THE SINTERING OF BOEMITE GEL

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The sintering of the compact gel prepared by peptization of boemite begins at 920 °C and involves conversion of θ-Al₂O₃ to α-Al₂O₃. The bulk density of gels sintered at temperatures up to 1350 °C decreases linearly with the degree of the θ-Al₂O₃ to α-Al₂O₃ conversion. The arising α-Al₂O₃ interferes with the sintering of the system over the temperature range studied (up to 1350 °C).

INTRODUCTION

The sol-gel method has been finding wide application in the preparation of oxidic materials with properties unattainable by classical processes, namely purity, precise chemical composition, homogeneity and a defined microstructure [1, 2]. The method is based on preparing sols of oxidic, hydroxidic or oxihydroxidic particles. This colloidal state of particles is generally attainable in two ways:

1. The use of true solutions of organometallic compounds, mostly alkoxides of metals, and creation of conditions for their hydrolysis and polycondensation [3]. In terms of the respective conditions, the system yields spatially branched, so-called fractal particles or those approaching the spherical shape [4]. In this way the true solution is converted to a colloidal one — i.e. a sol.

2. The coarsely dispersed system is converted to a colloidal solution by peptizing. During the course of the process, the aggregates of the particles break down to primary, originally colloidal particles [5]. The process is therefore the reverse of the former case, as the particles do not grow but are diminuted. The coarsely dispersed particles, aggregates, are obtained by rapid reaction of the alkoxide with excess water (up to 100-fold stoichiometric amount of water) at elevated temperature (50—90 °C) [6].

The possibility of choosing the process depends on the properties of the alkoxide of the respective elements from which a sol of its oxide is to be prepared. The decisive role is played by the rate of the hydrolysis and polycondensation of the respective alkoxide. The other procedure is only practicable with high rates of the conversion e.g. Al(OR)₃, Y(OR)₃ [6].

The boemite sol is mostly prepared by peptization of boemite which is a by-product of the manufacture of higher alcohols by Ziegler's method [7—9]. This product is an equivalent of hydrolyzates obtained from aluminium alkoxides.

Boemite gels are studied in relation with their practical application in the form of thin layers [10], ceramic diaphragms [11], grinding grains [12], catalyst carriers [13, 14] and ceramic powders [15].

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As the boemite gel consists of primary particles about 10 nm in size [9], it could be expected to sinter extensively at temperatures as low as 1100—1300 °C. However, practice shows [6—9] that without additions, the boemite gel sinters only at about 1600 °C, forming a substance approaching the theoretical density. The process involves great changes in volume which make the boemite gel unsuitable for the production of bulky corundum ceramics.

Heating up of boemite gel involves a series of topotactic phase conversions of \( \text{Al}_2\text{O}_3 (\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha) \) [16]. The present study is aimed at investigating the effect of \( \theta \cdot \text{Al}_2\text{O}_3 \rightarrow \alpha \cdot \text{Al}_2\text{O}_3 \) conversion on sintering at medium temperatures of up to 1350 °C.

**EXPERIMENTAL**

**Preparation of the boemite gel**

Use was made of powdered boemite (Condea-FRG) with a specific surface area of about 250 m² g⁻¹ and aggregate (cluster) sizes of less than 60 µm. The clusters comprise primary particles about 10 nm in size. Boemite of such properties is known [5] to peptize in an acidic medium (HNO₃, HCl, CH₃COOH, pH = 2 to 3), producing hydrosol. Its stability and the course of the peptization depend on temperature, intensity of agitating the dispersions, on boemite concentration and the type and concentration of the acid employed.

The boemite gels were prepared at 50 °C. The nitric acid (63 wt. %) was added dropwise while stirring the dispersion extensively. The stability of the sol (the time of gelation) is affected above all by the concentration of the acid, or by the ratio \( p = \text{HNO}_3 : \text{AlO(OH)} \) (Fig. 1). The stability of the sol decreases with the increasing ratio. The sol prepared contains approximately 2 wt. % of non-peptized particles which are separated from the system by centrifugation.

![Fig. 1. Time of gelation of the boemite sol vs. its concentration c (wt. % AlO(OH)) and weight ratio \( p = \text{HNO}_3 (63 \text{ wt. %})/\text{AlO(OH)} \), peptization at 50 °C, agitated dispersion.](image-url)
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With respect to the goals of this study and the times allowed for handling, sols containing 20 wt. % AlO(OH) with the ratio \( p = 0.06 \) were found suitable, as their gelation took approximately 40 minutes (Fig. 1). The gelation of the sols took place in Petri dishes on micropolythene sheets.

