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Influence of different amounts of hematite seedings on the temperature of phase transformation of transition aluminas into corundum¹

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Abstract

Corundum (α -Al₂O₃) is the only stable oxide in the aluminium–oxygen system and is characterized by its high mechanical and chemical stability. But there are some problems in producing very fine corundum powders. Usually α -Al₂O₃ is obtained from transition aluminas at temperatures in the range of 1100–1200°C. At this temperatures the dispersity of the corundum formed is reduced due to the start of grain growth processes. That is the reason for our investigations in preparing α -Al₂O₃ at lower temperatures. Therefore aluminium-secondary-butoxide was hydrolysed in water and seeded with different amounts of hematite. The dried powders were investigated for instance by using differential thermal analysis. A nearly linear relation between seeding amount and transformation temperature was found. The formation temperature of corundum was decreased by seeding with 10 wt% hematite from about 1100 to 970°C.

Keywords: Corundum; Seeding transformation; Hematite

1. Introduction

Corundum is the only stable oxide in the aluminium–oxygen system and is characterized by its high mechanical and chemical stability. As a rule, α -Al₂O₃ is obtained from transition alumina (κ -, γ -Al₂O₃) by phase transformation. The required transformation

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temperature lies between 1100 and 1200°C. Due to the sintering processes occurring at these temperatures and being related to grain growth, the dispersity of the formed corundum is reduced.

The aim of the present investigations was to prepare corundum at low temperatures in order to prevent sintering. An aluminium hydroxide sol was prepared from aluminium alcoholate and seeded with different amounts of hematite nuclei ($\alpha\text{-Fe}_2\text{O}_3$). The development of transformation temperature into corundum and the amounts of $\alpha\text{-Al}_2\text{O}_3$ obtainable are investigated as a function of the amount of nuclei.

2. Experimental

2.1. Sol preparation

Aluminium-secondary-butoxide ($\text{C}_{12}\text{H}_{27}\text{AlO}_3$) from FLUKA-Chemika AG, Buchs, was hydrolyzed by slow trickling into strongly stirred hot water (80°C). The molar ratio $\text{H}_2\text{O}/\text{ASB}$ was 100:1, which is sufficient for complete hydrolysis. The sols were flocculant and white, pH value was 8.2.

Six sols with different content of hematite were prepared. The content of iron oxide referred to the formed Al_2O_3 was 0, 1, 3, 5, 7 and 10 wt %.

The seeding of the samples was performed by adding the respective amount of salt $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Riedel-de Haen AG, Seelze-Hannover). Peptization of the sol particles was carried out by 1 N HNO_3 .

The iron salt was dissolved in nitric acid, and these solutions were added to the white aluminium hydroxide sols, such that the pH values of the seeded sols decreased to 3.6–3.9. The peptization of the sol particles was distinctly visible.

The grain size distribution of the peptized sols was performed by the use of a Microtrac Ultrafine Particle Analyzer from Leeds and Northrup. Fig. 1 shows the grain size

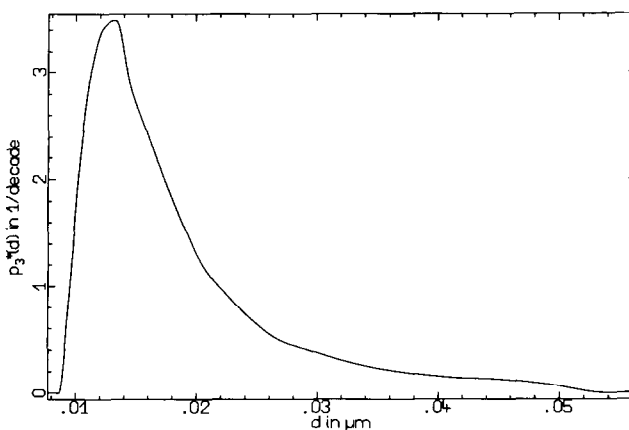


Fig. 1. Grain size distribution of the sol seeded with 5 wt% Fe_2O_3 .

Table 1
d-values of sols

Sol	<i>d</i> ₅₀ value in μm	(<i>d</i> ₉₀ - <i>d</i> ₁₀)/ <i>d</i> ₅₀
Sol unseeded	0.0159	0.987
Sol with 1 wt% Fe ₂ O ₃	0.0172	1.041
Sol with 3 wt% Fe ₂ O ₃	0.0137	1.153
Sol with 5 wt% Fe ₂ O ₃	0.0141	0.915
Sol with 7 wt% Fe ₂ O ₃	0.0139	0.870
Sol with 10 wt% Fe ₂ O ₃	0.0149	0.926

distribution of the sol seeded with 5 wt % of iron oxide. The *d*-values of the distributions necessary for characterizing the sols are given in Table 1.

