-$Al_2O_3$ ($\rho$ = 3.55 g/cm$^3$). The amount of boehmite remaining in compacts after pressure filtration was estimated following DTA and TG and recalculated to $\gamma$-$Al_2O_3$ amount. The theoretical densities of each type of compact were calculated from $\alpha$-$Al_2O_3$ and $\gamma$-$Al_2O_3$ contents (table 2). The relative densities presented in table 1 are related to these theoretical densities.

### The influence of boehmite content in sol on density of sintered samples

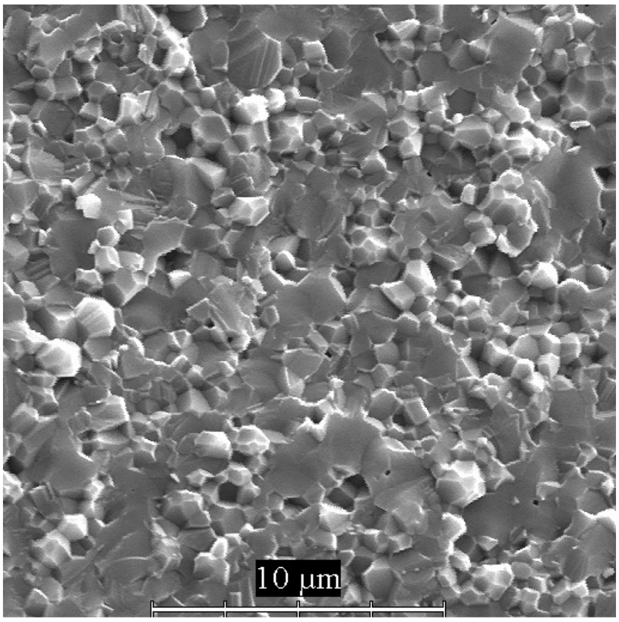
In any case, the sintered density is the determining criteria by the selection of the most suitable boehmite content in sol. The samples were sintered at 1350°C for 20 min and 1 h, respectively (the temperature and the holding times were chosen according to preliminary experiments). The sintered densities are presented in table 3.

The sintered density decreased slightly with enhanced boehmite content at both holding times, except the samples B0 and B5 at shorter holding time. The average grain size is reduced at shorten holding time. The microstructure of sintered samples was homogenous without noticable microstructural defects (figure 3).

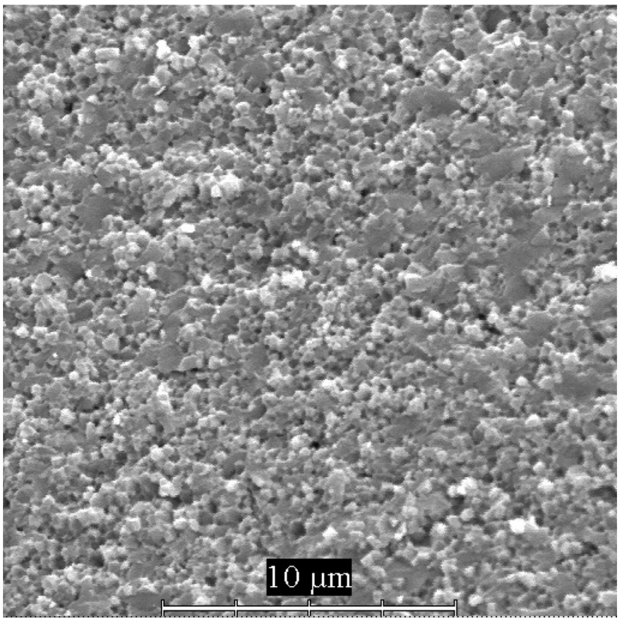
As can be seen from table 4, at shorter holding time the highest density was obtained for B5. At higher boehmite content (B10, B15) the sintered density decreased, also for B0 the density was lower. Following these results, it can be supposed that boehmite nanoparticles, especially in the case of B5, enhance the sintering. This assumption was confirmed by dilatometric measurement and subsequent kinetic analysis of sintering (the comparison of B0 and B5 sintering kinetics).