The gel disks obtained (about 11 cm in diameter and 1.2 cm in thickness) were dried for 10 days freely in air; during that time their weight and volume decreased approximately to half. Further drying under these conditions is very slow. During three months, the additional decrease of weight and volume amounts to only 4 \%. Still longer drying of the gel leads to losses in weight without any shrinkage [17].

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The compact boemite gel was sintered for 1 hour at 1350 °C following previous isothermal heating in the temperature range of \( \theta - \text{Al}_2\text{O}_3 \) to \( \alpha - \text{Al}_2\text{O}_3 \) conversion. As the study was aimed at studying the transformation proper, longer times of sintering were not needed. In agreement with the literature [16, 18], X-ray phase analysis proved that in the given system, \( \alpha - \text{Al}_2\text{O}_3 \) is formed from \( \theta - \text{Al}_2\text{O}_3 \).

The gel was sintered directly in the DTA apparatus (Netzsch 404) which allowed both the sintering and conversion to be quantified on the same specimens. The principle of the method for determining \( \alpha - \text{Al}_2\text{O}_3 \) is similar to the DTA method for establishing the nucleation of crystalline phases in glasses [19, 20]. One has to determine the height or the area of the exothermic DTA peak due to crystallization of \( \alpha - \text{Al}_2\text{O}_3 \) in terms of the time of the previous isothermal heating. The method is illustrated by Fig. 2. The gel is heated in the DTA apparatus so as not to disturb its integrity, namely at a rate of 5 °C per minute, up to 500 °C, at a rate of 10 °C between 500 and 1000 °C, and at a rate of 20 °C per minute above 1000 °C.

As the isothermal heating temperature (e.g. 1060 °C, 1080 °C) is close to the onset of the exothermic peak (1100 °C), the temperature is rapidly reduced down to the designated value, i.e. 1040 °C.

![Fig. 2. DTA of boemite gel, isothermal heating at 1040 °C for 3 hours.](image)

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to 1000 °C and from that level the DTA is restarted at a rate of 20 °C per minute. The increased heating rate allows the crystallization of α-Al₂O₃ between the isothermal heating temperature and the onset of the exothermal deflection to be neglected. If the isothermal heating is effected at temperatures below 1000 °C, the DTA is started at a rate of 20 °C per minute directly from this temperature.

The temperatures and times of isothermal heating were chosen so as to achieve the alumina conversion to the fullest possible degree during less that 15 hours. In this respect, the suitable temperatures were 1040°, 1060° and 1080 °C. At temperatures above 1080 °C, the conversion is too rapid and below 1040 °C it is too slow for the measuring method employed. As specimens with identical shape and weight were used in all the experiments (cylinders with a volume of about 0.2 cm³ and \( m = 0.3700 \pm 0.0002 \) g), similar DTA curves as regards shape and position of peaks were obtained at a constant peak temperature of 1195 ± 5 °C; the peaks differed in their height only (Fig. 3). The conversion degree was determined by measuring the height and area of these exothermal peaks [21] and verified by quantitative X-ray phase analysis. Under the constant measuring conditions and the relatively large weights of the specimens (0.3 g), the height of the DTA peaks was in satisfactory agreement with the results of quantitative X-ray phase analysis. In the present case, the measuring of peak height was therefore justified as a sui-

Fig. 3. Exothermal DTA peaks due to crystallization of α-Al₂O₃ (conversion of ω-Al₂O₃ to α-Al₂O₃) after isothermal heating at 1040 °C for 0, 1, 2 and 3 hours respectively.
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table method for determining the conversion of $\theta \rightarrow \alpha$-$\text{Al}_2\text{O}_3$ during isothermal heating according the simple equation:

$$\alpha_i = \frac{h_0 - h_i}{h_0},$$  

(1)

where $h_0$ is the height of the exothermal peak due to crystallization of $\alpha$-$\text{Al}_2\text{O}_3$ ($\theta \rightarrow \alpha$-$\text{Al}_2\text{O}_3$ conversion) without isothermal heating, and $h_i$ is the height of the peak during the $i$-th isothermal heating.

The density of the specimens was determined after conclusion of the complete DTA and sintering for 1 hour at 1350 °C, or only after isothermal heating, by measuring the buoyancy of specimens immersed in mercury.