Thereafter the sols were frozen in liquid nitrogen and dried in a freeze drier. After drying, highly voluminous and glittering powders were obtained.

To eliminate nitrate amounts, the powders were precalcined in a muffle furnace for 2 h at 500°C. It is supposed that during this heat treatment hematite was formed, which however could not be proved later.

Subsequently the samples were calcined in a muffle furnace for 2 h each at 950, 1000 and 1050°C in air.

3. Results and discussion

For the visualization of the $\theta \rightarrow \alpha$ -Al₂O₃ transformation, differential thermal analyses (DTA) of all samples were carried out. The DTA curves were recorded by means of the high temperature calorimeter type 1500 K from Setaram, Lyon, incorporating the DTA accessory. The device was equipped with a new computer-aided data processing unit. The DTA and temperature signal was submitted via a multiplexer to a digital multimeter M2001 from Keithley, and within 3 s both voltages were measured ten times with an integration time of 20 ms each. The mean values of the voltages were stored immediately after each measuring loop as ASCII data on to the hard disk. Temperature calibration of the Pt–PtRh thermoelements was performed by the determination of the transformation temperatures of K₂CrO₄, Au and Ni. The onset temperatures were determined by the use of the evaluation program TAWIN from Linseis: TU (K₂CrO₄) is 672 ± 0.5 K (must be 668 K); TU (Au) 1064 ± 0.5 K (must be 1064.43 K); TU (Ni) 1443 ± 0.5 K (must be 1455 K). The measuring conditions for all the calibration measurements were as follows: 5 K min⁻¹, 1.2 l argon min⁻¹, Pt crucible, corundum powder.

The temperature–voltage table of the thermoelement was fitted with three supporting values, such that the error of the onset temperatures given below was lower than 1 K.

Throughout the measuring curves all the samples showed a distinct exothermal peak during $\theta \rightarrow \alpha$ -Al₂O₃ transformation.

It can be concluded from the curves, that the transformation of corundum takes place at increasing hematite content at lower temperatures than with the unseeded sample.

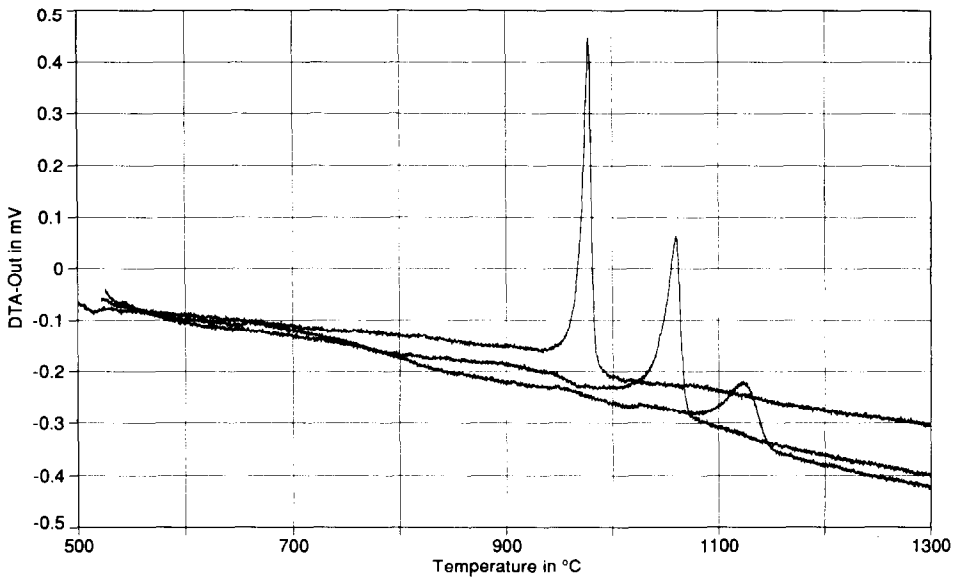


Fig. 2. DTA curves of the unseeded and 5 and 10 wt% α - Fe_2O_3 seeded sols.

Fig. 2 shows this relationship by means of three DTA curves of the samples with iron oxide contents of 0, 5 and 10 wt%. In this connection the curve with the highest peak corresponds to the one seeded with 10 wt% of α - Fe_2O_3 , the curve with the lowest and the peak at the highest temperature correspond to the unseeded powder.

