THE INFLUENCE OF THE PREFERRED ORIENTATION OF BOEHMITE CRYSTALLITES ON α-Al_2O_3 CRYSTALLIZATION

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Monolithic boehmite gels were prepared from commercial peptizable Condea product. The gels were modified by nanoparticle SiO_2 addition. Preferred orientation of boehmite crystallites in the gels and phase composition of sintered samples was observed by XRD analysis. To determine the effect of gel structure and eventually of SiO_2 addition on sintering and crystallization DTA, SEM and bulk density measurement were used. Boehmite crystallites align themselves spontaneously during gelation into preferred orientation state that can be avoided by ultrasonication or by the nanoparticle SiO_2 addition. The ordered or disordered gel microstructure has only marginal influence on high-temperature processes (crystallization, sintering). These processes are significantly influenced by addition of foreign SiO_2 nanoparticles, which decrease coordination of boehmite particles suppressing thus α-Al_2O_3 nucleation. Spread of SiO_2 on the surface of Al_2O_3 particles inhibits α-Al_2O_3 crystallization up to 1350°C.

INTRODUCTION

Boehmite, γ-AlOOH, is often employed as a precursor for preparation of catalysts, coatings, membranes and advanced alumina ceramics [1]. It is usually well peptizable, with particle size of a few nanometers. It is a by-product of petrochemical industry or it is obtained from aluminium alkoxide [2].

Particles of presently used boehmite are plate-like with plate length ~5 nm [3]. Different properties of each crystallographic plane in aqueous solution result in particle's interaction and preferred orientation. This results in fibers creation in solution, what is a reason of gelation in diluted boehmite dispersions (5-7 wt.%). Therefore it is not possible to prepare more concentrated dispersions than 18-20 wt.%. The preferred orientation of boehmite crystallites is even enhanced during gelation [3].

Preferred orientation of boehmite crystallites in monolithic gels was observed by Mange et al. [4], Popa et al. [5] using XRD technique. Primary plate-like crystallites are ordered in uniplanar arrangement with the (020) axis normal to the film layer.

Silica is known as a stabilizer of transient alumina phases. The stabilization effect depends on silica nature and its content. The mechanism of stabilization is not exactly explained yet. It is very possible that silica comes in intimate contact with alumina by surface diffusion [6].

The aim of this work was to investigate the effect of ordered or disordered gel microstructure on high-temperature processes of α-Al_2O_3 and mullite crystallization and subsequent sintering. Preferred orientation of boehmite crystallites takes place spontaneously so the microstructure disordering must be enforced. This can be accomplished by ultrasonication or by the addition of the foreign component, e.g. silica nanoparticles.

EXPERIMENTAL

Monolithic boehmite-SiO_2 gels (0, 1, 2, 3, 4, 5, 10, 20, 28 wt.% SiO_2 - sum of alumina and silica weights equal 100%) were prepared using commercial boehmite powder (Condea Pural SB, ~5 nm, Condea, Germany) and silica sol (Tosil, 30.wt % of silica, particles ~20 nm, TONASO Neštenice, Czech Republic). Water boehmite suspension was peptized by mixing with HNO_3 ($pH \cong 2.5$) at 55°C. Unpeptized part of boehmite was removed from the sol by centrifugation (9000 rpm, 10 min). Then the calculated amount of the silica sol was slowly added into the mixed dispersion of boehmite. The sol was poured onto a plastic plate. Thin layer of sol (2 mm) was gelled in about 20 min. A gel was allowed to dry at room temperature for 3 days, cracking spontaneously to planar fragments (1-3 cm^2) in a final stage of drying.

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Two another gels - boehmite gel with 3 wt.% SiO_2 with a particle size of 640 ±60 nm and pure boehmite gel, which was gelled during ultrasonication in a closed vessel above saturated $CaCl_2$ solution were prepared. These SiO_2 particles were prepared by sol-gel method using tetraethoxysilane (Fluka) as a precursor.

XRD analysis observed by Stoe θ/θ Difractometer-System STADIP was used to investigate the particle arrangement in dependence on composition and heat treatment in boehmite and boehmite-SiO_2 monolithic gels and also to determine the phase composition of sintered samples. The particle arrangement was observed on monolithic gels with thickness of 1 mm and diameter of 12 mm. The difractograms of monoliths were recorded with the incident beam normal to the monolithic plate. The first measurement was made after drying monolithic gels at room temperature (RT) and further after heating to 200, 400, 500°C at heating rate 10°C/min with holding time 15 min. The phase composition of sintered samples heated to 1340°C and to 1440°C at heating rate 10°C/min, without holding time was determined by standard XRD powder analysis. Preferred orientation was qualitatively evaluated by the comparison of the ratios of integral intensities of the boehmite diffraction lines (020) and (120).