Table 1. The relative density after calcination at 600°C/15 min; at heating rate 2°C/min in dependence on the dispersing medium and the applied pressure.

| Pressure (MPa) | Relative density (%) | | | |
|---|---|---|---|---|
| | B0 | B5 | B10 | B15 |
| 20 | 60.3 | 57.5 | 61.2 | 60.9 |
| 30 | 60.0 | 59.0 | 61.5 | 61.2 |
| 50 | 60.1 | 60.0 | 62.2 | 61.9 |



a)



b)

Figure 3. SEM images of fractured surfaces of samples prepared by pressure filtration of alumina suspension in 5 % boehmite sol (B5) and sintered 1 h (a) or 20 min (b) at 1350°C; heating rate 10°C/min.

Table 2. The boehmite content in green compacts, the $\gamma$-$Al_2O_3$ content in calcinated compacts and the theoretical densities of calcinated compacts prepared by pressure filtration of the various alumina - boehmite water suspensions.

| Suspension | The boehmite content in green compact (wt.%) | The $\gamma$-$Al_2O_3$ content in calcinated compact (wt.%) | The theoretical density of calcinated compact (g/cm$^3$) |
|---|---|---|---|
| B5 | 2.73 | 2.37 | 3.967 |
| B10 | 5.19 | 4.57 | 3.955 |
| B15 | 7.72 | 6.88 | 3.943 |

### The sintering kinetics of compacts prepared with and without boehmite addition

The sintering kinetics was evaluated from length - temperature dependences measured at non-isothermal conditions, namely at constant heating rates. Such non-isothermal kinetics is advantageous because of relatively high number of experimental data, small amount of specimen needed as well as simpler and faster measurements. With respect to the parameters of the available dilatometer, the sintering was provided only to 1250°C. This temperature limit enabled the densification from initial 60 % to 70.5-75.5 % of theoretical density only. Three heating rates of 2, 5 and 10°C/min were used in present experiments. The relative length - temperature dependences for both types of compacts are plotted in figure 4, where the effect of boehmite is illustrated at one heating rate.

For modelling of sintering kinetics following equation [16] was used

$$l_\tau = \sqrt[3]{l_0^3 - (l_0^3 - l_f^3)\frac{k\tau^n}{1+k\tau^n}} \qquad (2)$$

where $l_0$ is the sample length in time $\tau = 0$, $l_\tau$ is the actual sample length in time $\tau$, $l_f$ is the final length corresponding to the theoretical $\alpha$-$Al_2O_3$ density, $n$ is a para-meter independent on temperature (it is related to the sintering-controlled mechanism), $k$ a kinetic constant, which assumed to be dependent on temperature accor-ding to Arrhenius equation (3)

$$k = A\exp\left(-\frac{E}{RT}\right) \qquad (3)$$

where $A$ is a preexponential factor, $E$ the apparent activation energy, $T$ the absolute temperature. The time $\tau$ was calculated according to relation

$$\tau = \frac{t - t_0}{\beta} \qquad (4)$$

where $t$ is temperature in °C, $t_0$ is the temperature at which the densification begins and $\beta$ is a heating rate. It is not supposed any change either in sintering mechanism or in energy barrier of sintering, when the heating rate is changed in mentioned range (2-10°C/min). Therefore, all three dependences for each type of compact were evaluated together. The obtained results are presented in table 4.

Table 3. The relative densities and average particle size of sintered samples (1350°C/1 h; heating rate 10°C/min).

| Suspension | 20 min | | 60 min | |
|---|---|---|---|---|
| | Relative density (%) | Average particle size (nm) | Relative density (%) | Average particle size (nm) |
| B0 | 98,1 | 620 | 99,3 | 1020 |
| B5 | 98,9 | 560 | 99,1 | 1010 |
| B10 | 96,4 | 680 | 98,5 | 870 |
| B15 | 95,3 | 650 | 97,7 | 790 |

Table 4. The calculated parameters for non-isothermal sintering of compacts prepared by pressure filtration of B0 and B10.

