

ON ALUMINA PHASE TRANSFORMATION AND CRUST FORMATION

IN ALUMINUM CELLS

R. Oedegard, S. Roenning, S. Rolseth and J. Thonstad

Laboratories of Industrial Electrochemistry
and
SINTEF, The Foundation for Scientific and
Industrial Research
at
The Norwegian Institute of Technology
N 7034 TRONDHEIM-NTH
NORWAY

The catalytic effect of fluorides on the $Y \rightarrow \alpha\text{-Al}_2\text{O}_3$ phase transformation was studied by keeping commercial alumina samples with addition of different fluorides (2 wt%) for 30 minutes at various temperatures. After heat treatment the $\alpha\text{-Al}_2\text{O}_3$ content was analyzed by means of X-ray diffraction. The phase transformation occurred within a narrow temperature range (50°C) and the characteristic temperatures determined with different additives increased in the following order AlF_3 (800°C), Na_3AlF_6 (880), NaF (935), CaF_2 (980), no additive (1040), NaOH (1115). Aluminum hydrate showed higher transformation temperatures than the commercial aluminas. Dry scrubber alumina was transformed at about 785°C.

The coherence of crusts formed on top of cryolitic melts were studied by reheating the crust samples to a temperature well above the liquidus temperature of the bath phase. The experiments supports the notion that an alumina network is formed during the $Y\text{-}\alpha$ phase transformation which reinforces the crust on top of cryolite bath. Such strengthening was not observed when the initial content of $\alpha\text{-Al}_2\text{O}_3$ was above 50% or when the temperature was below $\approx 800^\circ\text{C}$.

Introduction

Alumina used for aluminum production in Hall-Heroult cells is mostly of the so-called "sandy" type which has a low content of fines (<20% -325 mesh) and a low content (<30 wt%) of the stable modification $\alpha\text{-Al}_2\text{O}_3$ (corundum). The metastable intermediate oxide phases ($\chi, \kappa, \gamma, \delta, \eta, \theta$ (1)) which in this paper are simply designated $Y\text{-Al}_2\text{O}_3$, have a grain morphology which makes the alumina more free-flowing than the high calcined "floury" type of alumina which consists essentially of $\alpha\text{-Al}_2\text{O}_3$. The metastable intermediate phases (Y) can be transformed to $\alpha\text{-Al}_2\text{O}_3$ by calcination at around 1200°C. However, it is well known that the phase transformation is catalyzed in the presence of fluorides (2,3). In the production of "fluory" alumina fluorides have in some cases been added as mineralizers to allow the calcination temperature to be lowered from 1200°C to 1100°C (2). It also makes the alumina less dusty (4) probably due to formation of larger grains (3). The use of a separate reactor to generate fluoride fumes for this purpose has been suggested (5).

A rapid conversion to $\alpha\text{-Al}_2\text{O}_3$ takes place also when alumina is added to liquid cryolitic melts (2,3,6). Less (7) showed that when a sandy alumina forms a crust on top of the bath, a network interlinked by $\alpha\text{-Al}_2\text{O}_3$ grains are formed which reinforce the crust. Abd El All et al. (8) found that such crust lumps when sinking to the bottom of the cell did not disintegrate readily, due to this sintered alumina network.

Phase Transformation Temperature

The catalytic effect of additives on the temperature at which the $Y\text{-}\alpha$ phase transformation occurs was studied for a commercial sandy alumina and for aluminum hydrate. Some physical properties of the sandy alumina (type A) are given in the appendix.

The alumina samples were intimately mixed with 2wt% of the additives prior to heat treatment. The content of $\alpha\text{-Al}_2\text{O}_3$ before and after heat treatment was controlled by X-ray diffraction according to the ISO specification (9). Two heat treatment techniques were used, differential thermal analysis (DTA) and heat treatment at constant temperature.

In the DTA measurements the standard sample was $\alpha\text{-Al}_2\text{O}_3$ and the heating rate was 50 °C/min. The exothermic heat of reaction of the $Y\text{-}\alpha$ phase transformation gave a peak on the curve which shows the temperature difference between the test sample and the

standard. The peak temperature was taken as the alumina transformation temperature for the DTA experiments. (X-ray analysis of the samples after the DTA experiments showed ~ 100% α - Al_2O_3).