α-Al_2O_3 and mullite crystallization temperatures in dependence on gel composition were examined by DTA, sdt 2960 (T.A.Instruments), up to 1440°C at a heating rate of 10°C/min. Dried and calcinated powders prepared from gels in amount of 20 mg were used for this measurement. Bulk density of sintered samples was measured on the principle of Archimedes law. The microstructure of fracture surfaces was observed by SEM (Tesla BS 300).

RESULTS

X-ray diffractograms of some monolithic gels after heating to 400°C (below the decomposition temperature of boehmite) given on figure 1 are characterized by the strong enhancement of the (020) peak intensity. This is manifestation of the preferred orientation of boehmite crystallites as described also in [4, 5]. The diffractograms indicated orientation of particles are the same for temperatures in the range RT - 400°C.

The most preferred orientation of boehmite crystallites in gels is gradually lost by increase of silica content. At 3-4 wt.% content of silica the difractograms are closer to the boehmite powder than to the boehmite gel. After the boehmite decomposition to γ-Al_2O_3 (500°C) there is no oriented arrangement of particles as is evident from figure 1.

As figure 2 shows, alignment of boehmite crystallites in diphasic AlOOH-SiO_2 gels depends on the size of silica particles. 3 wt.% of SiO_2 particles with particle size ~20 nm canceled oriented arrangement of boehmite crystallites, whereas the same amount of ~640 nm SiO_2 particles have no influence on crystallite orientation. If boehmite sol is gelled during ultrasonication by drying with saturated $CaCl_2$ solution, no oriented arrangement occurs, as is documented in figure 2.

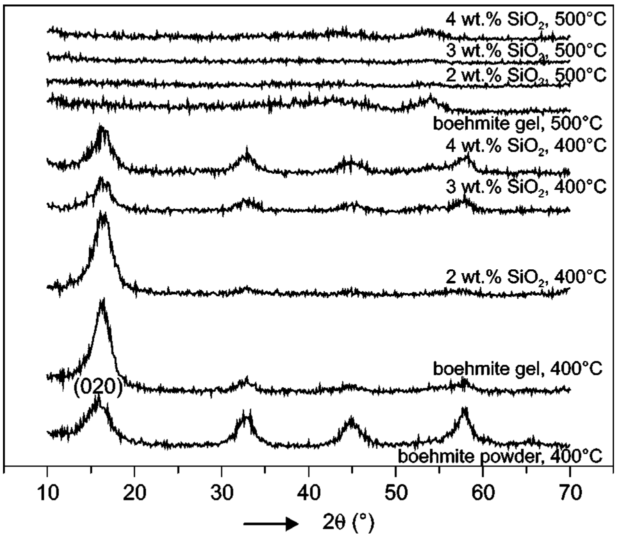


Figure 1. X-ray diffractograms of boehmite powder and gels (without and with SiO_2 addition) after heating to 400°C eventually to 500°C.

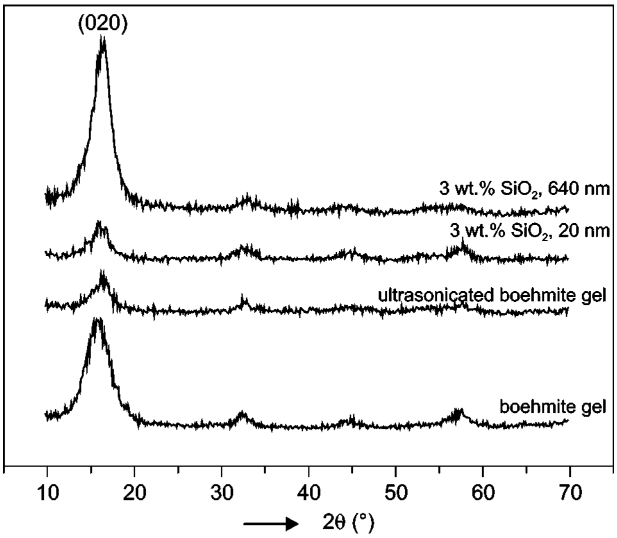


Figure 2. X-ray diffractograms of boehmite gel with 3 wt.% of SiO_2 addition (particle size of SiO_2 is ~20 and ~640 nm) and boehmite gel prepared by routine method and boehmite gel gelled during ultrasonification after heating to 400°C.