By means of the evaluation program the onset temperatures of the $\theta \rightarrow \alpha$ - Al_2O_3 transformation of all the curves were determined. Fig. 3 shows the dependence of this tem-

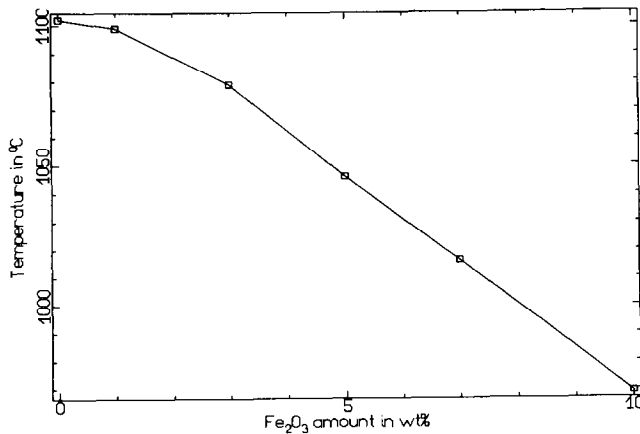


Fig. 3. Dependence of transformation temperature on seeding amount.

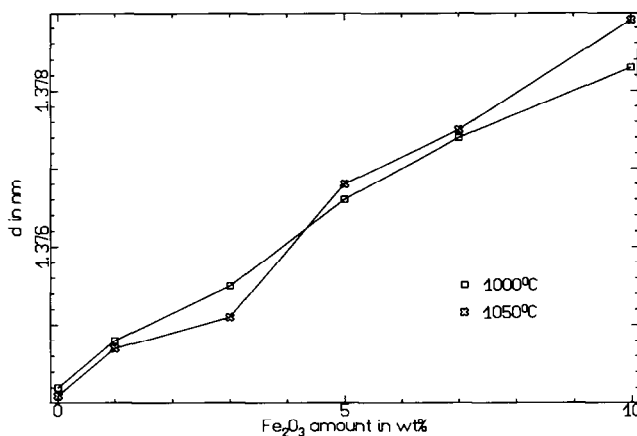


Fig. 4. Shift of the (300)-reflex.

perature each on the hematite content of the samples. A linear dependence of transformation temperature on iron oxide content is significant at least as regards α -Fe₂O₃ concentrations above 3 wt%. Thus it is possible to decrease the formation temperature of corundum from transition aluminas by seeding with 10 wt% of hematite nuclei from about 1100 down to about 970°C.

The deviation from linear behaviour at seeding amounts smaller than 3 wt% could be caused by impurities of the starting materials (ASB, iron nitrate), which under these conditions could be eventually act as foreign seed particles.

3.1. X-ray phase analysis

After calcining, the phase content of the powder was investigated by means of XRD. After calcining at 950°C all the samples showed a gradual corundum formation depending on hematite content. Furthermore, all the samples indicated reflexes of the transition aluminas γ , δ and κ -Al₂O₃, respectively.

The samples calcined at 1000°C showed in all cases a strong formation of corundum,

Table 2

Corundum yields as a function of α -Fe₂O₃ content and calcining temperature

Calcining temperature in °C	Corundum yields in wt%					
	0 wt% α -Fe ₂ O ₃	1 wt% α -Fe ₂ O ₃	3 wt% α -Fe ₂ O ₃	5 wt% α -Fe ₂ O ₃	7 wt% α -Fe ₂ O ₃	10 wt% α -Fe ₂ O ₃
950	2	1	10	43	52	76
1000	56	52	85	88	88	86
1050	99	100	96	91	88	84

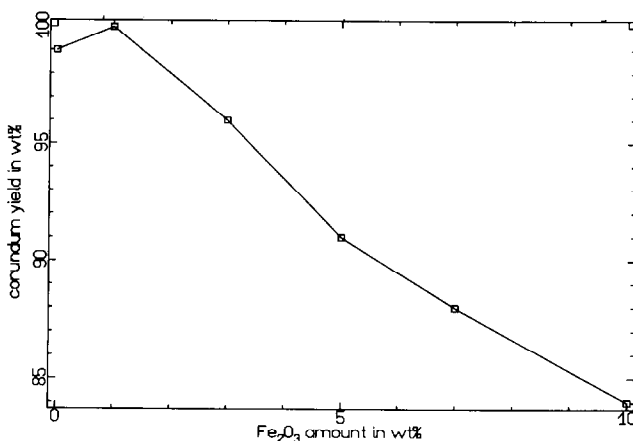


Fig. 5. Dependence of corundum yield on amount of seeding.

while the unseeded sample and that to which 1 wt% of α -Fe₂O₃ was been added still showed, besides strong corundum reflexes, traces of δ - and ϑ -aluminium oxide. With the samples treated at 1050°C only corundum peaks could still be found.