| The parameters of the kinetic equation | Suspension | |
|---|---|---|
| | B0 | B5 |
| $A$ (s$^{-1}$) | $1.208{\cdot}10^9 \pm 0.091{\cdot}10^9$ | $2.964{\cdot}10^7 \pm 0.664{\cdot}10^7$ |
| $E$ (kJ/mol) | 277.6 ± 1.2 | 245.4 ± 1.9 |
| $n$ | 0.1164 ± 0.0013 | 0.1853 ± 0.0226 |
| $l_0$ ( m) | 3153.1 ± 0.3 | 4273.3 ± 0.1 |
| $t_{01}$ [2°C/min] (°C) | 962 ± 48 | 373 ± 296 |
| $t_{02}$ [5°C/min] (°C) | 963 ± 50 | 605 ± 122 |
| $t_{03}$ [10°C/min] (°C) | 966 ± 51 | 991 ± 3 |

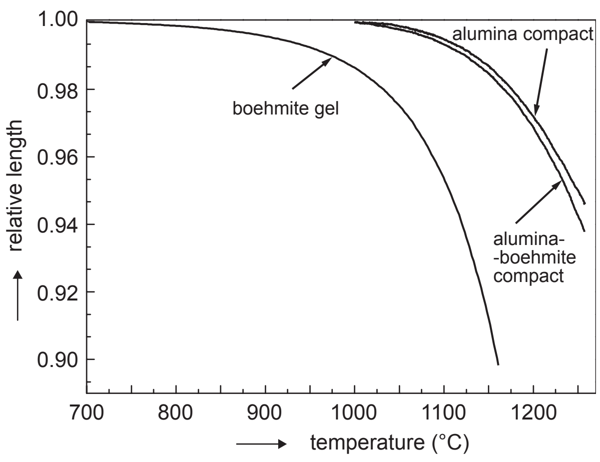


Figure 4. The experimental length - temperature dependences for compacts prepared from alumina - water suspension (B0) at heating rates 2, 5, 10°C/min.

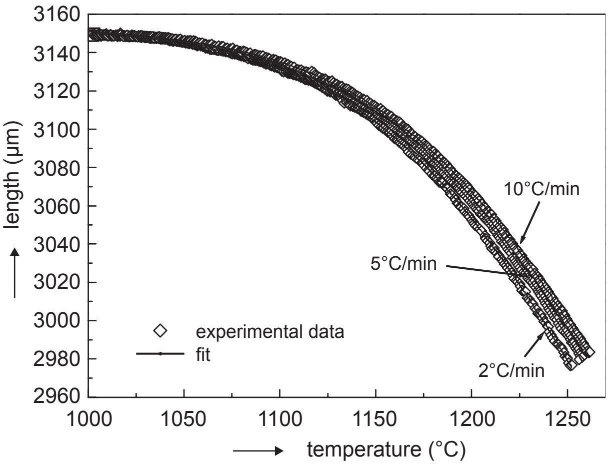


Figure 5. The experimental length - temperature dependences for compacts prepared from alumina - boehmite water suspension (B5) at heating rates 2, 5, 10°C/min.

The correlation of experimental and calculated length values is very good (0.99994 and 0.99987, respectively). In addition, plotted experimental and calculated dependences (figures 5 and 6) indicate that the fit using equation (2) is satisfactory. In term of comparing the sintering of the both compact types the parameters *E* and *n* are important. The values of n could be considered as very close. The activation energy of sintering for compact with small nanoparticle boehmite addition is slightly lower (245.4 kJ/mol) then for the compact without boehmite (277.6 kJ/mol).

## DISCUSSION

The enhanced handling strength of green compacts involves one of the advantages of using boehmite sol as a dispersant for alumina powders. Moreover, according to the result of kinetic analysis, the definite amount of boehmite (B5; 2.7 wt.% in green compact) affects positively the densification. The boehmite nanoparticles addition to alumina suspension results in lower energy barrier as can be seen from comparison of the apparent activation energy values.

The positive effect of boehmite nanoparticles is probably due to both different structure of transient alumina phases and their nanoparticle character with very high surface area. At heating, the transient alumina phases, raised from the boehmite particles, transform to α-alumina. The transient alumina phases sinter faster because of their defect structure. Moreover the driving force of sintering is enhanced because of higher surface area of nanoparticles. In consequence of transformation also the particle rearrangement contributing to densification may occur.