Crystallization temperature of α-Al_2O_3 and mullite in diphasic gels is well documented by DTA curves in figure 3. Exothermic peaks were assigned to α-Al_2O_3 or mullite crystallization according to the XRD analysis (figures 4, 5) after heating of the separate samples to 1340°C and 1440°C (the same heat treatment as by DTA). α-Al_2O_3 crystallization temperature increased gradually with increasing amount of SiO_2 up to 1367°C at 3 wt.% SiO_2. Mullite crystallization is recorded using DTA already at 10 wt.% of SiO_2. It is necessary to note that mullite crystallized at lower temperature (1327°C) than α-Al_2O_3 (1356°C). At higher SiO_2 addition, only mullite crystallization is recorded.

Table 1. Phase composition (XRD analysis) and temperature effects (DTA) of samples after heating to 1440°C at a rate of 10°C/min.

% SiO_2	Phases after heating		Temperature effects (DTA)
	to 1340°C (XRD)	to 1440°C (XRD)	
0	α-Al_2O_3	α-Al_2O_3	1178°C
1	α-Al_2O_3	α-Al_2O_3	1214°C
2	α-Al_2O_3	α-Al_2O_3	1245°C
3	α-Al_2O_3; δ-, θ-Al_2O_3	α-Al_2O_3, mullite	1367°C
4	δ-, θ-Al_2O_3	α-Al_2O_3, mullite	1364°C
5	δ-, θ-Al_2O_3, mullite	α-Al_2O_3, mullite	1360°C
10	mullite, θ-, α-Al_2O_3	α-Al_2O_3, mullite	1327°C, 1356°C
20	mullite, θ-Al_2O_3	mullite, θ-Al_2O_3	1316°C
28	mullite	mullite	1320°C

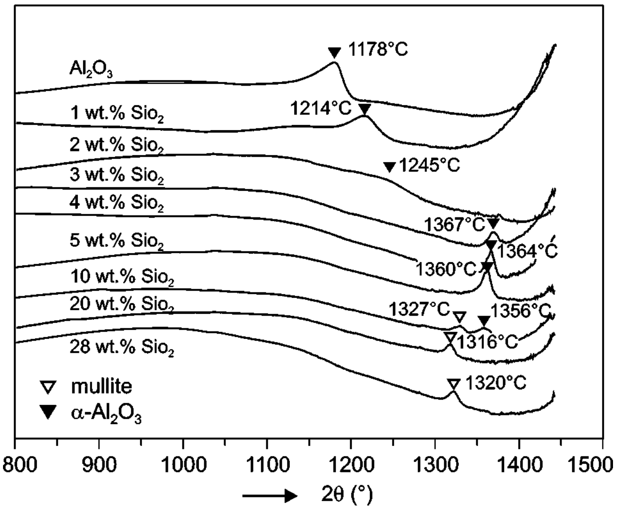


Figure 3. DTA of boehmite and boehmite-SiO_2 gels calcinated at 550°C.

Bulk density measured at room temperature after heating to 1440°C at the same heating as in DTA experiments in dependence on SiO_2 content showed three characteristic areas (figure 6). In the first area SiO_2 retards sintering of Al_2O_3, in the second SiO_2 accelerates the sintering process and in the third the bulk density increases continuously with increased mullite content in system.

As figure 7 shows, the disordered gel structure caused by ultrasonication during gelation has no influence on α-Al_2O_3 crystallization. On the other hand, as it was shown, the effect of SiO_2 particle size is dominant (figure 7, table 2). The relative densities of these gels after heating to 1440°C are showed in table 2.

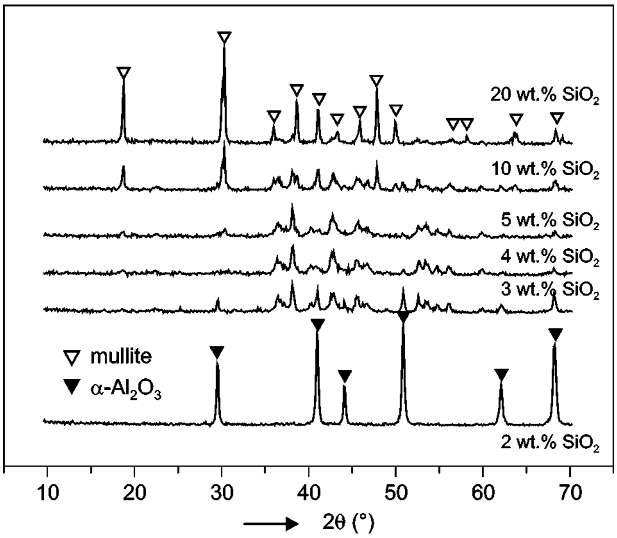


Figure 4. X-ray diffractograms of samples after heating to 1340°C at a rate of 10°C/min.

