ELSEVIER

Thermochimica Acta 266 (1995) 293–300

thermochimica acta

# Influence of fluorides on polymorphous transformation of $\alpha$-$Al_2O_3$ formation ☆

Živan Živković [a], Nada Štrbac [a], Jaroslav Šesták [b,*]

[a] *Technical Faculty, Belgrade University, 19210 Bor, Yugoslavia*
[b] *Institute of Physics, Czech Academy of Sciences, 18040 Prague, Czech Republic*

**Abstract**

Results of investigation into the influence of added fluorides ($AlF_3$, $CaF_2$, $MgF_2$, LiF, NaF and $Na_3AlF_6$, up to 10%) at the temperature of the polymorphous transformation $\gamma$-$Al_2O_3 \Rightarrow \alpha$-$Al_2O_3$ are presented. It was determined that, at a heating rate of 10°C $min^{-1}$, addition of 2% fluoride decreases the transformation temperature by 400°C for $AlF_3$, by 220°C for $MgF_2$, and by 130°C for $CaF_2$. The other fluorides have no effect. The mechanism of the influence is determined, and it can be explained by the formation of fluorine bridges between fluoride cations and aluminium on the $\gamma$-$Al_2O_3$ surface.

*Keywords:* Aluminium; Fluoride; Mechanism; Polymorphism

## 1. Introduction

$\alpha$-$Al_2O_3$ is produced by calcination of aluminium hydroxide [1]. It is known in the literature [2–4] that addition of low levels of $AlF_3$ decreases the temperature of the polymorphous transformation of $\alpha$-$Al_2O_3$ formation by about 300°C, which is of practical industrial interest.

Živković et al. [2] investigated the influence of $AlF_3$ (up to 10%) on the kinetics and mechanism of $Al(OH)_3$ and AlOOH dehydration and on the $\alpha$-$Al_2O_3$ polymorphous transformation temperature. In the literature [2–6], different mechanisms for the influence of added fluoride on decreasing the temperature of $\alpha$-$Al_2O_3$ forma-

* Corresponding author.

☆ Dedicated to Hiroshi Suga on the Occasion of his 65th Birthday.


*SSDI* 0040-6031(95)02335-6

tion are presented. According to one group of authors, water separated by dehydration of $Al(OH)_3$ reacts with the added fluoride, forming gaseous HF which enters the $\gamma$-$Al_2O_3$ crystal lattice, making its crystal bonds weaker, which decreases the activation energy for the polymorphous transformation $\gamma$-$Al_2O_3 \Rightarrow \alpha$-$Al_2O_3$. Accord-

