*Thermochimica Acta*, 32 (1979) 181–188

# THE EFFECT OF $AlF_3$ ON THE CALCINATION OF ALUMINIUM HYDROXIDE*

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(Received 27 July 1978; revised 3 October 1978)

## ABSTRACT

In this study, the effect of $AlF_3$ on the reaction temperatures of $Al(OH)_3$ and AlOOH dehydration and the crystallization process of $\alpha$-$Al_2O_3$ is considered. It was determined that the addition of up to 1 % $AlF_3$, under the conditions of calcination used and with a heating rate of 10° $min^{-1}$, has no influence on the dehydration reaction temperatures and that the crystallization temperature is lowered by about 200 K.

Study of the effect of added $AlF_3$ on the kinetics of $Al(OH)_3$ and AlOOH dehydration showed that there is some influence on the kinetic parameters of the process and on the temperature at which the reaction mechanism changes.

## INTRODUCTION

In industry, aluminium floride is continuously added in very small amounts during the calcination of aluminium hydroxide but still very little is known about the mechanism of its influence on the process.

Buldakov et al.[1] showed that the temperature of crystallization of $\alpha$-$Al_2O_3$ is lowered by adding $AlF_3$ with a simultaneous change in the type of surface of the calcined product. However, no data are available in the literature on the mechanism of the influence of $AlF_3$ on the calcination process of aluminium hydroxide.

Some authors[1, 2] conclude that on adding $AlF_3$, aluminium hydrofluoride is formed, and Varhegyi et al.[3] showed that $\beta$-$Al_2O_3$ is produced in the calcination process.

The present study attempts to explain the effect of added $AlF_3$ on most of the phase transformations that occur during the calcination process of aluminium hydroxide.

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* Presented at the 4th International Congress for the Study of Bauxites, Alumina and Aluminium, Athens, 9–12 October 1978.

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TABLE 1

BASIC CHARACTERISTICS OF THE ALUMINIUM HYDROXIDE USED

| *Specific weight ($kg\ m^{-3}$)* | *Specific surface ($m^2\ kg^{-1}$)* | *Impurities (%)* | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | *$SiO_2$* | *$Fe_2O_3$* | *$V_2O_5$* | *$TiO_2$* | *$P_2O_5$* | *Zn* | *$Na_2O$* |
| 2560 | 41.6 | 0.0108 | 0.026 | 0.0005 | 0.0039 | 0.0005 | 0.020 | 0.39 |

## EXPERIMENTAL

Commercial DTA, TG and X-ray equipment as well as an optical microscope that allows photography at higher temperatures were used.

DTA and TG measurements were carried out on equipment produced by Netzch, Model 409, which uses Pt–Pt/Rh thermocouples and fused alumina sample crucibles. All the research was done in an atmosphere of air with a heating rate of $10°\ min^{-1}$

X-Ray diffraction analysis was performed on Siemens equipment and recording was with Cu anti-cathode and Ni filters at a voltage of 40 kV and a current of 18 mA. For the detection of reflected emission, a scintillation detector was used.

Optical microscope Linseis 291 enabled a sample heating rate of $10°\ min^{-1}$ to be used and the samples to be photographed at elevated temperatures.

Samples of industrial $Al(OH)_3$ produced at Titograd, Yugoslavia, were used. Its basic characteristics are given in Table 1. The $AlF_3$ used as an additive was supplied by Merck.

## RESULTS AND DISCUSSION

### *The effect of $AlF_3$ on the temperature of phase transformation*

Živković[4] showed that the sequence of phase transformations in the calcination of $Al(OH)_3$ may be represented as

$$\alpha\text{-}Al(OH)_3 \rightarrow AlOOH \rightarrow \gamma \rightarrow \eta \rightarrow \theta \rightarrow \kappa \rightarrow \alpha\text{-}Al_2O_3$$

Only $Al(OH)_3$, AlOOH dehydration and the crystallization of $\alpha$-$Al_2O_3$ can be recorded by DTA. All other transformations occurring during the calcination of $Al(OH)_3$ were not measurable by this method even with very sensitive DTA equipment. The effect of added $AiF_3$ will therefore be discussed only up to the temperature required for the dehydration of $Al(OH)_3$ and AlOOH and the crystallization of $\alpha$-$Al_2O_3$.