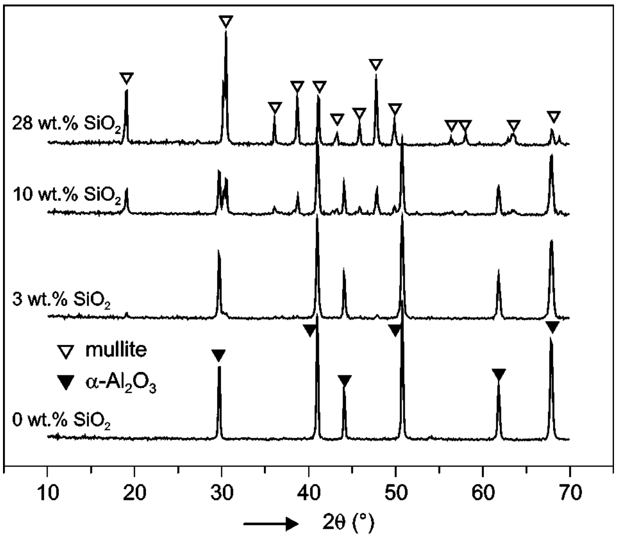


Figure 5. X-ray diffractograms of samples after heating to 1440°C at a rate of 10°C/min..

Table 2. Relative densities (actual density divided by theoretical density) of samples after heating to 1440°C at a rate of 10°C/min.

Type of gel	Boehmite gel	Boehmite gel gelled during ultrasonification	Boehmite gel (3 % SiO_2, ~20 nm)	Boehmite gel (3 % SiO_2, ~640 nm)
Relative density (%)	75.2	74	83.4	74

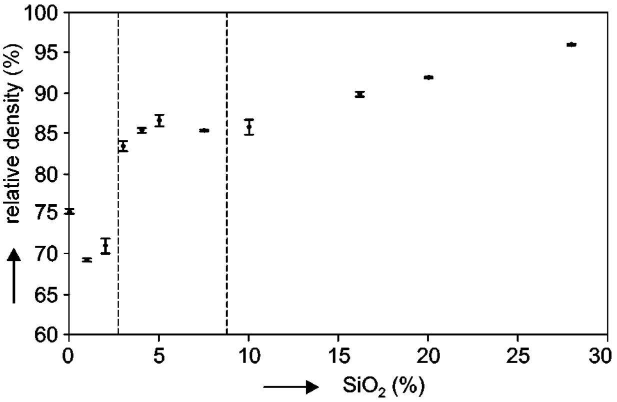


Figure 6. Relative densities of gels heated to 1440°C at a rate of 10°C/min.