Reflexes of hematite and of other Fe₂O₃ modifications could not be detected. A reason for their absence could be found in a possible insertion of iron atoms as a solid solution into the aluminium oxide lattice. Possible confirmation of this phenomenon could be the shift of the d -values of corundum reflexes as a function of iron content, which was found in the samples calcined at 1000 and 1050°C.

As an example of the large variety of corundum reflexes the (300)-reflex is presented. Fig. 4 shows the shift of this d -value as a function of α -Fe₂O₃ content.

By means of quantitative X-ray phase analysis and by the use of a calibration curve, the corundum content presented in Table 2 could be determined in the decomposition products. The highest achievable corundum yield in all cases was 100 wt%.

The shift of the temperatures for corundum formation from the results of DTA, where phase transformation, for example, occurred with 10 wt% seedings only at temperatures of 970°C, could be explained by holding times during calcining and by the time dependence of crystallization and nucleation.

The relationship between maximum achievable corundum yield and seeding amount after a heat treatment at 1050°C, which is presented in Fig. 5, seems to be interesting. It is evident that by an increasing amount of hematite nuclei, the temperature of phase transformation of $\theta \rightarrow \alpha$ -Al₂O₃ decreases, but by this Fe₂O₃ addition, finally, the complete crystallization of α -Al₂O₃ is hindered.

3.2. Specific surface area

The BET measurements showed that it is impossible to prepare very fine α -aluminas by means of this method. If the corundum formation of all the samples at 1050°C is finished, also their surface has been decreased down to values below 10 m² g⁻¹.

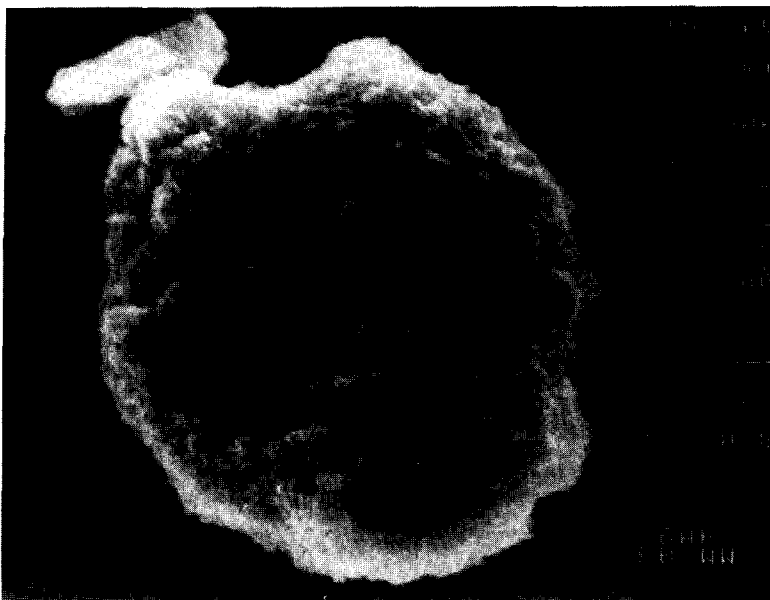


Fig. 6.

3.3. Profile analysis

From the reflexes of X-ray phase analysis the crystallite sizes of the transformed powders were determined by means of an analysis of the half-widths of the corundum peaks. It was 75 ± 17 nm for the samples calcined at 1000°C and 84 ± 24 nm for those calcined at 1050°C . A relationship between the size of primary particles and seeding amount could not be recognized.

The small crystallite sizes can be observed distinctly in Fig. 6.

4. Conclusions

The aim of the present investigations was to prepare corundum at relatively low temperatures. An aluminium hydroxide sol obtained from aluminium secondary butoxide (ASB) was seeded with hematite nuclei, which were added to the sol as $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The calcining of the powders led to a distinct and nearly linear dependence of transformation temperature on Fe_2O_3 content as well as to a relationship between the amount of $\alpha\text{-Al}_2\text{O}_3$ formed to the seeding rate.

By the use of 10 wt% $\alpha\text{-Fe}_2\text{O}_3$ seedings, the temperature of corundum formation could be decreased in contrast to the unseeded sample by 130°C to about 970°C . Since this Fe_2O_3 amount presumably affects the chemical stability of the corundum formed, a maximum seeding of 3–5 wt% of hematite is recommended, because in this case at a heat treatment at 1000°C , corundum yields of nearly 90 wt% could be obtained.

The specific surface areas of the transformation products are insufficient. With corundum contents above 80 wt% these are a maximum of $10 \text{ m}^2 \text{ g}^{-1}$ within the range of alpha aluminas (ALCOA A16), which are already in commercial use; however, in the present investigations the milling process could be eliminated.

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