Figure 1 shows DTA curves for $Al(OH)_3$ with different quantities of added $AlF_3$ at a heating rate of $10°\ min^{-1}$ in an atmosphere of air. From the results obtained, it may be seen that addition of $AlF_3$ to $Al(OH)_3$, in the process of calcination, the

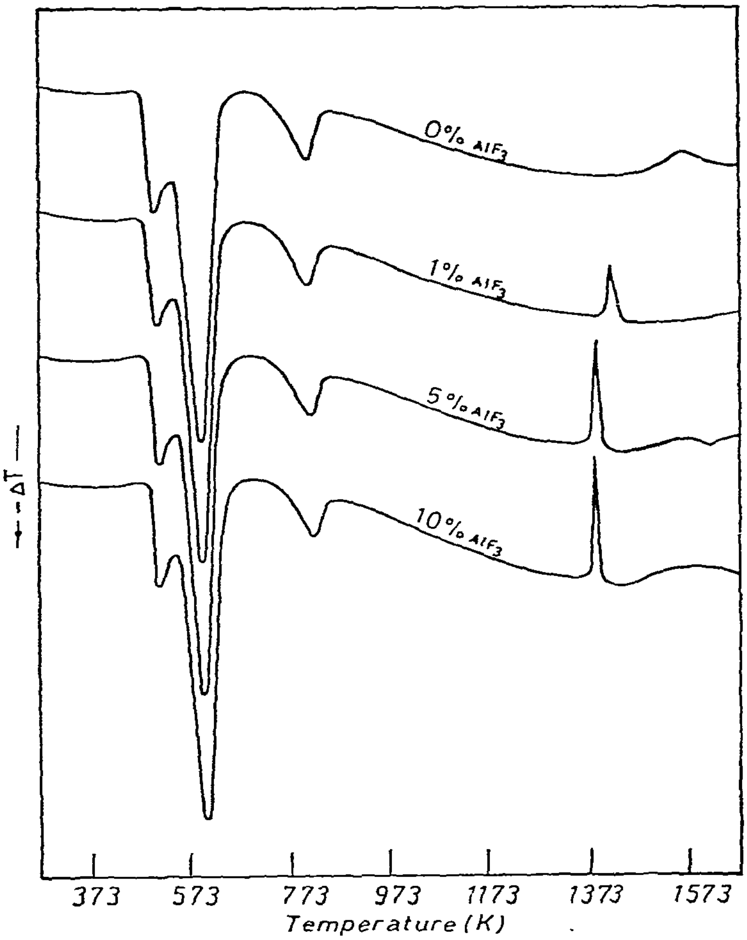

Fig. 1. DTA curves for aluminium hydroxide with different amounts of added $AlF_3$.

dehydration temperatures of $Al(OH)_3$ and AlOOH are not changed and that the exothermal peak, which corresponds to the crystallization of $\alpha$-$Al_2O_3$ occurs at a lower temperature.

It is evident that addition of $AlF_3$, even in very large quantities up to 10%, has no influence on the dehydration temperatures of $Al(OH)_3$ and AlOOH, and has a very significant influence on the crystallization temperature of $\alpha$-$Al_2O_3$ only for additions of up to 1 %. With an addition of this magnitude, the crystallization temperature of $\alpha$-$Al_2O_3$ is lowered by about 200 K which is important for fuel economy in industrial $Al(OH)_3$ calcination plants.

On the basis of X-ray analysis, it was concluded that, in all cases, a very clearly defined $\alpha$-$Al_2O_3$ phase is obtained. In the samples to which $AlF_3$ was added, a further well-defined phase was observed with additions of 5 and 10% $AlF_3$ (this was the reason for such large additions), but based on ASTM standards, we were unable to define it. It is possible that this phase catalytically influences the crystallization of $\alpha$-$Al_2O_3$, resulting in a lowering of the temperature of this reaction.

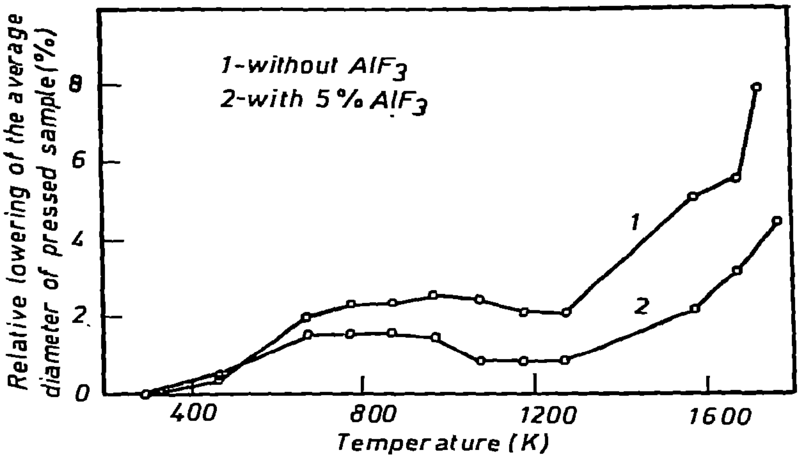

Fig. 2. The relative change in the mean diameter of pressed aluminium hydroxide as a function of the calcination temperature.