RESULTS AND DISCUSSION

Following isothermal heating at 1040 °C, 1060 °C and 1080 °C, the bulk density of boemite gel increases in terms of time (Fig. 4) to an approximately equal value of $2.2 \times 10^3$ kg m$^{-3}$ for all the three temperatures. It is interesting to note that this value was approached from above by bulk densities of gels which had been subject to isothermal heating and subsequent sintering at 1350 °C. The highest bulk density of $2.95 \times 10^3$ kg m$^{-3}$ (75 % of theoretical density) was exhibited by a specimen which had been sintered directly without any isothermal heating. The isothermal heatings before the sintering proper are therefore responsible for a decrease of the resultant bulk density. The gels which had been heated isothermally for the longest periods of time (2 hrs - 1080 °C, 5 hrs. - 1060 °C and 13 hrs - 1040 °C) did not virtually change their bulk density, not even after subsequent sintering at 1350 °C. The bulk densities of these specimens

Fig. 4. Bulk density $p_p$ vs. temperature and time of isothermal heating.
1 — (curves a, b, c — isothermal heating) a — 1040 °C; b — 1060 °C; c — 1080 °C and sintering for 1 hour at 1350 °C in the DTA apparatus.
2 — (curves d, e, f — isothermal heating only) d — 1040 °C; e — 1060 °C; f — 1080 °C.
are very similar but their microstructure is quite different. Following isothermal heating, these specimens contain approximately 45% of pores by volume. According to mercury porometry (Carlo Erba, type 1520) all the pores have radii smaller than 5 nm. In contrast to this, the specimens sintered subsequently at 1350 °C contained an approximately identical volume of pores, but their size was substantially larger, as the radii attained up to 200 nm. The result was also proved by the scanning electron microscope (Tesla BS-300) (Figs. 7 and 8). The fracture surface of sintered specimens (Fig. 8) exhibits pores of approximately the same size. The micrographs are characterized by occurrence of vermicular structural formations which are also mentioned in [7]. During the isothermal heating, the formations appear just as nuclei (Fig. 7). Some nucleation of vermicular formations probably takes place during the isothermal heating.

Crystallization of α-Al₂O₃ or conversion of 0-Al₂O₃ to α-Al₂O₃ takes place during isothermal heating. The degree of the conversion increases with temperature and the time of holding (Table I).

**Table I**

<table>
<thead>
<tr>
<th>Crystallization of α-Al₂O₃ (conversion — (α) of 0-Al₂O₃ — α-Al₂O₃) in boemite compact gel vs. temperature and time of isothermal heating</th>
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The bulk density of sintered specimens decreases linearly with conversion during isothermal heating (Fig. 5). From this finding it follows that the sintering is slowed down by increasing conversion, i.e. by an increasing content of α-Al₂O₃ in the specimens, being completely terminated as soon as the specimen contains α-Al₂O₃ alone.

According to the results described, boemite gel should sinter extensively at temperatures below about 1100 °C only if the crystallization of α-Al₂O₃ would not take place at the same time.

With this in mind, the authors carried out isothermal heating at gradually lower temperatures (1020°—500 °C). The isothermal heating was followed by sintering for 1 hour at 1350 °C. The isothermal heating took at the most 20 hours.

Fig. 6 and Table I indicate that although the bulk density increases with the decreasing degree of conversion, as soon as the conversion approaches zero, the increase in apparent density will virtually stop for reasons of kinetics. From this it follows that the sintering of 0-Al₂O₃ is directly associated with its conversion to α-Al₂O₃.
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**Fig. 5.** Bulk density \( \rho_v \) of originally boemite gel after isothermal heating and sintering (Fig. 4) vs. degree of \( \alpha \) conversion \((\theta-Al_2O_3 \rightarrow \alpha-Al_2O_3)\) during isothermal heating \((1040^\circ C, 1060^\circ C \text{ and } 1080^\circ C)\).

**Fig. 6.** Bulk density and conversion degree \((\theta-Al_2O_3 \rightarrow \alpha-Al_2O_3)\) in the originally boemite gel vs. temperature of isothermal heating over the range of 500 to 1080 \(^\circ\)C under constant sintering parameters of 1 hour at 1350 \(^\circ\)C.

CONCLUSION

The sintering of boemite gel in compact state begins at about 920 \(^\circ\)C when the material consists of the \(\theta-Al_2O_3\) phase. The sintering process involves conversion of \(\theta-Al_2O_3\) to \(\alpha-Al_2O_3\). The increasing degree of conversion due to isothermal
heating over the range of 960—1080 °C will slow down or completely terminate the sintering process up to the temperature of 1350 °C. Under these conditions, the material is densified solely as a result of the sintering of α-Al₂O₃. Up to the limit temperature investigated, 1350 °C, the α-Al₂O₃ virtually failed to sinter in the original boehmite compact gel. The sintering is connected with a distinct increase in pore size (the radii increase from 5 to 200 nm) without exhibiting any substantial change in volume.

References


SPEKANIE BÔHMITOVOHO GÉLU
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Bôhmítové gely pripravené sôl-gel procesom sa študujú v súvislosti s ich praktickými aplikáciami vo forme tenkých vrstiev [10], keramických membrán [11], brúsnych zín [12], nosičov katalyzátorov [13, 14] a keramických práškov [15].