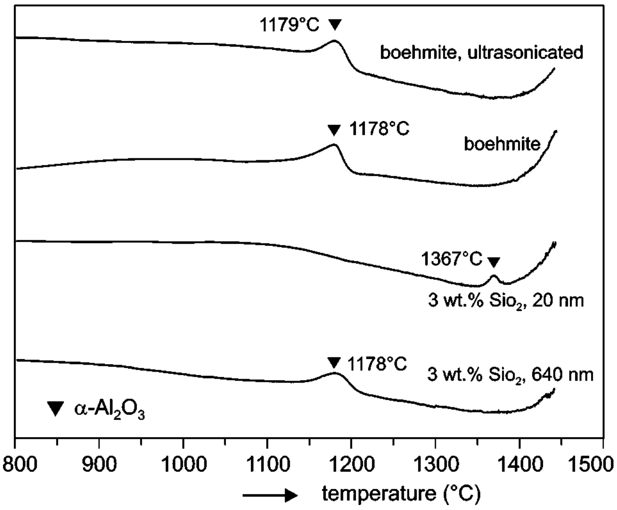
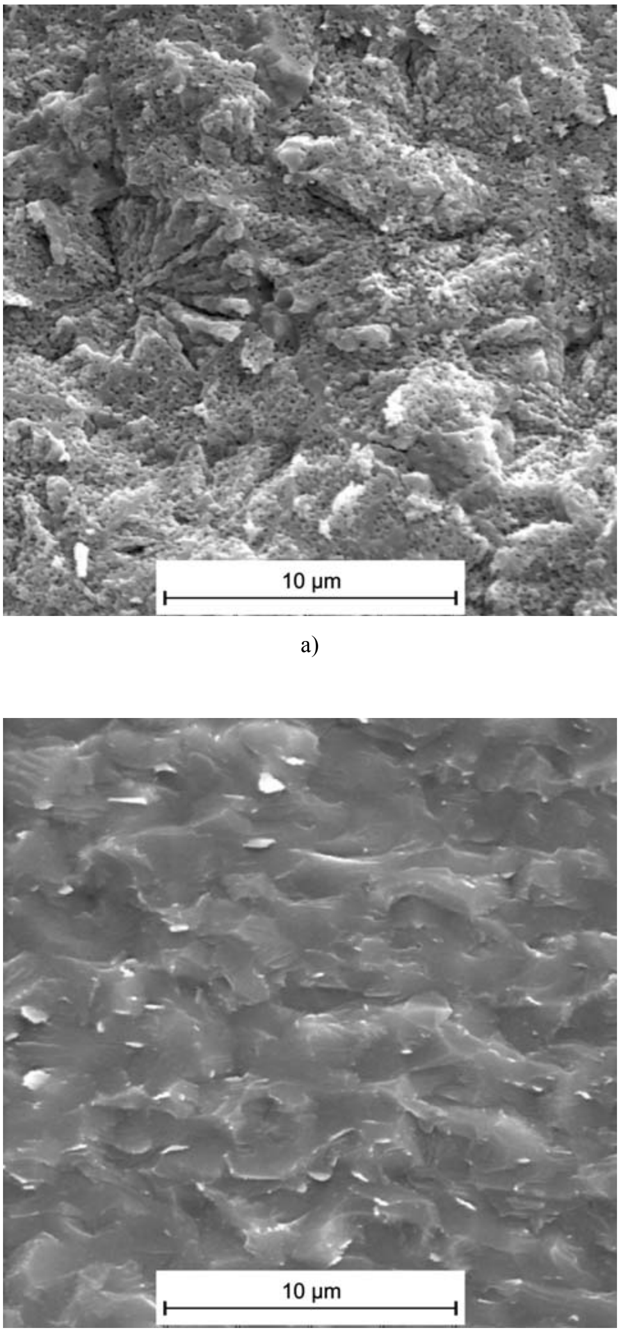


Figure 7. DTA curves of boehmite gels and boehmite gels with 3 wt.% of SiO_2 calcinated at 550°C.

SEM micrographs show microstructures (fracture surfaces) of pure boehmite gel and boehmite gels with 28 % of SiO_2 after heating to 1440°C (figure 8). The microstructure of fractured surfaces varies continuously with increased SiO_2 content from known vermicular porous microstructure [11], which vanishes at 3 % of SiO_2 and at 28 % of SiO_2 up to characteristic dense mullite microstructure (figure 8D).



a)

b)

Figure 8. SEM micrographs of boehmite gel (a), boehmite gel with 28 wt.% SiO_2 - mullite (b) heated to 1440°C at a rate of 10°C/min.

DISCUSSION

The interactions between plate-like boehmite crystallites cause bonding of these crystallites to fibers in sol and also their preferred orientation in gels [3, 4, 5]. In this work we focused on the effect of preferred crystallite orientation on high-temperature processes. To avoid this preferred orientation we applied either ultrasonication during sol gelation, or the addition of SiO_2 nanoparticles (~20 nm) to the sol.

Our results show that spontaneous preferred orientation in gels has no influence on high-temperature processes - crystallization and sintering. Pure boehmite gel with ordered or disordered gel microstructure crystallizes (α-Al_2O_3) and sinters to material with the same properties (bulk density, microstructure).

When the gel microstructure is disordered by SiO_2 nanoparticles at least 3 wt.% the high temperature processes are significantly influenced. It means, that the high-temperature processes are influenced not by crystallite orientation but by the presence of foreign particles in a system in our case SiO_2. The presence of these particles increases α-Al_2O_3 crystallization temperature from 1178°C without SiO_2 to 1367°C with 3 wt.% of SiO_2. Thus SiO_2 addition enhanced the stability of transient Al_2O_3 phases at high temperatures, which creates possibility to utilize this effect in catalysis [7] and Al_2O_3 fibers preparation [8].