### *The effect of $AlF_3$ on dimensional change of the sample*

As the phase recorded by means of X-ray analysis is formed at much lower temperatures, it was investigated by the dimensional change of pressed samples of aluminium hydroxide with 0 and 5% added $AlF_3$. These were compressed and heated under the same conditions and their diameters recorded at different temperatures.

The diameters of the compressed samples were measured at three different places and an average taken to obtain the variation with temperature. In both samples, the mean diameter decreased with increasing temperature.

The relative lowering of the mean diameters of compressed samples of aluminium hydroxide containing 0 and 5% $AlF_3$ is shown in Fig. 2. It can be seen that the relative decrease for samples containing no $AlF_3$ is about twice that for samples containing 5% $AlF_3$ above about 700 K. Up to this temperature, the changes are similar. It is believed that at about 700 K a new phase is formed in the $Al_2O_3$–$AlF_3$ system in the presence of the remaining $Al(OH)_3$ and AlOOH which influences further calcination.

The further behaviour of samples with added $AlF_3$ with increasing temperature is different from that of samples containing no $AlF_3$ up to a temperature of about 1300 K. With further increase to 1750 K, the tendency for the average diameter to decrease is again observed in both cases. The anomalous behaviour in the temperature range from 700 to 1300 K can be explained as the influence of the phase formed in the $Al_2O_3$–$AlF_3$ system. This has some effect on the phase transformations during calcination, which are mainly completed by 1300 K.

### *The effect of $AlF_3$ on the kinetic of dehydration of $Al(OH)_3$ and AlOOH*

The kinetics of dehydration of $Al(OH)_3$ and AlOOH in non-isothermal conditions were studied by Živković and Dobovišek[5]. Using the same procedure as for the explanation of the experimental thermogravimetric results, the effect of the addition of $AlF_3$ on the kinetics of these processes is discussed.

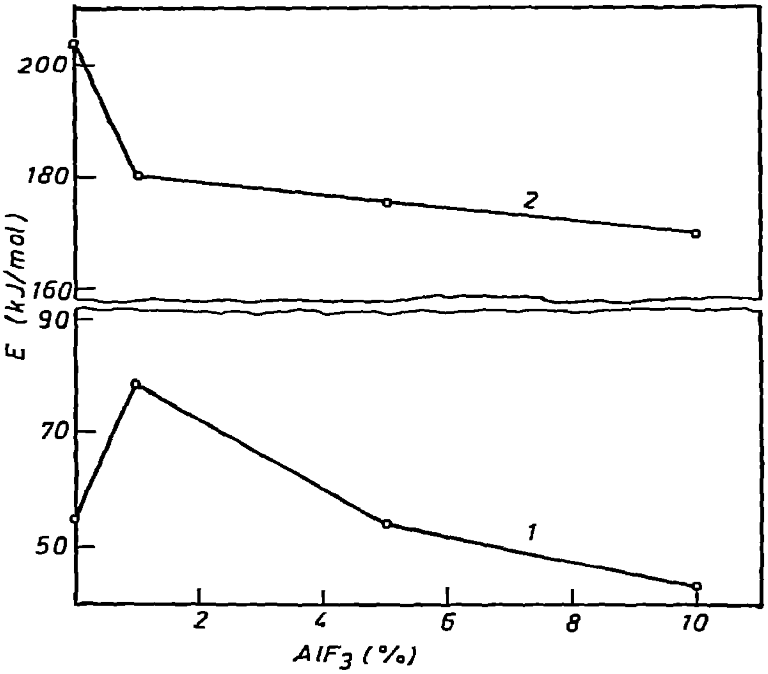

Fig. 3. Dependence of the activation energy for the dehydration of $Al(OH)_3$ on the amount of $AlF_3$ added. (1) Diffusion limited state of reaction; (2) kinetic limited state of reaction.