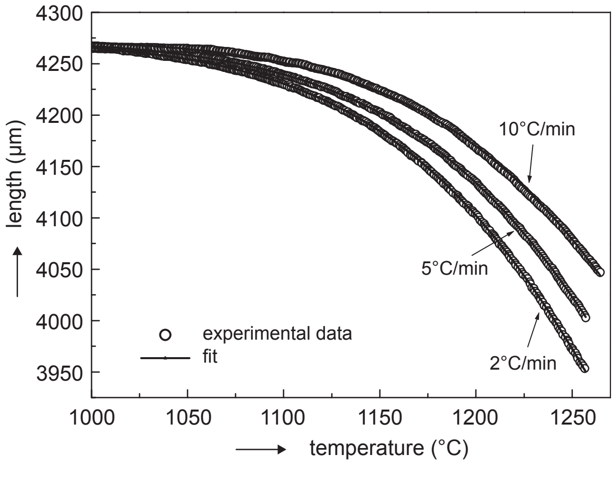


Figure 6. The experimental and calculated length - temperature dependences for compacts prepared from alumina - water suspension (B0) at heating rates 2, 5, 10°C/min.

Following these considerations the higher amount of boehmite in system should also positively affect the sintering. However, the sintered densities of samples prepared by pressure filtration from B10 and B15 (tables 3 and 4) are lower.

The understanding of present results comes out from the idea that boehmite acts primarily as a dispersant in the suspension (it coats and separates much larger alumina particles). According to the preliminary rough calculation based on average alumina and boehmite particle size, the 5 wt.% of boehmite in used sol is sufficient to cover the surface of alumina particles in suspension.

Whereas the suspension B5 exhibits Newtonian behaviour, the rheological character of B10 changes to pseudoplastic. Pseudoplastic behaviour corresponds to suspensions created by weakly attractive network of particles or by isolated clusters. Hence at higher boehmite content the flocculation of probably both alumina and boehmite particles occurs; this means that the suspension consists of weakly aggregates. Therefore, the higher viscosity and pseudoplastic behaviour of B10 is a result of the clusters formation.

At sintering the densification of the particles in cluster (aggregate) is preferred, then the later densification of the clusters requires more energy, which results in lower sintered density at the same sintering conditions comparing to the compacts with lower boehmite content (B5). This means that the nanoparticles influence positively sintering only within the clusters, which decreases the overall sinterability of the compact.

## CONCLUSION

The rheological behaviour of alumina - water suspension and alumina suspension in 5 % boehmite sol (B0, B5), showed to be Newtonian. The viscosity of suspensions with higher boehmite content was higher and decreased with increasing shear rate (pseudoplastic behaviour). This corresponds to weakly attractive clusters formation, which results in lower sintered density.

Boehmite nanoparticles act as a lubricant, a binder as well as a sintering aid, when presented in certain small amount (~ 2.7 wt.% in the compacts). The positive influence on sintering is evident only in case when boehmite nanoparticles only cover the surface of alumina and are not present as separate boehmite domains.

The kinetic analysis confirmed the positive effect of boehmite on sintering. The certain addition of boehmite nanoparticles decreases the sintering energy barrier of compacts prepared by pressure filtration. The positive influence is evident in both higher sinterability of transient alumina phases and the nanometer particle size.

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## KORUNDOVÁ KERAMIKA PRIPRAVENÁ TLAKOVOU FILTRÁCIOU PRÁŠKU $Al_2O_3$ DISPERGOVANÉHO V BÖHMITOVOM SÓLE

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Predmetom článku je príprava korundovej keramiky beztlakým spekaním kompaktov pripravených tlakovou filtráciou elektrostaticky stabilizovaných suspenzií. Stabilizácia suspenzií reguláciou medzičasticových síl zabraňuje tvorbe aglomerátov. Disperzným prostredím pre $Al_2O_3$ častice bol nanočasticový böhmitový sól, ktorý navyše pôsobí ako lubrikant, zvyšuje manipulačnú pevnosť surových kompaktov a tiež ich spekateľnosť. Kinetická analýza spekania potvrdila pozitívny účinok malého prídavku böhmitu (2.7 hm.% v surovom kompakte). Väčšie množstvo böhmitu má naopak negatívny efekt; spôsobuje flokuláciu suspenzií a pokles objemovej hmotnosti spekaných teliesok.