For the heat treatment at constant temperature the samples of alumina (predried at 400°C) mixed with 2wt% additives were held for 30 minutes in sintered alumina crucibles at constant temperature in nitrogen atmosphere. The heat treatment temperature was varied systematically in order to identify the temperature range where the phase transition took place. The time of heat treatment at constant temperature was also varied in some experiments to determine the rate of the $\gamma \rightarrow \alpha$ transformation. The temperature was varied from 740°C to 800°C and the time from 5 min. to 7 hours. These tests were performed with addition of 2 wt% AlF_3 .

In order to test whether HF has any specific catalytic effect some samples of alumina without additives were exposed to HF for 1/2 to 4 hours at constant temperature in the range 300-900°C. The alumina samples were housed in sintered alumina crucibles inside a steel container in a furnace. A 50-50 mixture of HF+He was passed through steel tubes into the bed of alumina.

Results

Fig. 1 shows a DTA curve for a sample with 2wt% CaF_2 addition. An exothermic heat of reaction due to the $\gamma \rightarrow \alpha$ transformation is evident. The pre-peak shift of the curve is probably due to a difference in heat capacity between the test sample and the reference. Table I gives phase transformation temperatures (marked with T_{tr} in Fig. 1) taken from DTA experiments with various additives to the same type of alumina (A).

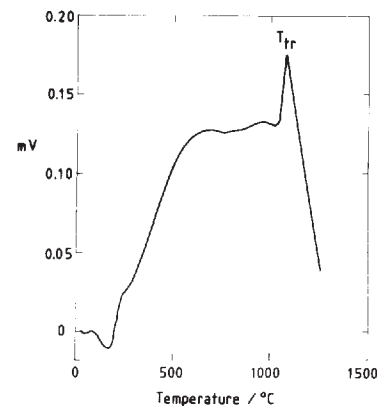


Fig. 1. DTA curve (temperature versus differential thermocouple reading) for the heat treatment of a commercial "sandy" alumina (type A) with 2 wt% CaF_2 additon. Netzsch STA-409 equipment.

Table I. DTA phase transformation temperatures for a commercial "sandy" alumina (type A) with various additives (2 wt%). Rate of temperature rise 50°C/min.

Additive	Phase transformation temperature (°C)
AlF_3	925
NaF	1040
CaF_2	1075
None	>1200

Results from the experiments with heat treatment at constant temperature are given in Fig. 2 in the form of plots of % α - Al_2O_3 versus temperature for various additives. The fact that the curves do not approach 100% is probably partly due to differences in the X-ray diffraction peak intensity compared to that of the standard corundum sample.

Phase transformation temperatures corresponding to the 50 wt% α - Al_2O_3 level in Fig.2 are listed in Table II. Experiments with addition of NaCl gave a curve very similar to that with NaOH addition.

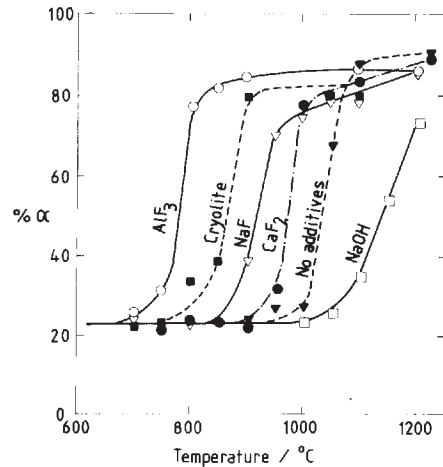


Fig. 2. The content of α - Al_2O_3 versus the temperature of heat treatment (30 minutes) for a "sandy" alumina (type A) mixed with 2 wt% of the compounds indicated on the curves.

Table II. Phase transformation temperatures for heat treatment of a commercial "sandy" alumina (type A) with various additives (2 wt%). The transformation temperatures are taken from Fig. 2 for 50% α - Al_2O_3 .

Additive	Phase transformation temperature (°C)
AlF_3	800
Na_3AlF_6	880
NaF	935
CaF_2	980
None	1040
NaOH	1115

An alumina sample that had been used for dry scrubbing of fluoride emissions from aluminium cells showed a phase transformation temperature of 785°C. This alumina contains chemisorbed HF, fluoride condensates and dust.