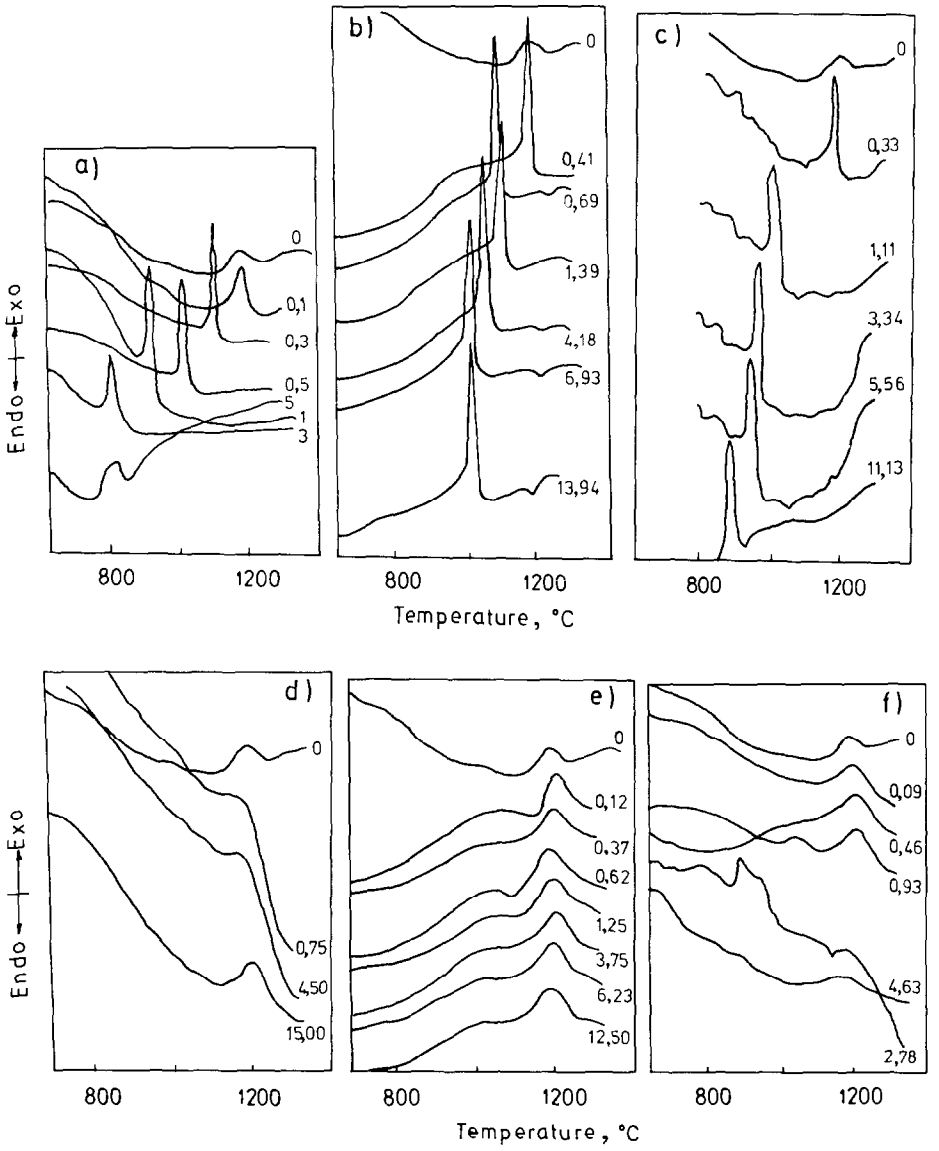


Fig. 1. Part of the DTA curves for $\alpha$-$Al_2O_3$ formation with different amounts of added fluorides: a, $AlF_3$; b, $CaF_2$; c, $MgF_2$; d, NaF; e, $Na_3AlF_6$; f, LiF. Heating rate, 10°C $min^{-1}$; numbers on the curves indicate the amount of fluoride in the initial $Al(OH)_3$ sample.

ing to another group of authors, fluoride forms solid solutions with aluminium oxide.

The influence of the fluorides $AlF_3$, NaF, $Na_3AlF_6$, $MgF_2$, $CaF_2$ and LiF (up to 10%) in a cell for electrolytical production of aluminium at the temperature of the polymorphous transformation of $\alpha$-$Al_2O_3$ formation is investigated in this paper. By comparative analysis of the results obtained, an attempt to define the mechanism of processes in the system $\gamma$-$Al_2O_3$–F (F is $AlF_3$, NaF, $Na_3AlF_6$, $CaF_2$, $MgF_2$ and LiF) is made.

## 2. Experimental

Industrial aluminium hydroxide produced by KAP (Aluminium Combine Podgorica, Yugoslavia) was used for the experimental investigations. Added fluorides were of analytical grade, and they are also used under industrial conditions in KAP.

Simulation of the calcination process with added fluorides was carried out on a Derivatograph 1500 (MOM, Budapest).

X-ray diffraction analysis was done with a Siemens diffractometer. Recordings were made with a Cu anticathode, the radiation being filtered with nickel filters.

The IR spectra were recorded with a Perkin-Elmer 983G spectrophotometer, using the pellet method. The pellets were prepared by mixing 0.3 mg of the sample with 150 mg of KBr.

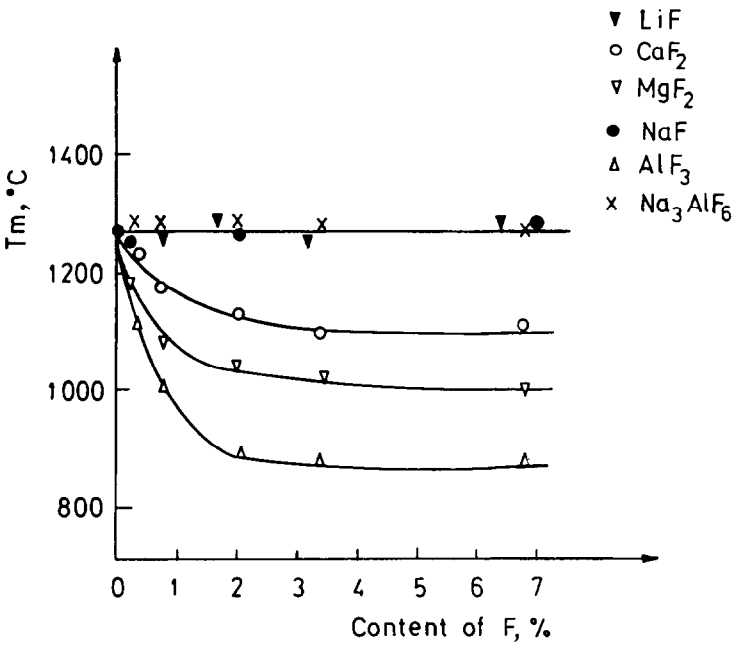


Fig. 2. The influence of the different fluorides on the temperature of the polymorphous transformation $\gamma$-$Al_2O_3 \Rightarrow \alpha$-$Al_2O_3$; heating rate 10°C $min^{-1}$.