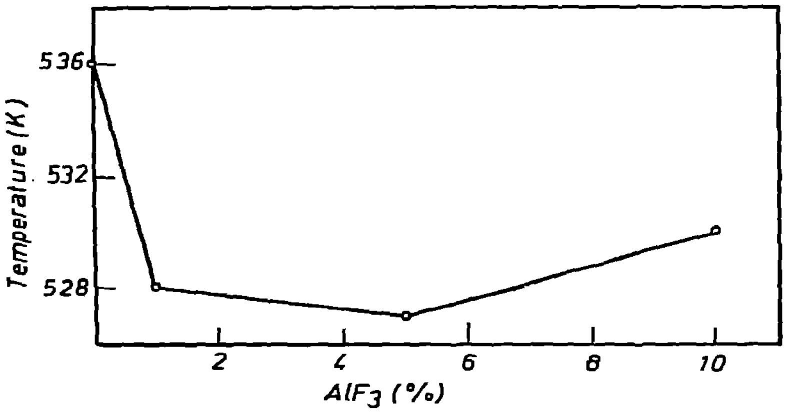

Fig. 4. Dependence on the added amount of $AlF_3$ of the temperature at which the reaction mechanism for the dehydration of $Al(OH)_3$ changes.

Figure 3 illustrates the change in activation energy, $E_1$ and $E_2$ for the dehydration of $Al(OH)_3$ and Fig. 4 the temperature at which the reaction mechanism changes, both as functions of the amount of $AlF_3$ added.

From the results, it can be seen that even with a small amount of added $AlF_3$ (less than 1 %), $E_1$ is increased but then decreases with the addition of larger amounts of $AlF_3$. The value of $E_2$ has a tendency to decrease with addition of $AlF_3$, the decrease being most marked by amounts up to 1 %. The temperature at which the reaction mechanism changes varies in the same way, although additions of up to 1 % $AlF_3$ have an even greater effect.

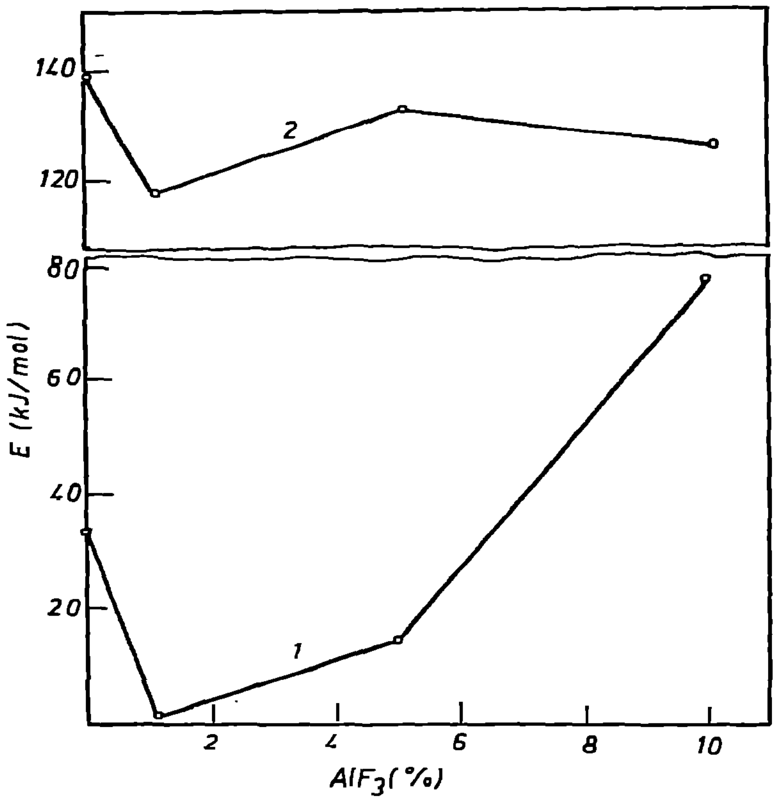

Fig. 5. Dependence of the activation energy for the dehydration of AlOOH on the amount of $AlF_3$ added. (1) Diffusion limited state of the reaction; (2) kinetic limited state of the reaction.

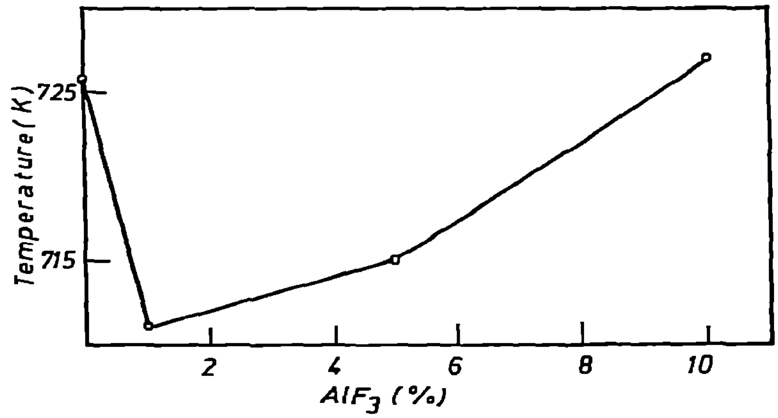

Fig. 6. Dependence on the added amount of $AlF_3$ of the temperature at which the reaction mechanism for the dehydration of AlOOH changes.