In addition to commercial "sandy" alumina some samples of aluminum hydrate were also tested. The hydrate was predried at 400°C for 24 hours and subjected to the same experimental procedure as for Fig.2. The α - Al_2O_3 content versus the heat treatment temperature for these samples is shown in Fig.3. Table III gives phase transformation temperatures taken from Fig.3 for α - $\text{Al}_2\text{O}_3 = 50\%$. In one experiment the predried aluminum hydrate was mixed with 15 wt% aluminum hydrate that had been heat treated at 1250°C for 24 hours (100% α - Al_2O_3). The mixture was then heat treated for 30 minutes at various temperatures from 1080°C to 1200°C. The resulting phase transformation temperature was found to be the same as that for aluminum hydrate without any additions.

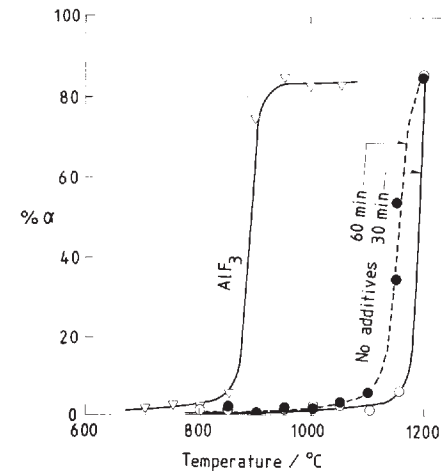


Fig. 3. The content of α - Al_2O_3 versus the heat treatment temperature for aluminum hydrate (predried at 400°C). The heat treatment time was 30 min. for the experiments with 2 wt% AlF_3 addition (∇) and 30 (o) and 60 min (o) for experiments without any additions. The initial α - Al_2O_3 content was zero.

Table III Phase transformation temperatures taken from Fig.3 for heat treatment of aluminum hydrate and corresponding data for "sandy" alumina (Table II).

Additive	Phase transformation temperature (°C)	
	hydrate	"sandy" alumina
AlF ₃	900	800
None (30 min)	1190	1040
None (60 min)	1160	

In order to determine the kinetics and the activation energy for the $\gamma \rightarrow \alpha$ phase transformation for "sandy" alumina (type A) with 2wt% AlF₃ addition, a detailed study was made of the α -Al₂O₃ content versus time of heat treatment at constant temperature. Fig. 4 shows experimental results for three different temperatures, 740°C, 769°C and 800°C. The experimental results were fitted to a model assuming a first order reaction. The full lines in Fig. 4 represent the best fit for this model. The agreement with the experimental data is good except for the initial "incubation" period which increases with decreasing temperature. The natural logarithm of the rate constants derived from this treatment are plotted as a function of the reciprocal absolute temperatures in Fig. 5.

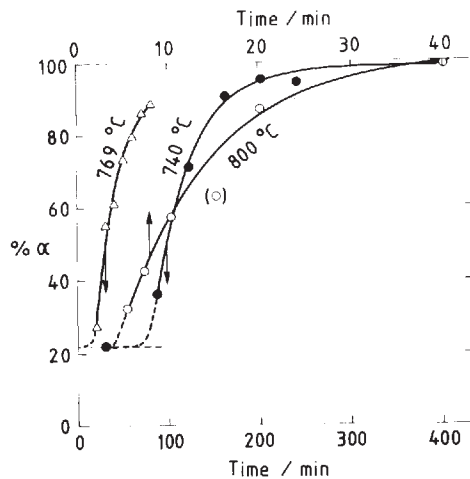


Fig. 4. The content of α -Al₂O₃ versus time of heat treatment at constant temperatures (°C) as indicated on the curves for "sandy" alumina (type A) with 2 wt% AlF₃ addition. The full lines represent the best fit for a first order reaction model.