Práca je zameraná na sledovanie vplyvu konverzie θ-Al₂O₃ → α-Al₂O₃ na spekanie pri stredných teplotách do 1350 °C.

Bôhmítový sôl (20 % hmot.) sa pripravoval peptizáciou bôhmítového prášku zn. Condea (250 m² g⁻¹) kyselínou dusičnou pri teplote 50 °C za intenzívneho mišania (obr. 1).

Konverzia θ-Al₂O₃ → α-Al₂O₃ a spekanie kompaktného gélu (sušený 10 dní na vzduchu) sa sledovali priamo pomocou DTA prístroja (Netzsch 404) (obr. 2). Používali sa tvarove (valceky ~0,2 cm³) a hmotnostne (0,3170 ± 0,0002 g) rovnaké vzorky. Ako sa potvrdilo rtg-fazovou analýzou, za podmienok merania, konverziu θ → α-Al₂O₃ je možné sledovať pomocou výšok (rov. (1)) exotermických DTA výhybek kryštalizácie α-Al₂O₃ (obr. 2, 3).

Spekanie kompaktného gélu začína pri teplote ~920 °C a je bezprostredne sprevádzané konverziou θ → α-Al₂O₃. Konverziu — narastaním podielu α-Al₂O₃ vo vzorkách spekanie ma—
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In our laboratory we studied gels of boehmite. We investigated the conversion of the gel (by the sintering method, 10% of boehmite) in the temperature range from 500°C to 1080°C. We also studied the sintering process at constant temperature for 3 hours. The gel was prepared from boehmite powder (20% by weight of Al₂O₃) and water. The gel was then heated in a furnace at temperatures ranging from 500°C to 1080°C. The results were analyzed using X-ray diffraction and scanning electron microscopy.

We found that the conversion of boehmite to 

α-Al₂O₃ (conversion 100%) occurs at temperatures above 1040°C. The sintering process is accompanied by a decrease in the specific surface area of the gel and an increase in its density. The sintering process is accompanied by a change in the microstructure of the gel, which is characterized by the formation of 

α-Al₂O₃ crystals.

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Kníha obsahuje tri samostatné kapitoly, z ktorých prvá (73 strán) je venovaná problematike syntézy diamantu a kubickeho nitridu boru účinkom razovej vlny. Pozornosť je proprie fyzike razovej vlny a jej generovania najmä fazovým premenám grafitu a hexagonalneho nitridu boru pri účinkoch razovej vlny, ktorých znalosť umožňuje optimalizáciu experimentálnych podmienok v smere zvýšenia velkosti rozmerov produktov a ich výtažkov.

Druhá kapitola (38 strán) pojednáva o termokapilárnom prudení v taveninách a jeho vplyvu na podmienky rastu monokrystalov. Vplyv prudenia vyvolaného gradientom povrchového napätia sa prejavuje najmä v malých objemoch taveniny (nap.: pri pestovani tvarovaných monokrystalov - Si pašky), v blizkosti voľných povrchov veľkého objemu taveniny alebo pri pestovani monokrystalov v bezbiažovom stave.

Posledná kapitola (80 strán) sa zaobiera elektrooptickými vlastnosťami kryštálov. V úvodnej časti sa diskutujú fyzikálne aspekty určujúce veľkosť elektrooptických efektov a experimentálne metódy ich merania. Látkovo sú zahrnuté skupiny kryštálov ABO₃ (perovskity), tetragonálne bronzy (AₓBₓCₓR₁₀₀₀₉₀), ionové kryštály obsahujúce molekulárné skupiny (KH₃PO₄—KDP) a polovodiče (Si, Ge, AB zlúčeniny). Hlavná pozornosť je zameraná na rôzne typy elektrooptických modulátorov a na nové poznatky z oblasti ich prípravy. Záverom sa vysvetľujú javy elektrooptickej bistability, elektroabsorpcie a fotorefraktivného efektu ako základu holografickej pamäti.

Už z podtitulu knihy je zrejmá špecifickosť jednotlivých kapitol, ktoré naprieč tomu, že sú písané zrozumiteľnou formou a pri štátase z menej priľahlých oblastí, nájdú uplatnenie predošvetkým v okruhu špecialistov a to nielen vlastným textom ale aj prostredníctvom literárnych odkazov (v 1. kapitole 242, v 2. 162 a v 3. 238). Kníha je vhodná ako zdroj sústredených informácií aj pre tých, ktorí sa rozhodli aktívne vstúpiť do niektorého z uvedených oblastí.
Fig. 7. Fracture surface of gel during isothermal heating at 1040 °C for 13 hours.

Fig. 8. Fracture surface of gel after isothermal heating for 13 hours at 1040 °C and sintering for 1 hour at 1350 °C.