Similar results for the dehydration of AlOOH are presented in Figs. 5 and 6. They show the same effect as in the dehydration of $Al(OH)_3$ with additions of small amounts of $AlF_3$ having the biggest influence. However, in this case, larger amounts also have an effect. This shows that, at these temperatures, the formation of the new phase described earlier has some influence on the dehydration process of AlOOH.

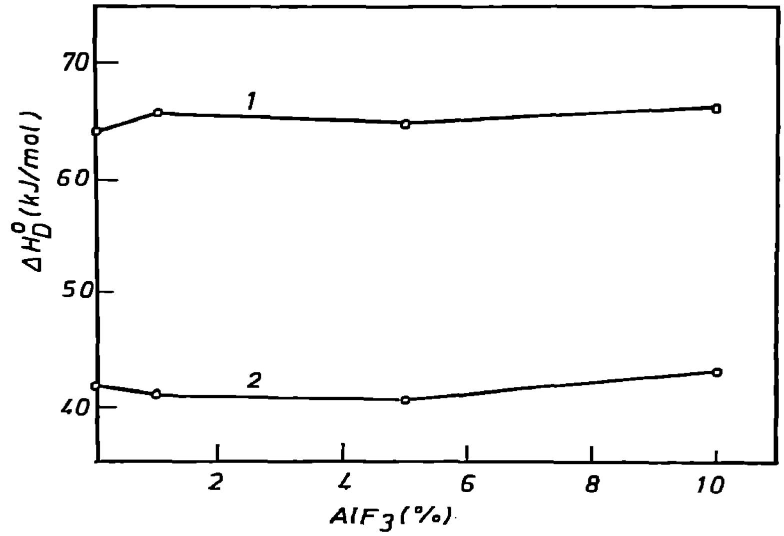

Fig. 7. The dependence of $\Delta H_D^0$ for the dehydration of $Al(OH)_3$ and AlOOH on the amount of added $AlF_3$. (1) Dehydration of $Al(OH)_3$; (2) dehydration of AlOOH.

The value of $E_1$ has a tendency to increase with added $AlF_3$, but $E_2$ maintains a constant value. At the same time, the temperature at which the reaction mechanism changes usually increases linearly with increasing amount of added $AlF_3$ up to 1 %. It is believed that this shows that the newly formed phase influences the initial rate of reaction, and with its moving in the kinetic range, e.g. when the reaction rate is surface-limited, the influence of $AlF_3$ is decreased.

It is evident that $AlF_3$ has some influence on the dehydration processes of $Al(OH)_3$ and AlOOH. However, for definite conclusions on the mechanism of this effect, further investigations are required.

Parallel with this and based on TG results using the method of Stenin et al.[6], we determined the heat necessary for the dehydration process of $Al(OH)_3$ and AlOOH, $\Delta H_D^0$, as a function of the amount of added $AlF_3$. The results are shown in Fig. 7.

Based on these results, it is evident that added $AlF_3$ has no influence on the amount of heat necessary to carry out the dehydration of $Al(OH)_3$ and AlOOH, but only on the kinetic conditions necessary for the process to take place.

## CONCLUSIONS

Based on the experimental results, we can draw the following conclusions.

(1) With additions of $AlF_3$ up to 1 %, the temperature of crystallization of $\alpha$-$Al_2O_3$ is decreased by about 200 K. Increasing amounts of $AlF_3$ have no influence on the temperature of this phase transformation. Added $AlF_3$ has no influence on the temperature at which other phase transformations, which occur during the process of calcination, take place.

(2) Adding $AlF_3$ leads to the formation of a new phase in this system at about

700 K, which is believed to have a catalytic influence on the crystallization of $\alpha$-$Al_2O_3$. It is not possible to identify the new phase according the ASTM standards.

(3) In the calcination of aluminium hydroxide, $AlF_3$ shows some influence even on the dehydration of $Al(OH)_3$ and AlOOH, which is included in its effect on the kinetic parameters for these processes. For this reason, this influence is more effective in the dehydration of AlOOH because, at this temperature, we have the formation of a new phase which is more effective than $AlF_3$ for the dehydration of $Al(OH)_3$.

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