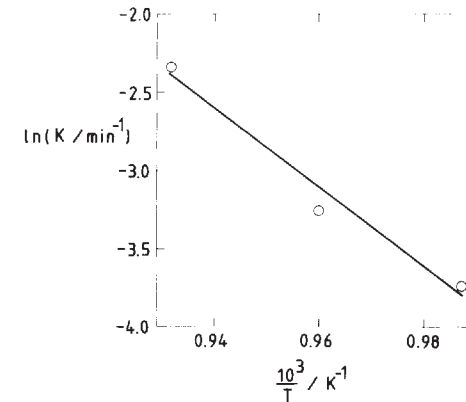


Fig. 5. Natural logarithm of the rate constants for the $\gamma \rightarrow \alpha$ transformation plotted versus the reciprocal absolute temperatures for oxide A with 2 wt% AlF₃ present.

In experiments where alumina (type A) was heated at different temperatures (300°C - 600°C) in an equimolar mixture of HF and He for 60 minutes, only formation of AlF₃ and no increase in the α -content was observed by X-ray diffraction analysis. In some experiments there was in fact a decrease in the α -content from the initial 22 % to \approx 10%. When the heat treatment temperature was increased to 900°C both AlF₃ formation and transformation to α -Al₂O₃ was observed.

Crust Formation

When cold alumina is added to molten bath in such amounts that it accumulates on the surface of the melt, a solid crust is formed on top of the melt, provided that the surface is cooled below its liquidus temperature. This crust consist of alumina embedded in frozen bath.

In order to test the coherence of such crust when heated above the liquidus temperature of the bath phase, crust samples were lifted off the cryolite bath as soon as they were soaked by the melt, using a strainer made of molybdenum wire. The samples were reheated in nitrogen atmosphere to a temperature well above the liquidus temperature of the bath for 90 minutes. Some crust samples underwent only minor dimensional changes during this treatment in contrast to other samples which collapsed, forming a cryolite-alumina sludge. The former group was designated high temperature coherent crusts. Generally it was found that samples made from "floury" alumina collapsed during this test,

whereas "sandy" alumina formed high temperature coherent crusts. To test the long term stability of crust formed by adding "sandy" alumina (type E) to molten cryolite at 985°C a piece of such crust was suspended in a platinum wire and submerged in a cryolite/alumina sludge (40 wt% alumina and 60 wt% cryolite) at 1000°C. After 48 hours the wire was pulled out of the sludge, and the crust sample came out intact, as shown in Fig. 6.

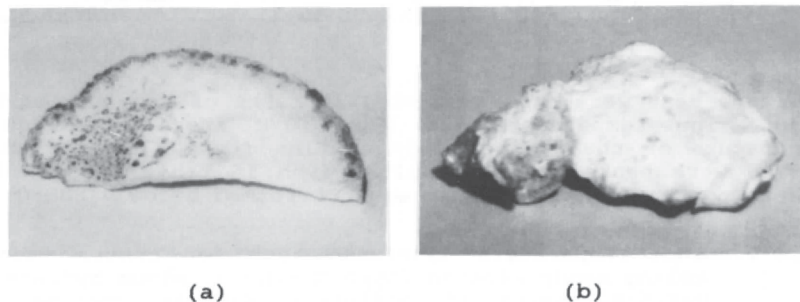


Fig.6. Sample of high temperature coherent crust before (a) and after (b) exposure in a cryolite-alumina sludge at 1000°C for 48 hours.

A series of coherence tests as describes above were conducted using sandy alumina with variable contents of $\alpha\text{-Al}_2\text{O}_3$. The alumina samples were prepared by mixing the virgin alumina with varying proportions of the same type of alumina which had been converted to 100% $\alpha\text{-Al}_2\text{O}_3$ by heat treatment at 1250°C for 24 hours. As shown in Table IV a high temperature coherent crust is formed only when the initial content of $\alpha\text{-Al}_2\text{O}_3$ is below 40-50%. The fluoride phase in these crust was extracted by leaching in a 30 wt% aluminum chloride solution. X-ray analysis of the remaining alumina phase showed it to contain only $\alpha\text{-Al}_2\text{O}_3$.

Table IV Test of the high temperature coherence (see text) of crusts prepared by adding aluminas with varying initial $\alpha\text{-Al}_2\text{O}_3$ contents to the surface of a alumina saturated cryolite melt at 985°C.