The influence of colloidal SiO_2 particles can be divided into several areas. While boehmite crystallites are positively charged in sol (*pH* ~3) [9], SiO_2 particles have negative charge in utilized solution (*pH* ~9,5) [10]. This leads to their mutual attachment after mixing the sols. Boehmite crystallites in boehmite sol without any addition are ordered into parallel orientation. SiO_2 particles in boehmite sol caused creating of the structure likely comprised of relative large SiO_2 particles with several smaller plate-like boehmite crystallites attached by the crystallographic plane with the highest surface energy [14]. Such attachment of boehmite crystallites on surface of SiO_2 was assumed according to the surface properties of boehmite crystallites. Thus single-phase continuous "complex" sol $(AlOOH)_x$ - $(SiO_2)_{1-x}$ arises from two-phases sol (AlOOH, SiO_2).

The effect of SiO_2 can be treated therefore as steric up to the temperature high enough for ionic diffusion. Even though a certain motion of particles (particle reorganization) occurs during initial stage of sintering, the identity and mutual coordination of SiO_2 and Al_2O_3 particles do not change at least up to 1000°C only the separation distance decreases.

It is known that α-Al_2O_3 nucleation depends on boehmite particle coordination in gel [11]. SiO_2 nanoparticles decrease definitely this coordination hence the nucleation and crystallization of α-Al_2O_3 is significantly shifted to higher temperatures.

At the temperatures higher than 1100°C we can suppose a spread of SiO_2 nanoparticles on the surface of Al_2O_3 particles. It means that steric effect is shifted to the field of boundary area in accordance with work [12]. The thickness of glassy grain boundary phase increases with increased amount of SiO_2 in system and this leads to primary crystallization of mullite even before α-Al_2O_3 crystallization (figure 3). This result is not consistent with the work [13].

Initial steric effect of SiO_2 is dominant for processes in the entire temperature range, RT-1440°C. The influence of SiO_2 particles on coordination of boehmite crystallites in gels and also on high-temperature processes decreases with increased particle size. By adding 3 wt.% SiO_2 (~640 nm) no influence was observed, neither on preferred orientation of boehmite crystallites nor on crystallization and sintering processes (figure 1). In this case phase transformation of Al_2O_3 occurred before spreading of SiO_2 due to longer diffusion way.

CONCLUSIONS

Boehmite crystallites show preferred orientation in monolithic gels, which vanished during boehmite decomposition (~450°C) to γ-Al_2O_3. The preferred orientation is prevented by adding at least 3 wt.% of SiO_2 nanoparticles or by ultrasonication during gelation.

The arrangement of boehmite crystallites has only marginal influence on their crystallization and sintering. These processes can be significantly influenced by SiO_2 nanoparticles, which decrease the coordination of boehmite crystallites and so enhance the crystallization temperature of α-Al_2O_3. SiO_2 particles of the size ~640 nm does not affect the coordination of ~5 nm boehmite crystallites, therefore no changes in high-temperature processes were observed by their addition.

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VLIV PŘEDNOSTNÍ ORIENTACE BOEHMITOVÝCH KRYSTALITŮ NA KRYSTALIZACI α-Al_2O_3

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Monolitické boehmitové gely byly připraveny z komerčních peptizovatelných produktů firmy Condea. Gely byly modifikovány přídavkem nanočástic SiO_2. Přednostní orientace boehmitových krystalitů v gelech a fázové složení sintrovaných vzorků bylo sledováno rtg difrakční analýzou. Ke zjištění vlivu struktury gelu a případně i přídavku SiO_2 na sintrování a krystalizaci byly použity metody DTA, SEM a měření objemové hmotnosti. Boehmitové krystality se samovolně uspořádávají během gelace do přednostně orientovaného stavu, čemuž lze zabránit účinkem ultrazvuku nebo přídavkem nanočástic SiO_2. Uspořádaná nebo neuspořádaná mikrostruktura gelu má jen okrajový vliv na vysokoteplotní procesy (krystalizace, sintrování). Tyto procesy jsou významně ovlivněny přídavkem cizorodých nanočástic SiO_2, který snižuje koordinaci boehmitových částic a tak potlačuje nukleaci α-Al_2O_3. Rozptyl SiO_2 na povrchu částic Al_2O_3 inhibuje krystalizaci α-Al_2O_3 až do 1350°C.