Alumina, type	% $\alpha\text{-Al}_2\text{O}_3$ in virgin alumina	Maximum % $\alpha\text{-Al}_2\text{O}_3$ in coherent crusts
B	28	35-40
C	24	40-45
E	26,5	50-55
D	12	40-45

Coherence test were also conducted in baths of varying NaF/AlF₃ ratio. The temperature was kept 10°C above the liquidus temperature of the melt. Sandy alumina (type E) and aluminum hydrate were tested. The results given in Table V, show that high temperature coherent crust was not formed below $\approx 800^\circ\text{C}$.

Table V. High temperature coherence test for crusts made by adding sandy alumina (type E) and aluminum hydrate to NaF/AlF₃ melts of different NaF/AlF₃ ratios (see text).

NaF/AlF ₃ mole ratio	Bath temperature (°C)	High temperature coherence	
		Alumina (type E)	Aluminum hydrate
3.00	1020	yes	yes
1.86	945	yes	-
1.80	911	yes	yes
1.70	850	yes	no
1.60	777	no	-

X-ray analysis of the alumina phase in the crust showed that in the two cases in Table V where the formed crust was not coherent, little or no phase transformation had taken place, whereas it was more or less complete for the other samples.

A crust formed by adding alumina (type E) to the surface of molten FLINAK (46.5 mole% LiF, 42 mole% KF and 11.5 mole% NaF) at 500°C proved not to be coherent at temperatures above the melting point of FLINAK. An X-ray test showed that no phase transformation had occurred in this case.

Discussion

Comparison of Tables I and II shows that the DTA and the heat treatment experiments gave the same ranking of the fluoride additives with respect to the effect on transformation temperature. Listed in the order of decreasing catalytic effect the ranking is $AlF_3 > Na_3AlF_6 > NaF > CaF_2$. However, the transformation temperatures were considerably higher in the DTA experiments. This is probably due to a rather slow formation of nuclei of $\alpha-Al_2O_3$ crystals. The heating rate being quite fast (50°C/min) in the DTA experiments, the time to attain significant nucleation at the right temperature was probably insufficient. One should also expect that the transformation temperatures given in Table II to decrease with increasing duration of the heat treatment at constant temperature.

There seems to be no commonly accepted explanation of the nature of the catalytic effect of fluorides on the $Y \rightarrow \alpha$ phase transformation (10). It has been suggested that a reaction of the fluorides with the OH groups of the hydrate or low calcined "sandy" alumina by formation of HF, accelerate the dehydration and thereby the recrystallization (10,11). The ranking of the fluorides with respect to their catalytic effect is the same as for the tendency to hydrolyze for the same fluorides. This supports the notion that a hydrolysis reaction may be a step in the catalytic reaction for the fluorides. Belyaev et al. (2) has suggested that HF, formed by the hydrolysis reactions of the fluorides, is the catalytic active specie. The heat treatment experiments of alumina A in a HF+He atmosphere do not support this mechanism. The observed increase in the $\alpha-Al_2O_3$ content when sandy alumina (type A) was heated at 900°C in HF-He atmosphere could be due to the catalytic effect of AlF_3 formed during the initial period of the experiment.

There is a marked difference in phase transformation temperature for aluminum hydrate compared to commercial "sandy" alumina as shown in Table III. The $\alpha-Al_2O_3$ which is already in the "sandy" alumina probably acts as nuclei for further $Y \rightarrow \alpha$ phase transformation. On the other hand addition of 15% precalcined hydrate (100% $\alpha-Al_2O_3$) to aluminum hydrate did not change the phase transformation temperature. A more intimate contact between the α and Y crystals in the "sandy" alumina compared to the mechanical mixture in the latter case may explain this difference.

The observed inhibition of the $Y \rightarrow \alpha-Al_2O_3$ phase transformation in the presence of NaOH and NaCl may be related to

formation of some β -alumina ($Na_2O \cdot 11Al_2O_3$). The β -phase was detected by X-ray analysis of these samples. The presence of β -alumina within a grain may create a disorder effect that will slow down the conversion of Y into α -alumina.

Alumina which had been used for dry scrubbing showed the lowest phase transformation temperature (785°C) of all materials tested. This can be explained by the fact that the surface of this alumina is covered to some extent by adsorbed fluorides (12).

The heat of activation for the transformation reaction to $\alpha-Al_2O_3$ is calculated from the slope of $\ln k$ versus $1/T$ plot in Fig 5 and is found to be 50 ± 9 kcal/mol. The results of the present work disagree with those of Steiner et al. (13) that studied the transformation of $Y-Al_2O_3$ without any additives and reported zero order kinetics and a heat of activation of 116 ± 5 kcal/mol. On the other hand Clark and White (14) observed first order kinetics and a heat of activations of 79 kcal/mol in experiments without additives. Steiner et al. (13) suggest that the disagreement in results compared to those of Clark and White could be due to differences in level and type of impurities. To distinguish between a zero and first order reaction it is very important to examine closely the transformation of the last 10-20% of the starting material. Some of the curves of Steiner et al. (13) may be interpreted to be slightly curved for high α -content, for other curves the fraction transformed is not high enough to distinguish between a zero order transformation and a 1. order. Therefore 1. order kinetics for the $Y \rightarrow \alpha$ transformation of a Y -alumina without any additives, can in our opinion, not be excluded from the data of Steiner et al. In the present work, with addition of 2wt% AlF_3 , a distinct 1. order transformation has been observed (see Fig.4). The low heat of activation found in the present work would be expected since the reaction is catalyzed.

A crust which is formed when alumina is added to the melt can be held together by

- A. Frozen bath only
- B. Frozen bath plus a network of recrystallized alumina.

In the latter case (B) the crust will be coherent even at temperatures above the liquidus of the bath phase. The mechanical strength of this network is rather limited, however, and it is easily crushed when being touched by a rod. As shown in Table IV there is an upper limit for the $\alpha-Al_2O_3$ content of the added alumina above which a network of recrystallized alumina is not formed in the crust. A similar observation was made by Johnston and Richards (15) for aluminas containing 66-92% $\alpha-Al_2O_3$. According to Less (7) a network of interlinked alumina platelets are formed during the $Y \rightarrow \alpha$ transformation. Johnston and Richards (14) elaborated on this mechanism and

suggested that the process takes place just above the liquid bath level. As alpha crystals form and grow they tend to crosslink with alpha crystals from adjacent grains forming an interlocking matrix of α -alumina. Fischer (16) observed that the lower part of the alumina layer resting on top of the crust in aluminum cells tended to sinter. This phenomenon can easily be demonstrated in the laboratory by exposing sandy alumina to bath fumes to catalyze the γ - α conversion. The formation of a coherent alumina network can then be described simply as a sintering process with "necking" between adjacent grains and simultaneous grain growth. A dissolution and precipitation mechanism via the cryolite bath as suggested by Townsend and Boxall (17) does not seem to be a prerequisite for coherent alumina network formation.

However, the bath still plays an important role in the formation of an alumina network. First of all it provides the catalyzing agent and secondly the frozen bath renders the time and stability needed to allow sintering to occur. If a frozen crust is not formed when adding alumina to the bath surface a coherent network will not be established either. The reason for this is twofold, firstly the movement of the alumina and the bath will tend to break up any links being formed, and secondly the alumina grains quickly become wetted by the bath, preventing intergranular contact.

It is also evident that if the temperature of the bath is below the γ - α phase transformation temperature in a given medium, no coherent network is formed, as can be seen from Table V and from the experiment with FLINAK melt. The fact that a high temperature coherent crust was not formed when adding alumina to a melt with NaF/AlF₃ molar ratio 1.60 at 777°C is in agreement with Table II concerning phase transformation temperatures in presence of AlF₃ and Na₃AlF₆. The temperature of the melt was below the phase transformation temperature which one would expect to lie between those obtained in the presence of AlF₃ (800°C) and of Na₃AlF₆ (880°C). Zivkovic et al. (10) has shown that increased addition of AlF₃ from 1 to 10% had only a slight effect on the transformation temperature. The observed long term stability of crust immersed in molten cryolite/alumina sludge is in good agreement with the work of Abd El All et al. (8) who found that crust samples maintained their shape for a long time at the bottom of a crucible containing molten cryolite at 1000°C.

Acknowledgement

Financial support from the Royal Council for Scientific and Industrial Research and from the Norwegian Aluminium industry is gratefully acknowledged.

References

1. K. Wefers and G. M. Bell: "Oxides and Hydroxides of Aluminum", Technical Paper No. 19, Aluminum Company of America, 1972.
2. A. I. Belyaev, M. B. Rapoport, L. A. Firsanova, *Metallurgie des Aluminiums*, p33; VEB Verlag Technik, Berlin 1956.
3. I. S. Kachanovskaya, V. I. Osovik and T. N. Kukhotkina, "Phase Transformation and Alumina Dissolution in Cryolite", *Tsvet. Met.*, 12 (10), 44 (1971).
4. W. Fulda and H. Ginsberg, *Tonerde und Aluminium*, Vol. 1, p. 98; Walter de Gruyter & Co, Berlin 1951.
5. M. Koster and H. Ginsberg, "Verfahren zur Calcination von Aluminiumhydroxide", *Deutsche Auslegeschrift* Nr. 1159418, 1963.
6. G. Winkhaus, "On the Dissolution of Alumina in Cryolite Melts", Paper presented at 99th AIME Annual Meeting, 1970, Paper No A70-25.
7. L. N. Less: "The Crusting Behavior of Smelter Aluminas", *Met. Trans. B.*, 8B, 219 (1977).
8. S. Abd El All, J. Gerlach and U. Henning: "Verhalten von Pulverschuttungen aus Aluminiumoxiden in Fluoridschmelzen und Eigenschaften der Reaktionsprodukte", *Erzmetall*, 33, 504 (1980).
9. Int. Stand. Org., ISO/TC47/GT 48, USA 51, NO. 476; Int. Stand. Org., ISO/TC47/WG 8, Germany 34, May 1969, no. 462.
10. Z. D. Zivkovic, N. Pacovic and M. Filipovic, "The Effect of AlF₃ on the Calcination of Aluminium Hydroxide", *Thermochimica Acta*, 32, 181 (1979).
11. L. A. Pashkevich, G. N. Gopienko and G. A. Zavaritskaya, "Effect of Mineralizer Batches on Aluminium Oxide Transformation to α -Modification", *Tsvet. Met.*, 12 (2), 43 (1971).
12. K. Grjotheim and B. J. Welch, *Aluminium Smelter Technology*, p. 108; Aluminium-Verlag GmbH, Dusseldorf, 1980.
13. C. J. P. Steiner, D. P. H. Hasselman, and R. M. Spriggs "Kinetics of the Gamma-to -Alpha Alumina Phase Transformation"; *J. Amer. Ceram. Soc.*, 54 (8), 412-13, (1971).
14. P. W. Clark and J. White, "Some Aspects of Sintering", *Trans. Brit. Ceram. Soc.*, 49, 305-33 (1950).

15. T. J. Johnston & N. E. Richards, "Correlation Between Alumina Properties and Crusts", *Light Metals 1983*, pp. 587-593. AIME Annual Meeting 1983.
16. J. F. Fischer, "Verhalten einiger Fremdoxyde in der Technischen Aluminium-Elektrolyze", *Angew. Chemie*, 20, 17-23, (1948).
17. D. W. Townsend and L. G. Boxall, "Crusting Behavior of Smelter Aluminas", *Light Metals 1984*. p 649. AIME Annual Meeting 1984.

Appendix

Some physical properties of the "sandy" type commercial aluminas used in the present investigation.

TYPE	A	B	C	D	E
Bulk density, packed g/cm ³	1,10	1,29	1,19	1,22	1,17
Bulk density, loose g/cm ³	0,93	1,03	0,99	0,99	1,06
% α -alumina	22,5	28,0	24,0	12,0	26,5
Spes. surface area, m ² /g	73,3	67,3	65,8	45,9	54,4
Angle of repose, degrees	34,4	34,4	33,9	34,7	34,4
LOI, 300-1000°C, %	0,74	0,26	1,06	0,26	0,56
Abs. density, g/cm ³	3,55	3,51	3,61	3,48	3,56
Sieve fractions -43 μ m, %	9,4	20,5	8,9	10,3	7,5
+105 μ m %	1,5	14,4	20,1	34,2	23,8