The scanning electron microscopic investigation of the calcinated products was carried out on a Cambridge microscope.

## 3. Results and discussion

DTA curves for $Al(OH)_3$ with the fluorides (up to max. 10%) were recorded to determine the influence of different amounts of added fluorides. The results obtained (part of the DTA curve which presents the process $\gamma$-$Al_2O_3 \Rightarrow \alpha$-$Al_2O_3$) are shown in Fig. 1.

The results obtained, summarized in Fig. 2, clearly show that adding fluorides up to 2% relative to the initial mass of $Al(OH)_3$, decreases the temperature of the polymor-

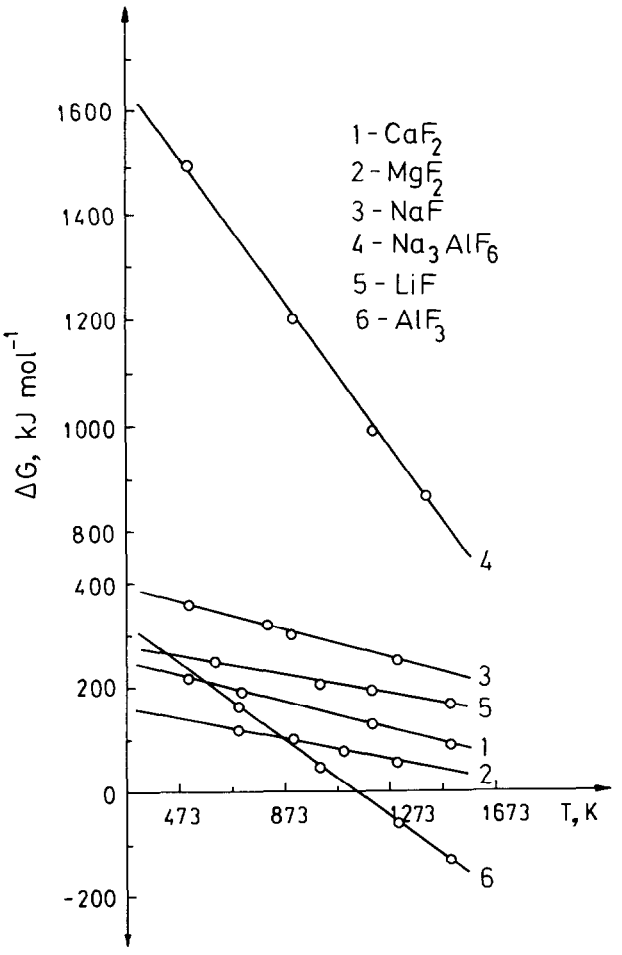


Fig. 3. The dependence $\Delta G_T^{\circ}$ against $f(T)$ for reaction (1) with the different fluorides used.

phous transformation in the following way: $AlF_3$ by 400°C, $MgF_2$ by 220°C, and $CaF_2$ by 130°C. It can also be concluded that adding NaF, LiF and $Na_3AlF_6$ does not influence the temperature of the process.

The possible influence of HF, formed by reaction, can be written in general as

$$3H_2O + 6MeF = 3Me_2O + 6HF \quad (1)$$

where $H_2O$, a product of $Al(OH)_3$ dehydration, can be neglected because all reactions of type (1), when the fluorides $AlF_3$, $MgF_2$, $CaF_2$, NaF, $Na_3AlF_6$ and LiF are used, are thermodynamically impossible in that direction at calcination temperatures. From the plot of $\Delta G_T^{\circ}$ versus temperature in Fig. 3, it can be seen that for all cases in the investigated temperature range, $\Delta G_T^{\circ} > 0$.

The experimental proof of this is shown in the DTA curves in Fig. 4, where the curves for fluoride homogenized with $\gamma$-$Al_2O_3$ (no $H_2O$ was present in the system) are shown, i.e. no conditions for reaction (1) were available. Almost the same decrease in polymorphous transformation temperature with added $AlF_3$, $MgF_2$ and $CaF_2$, and the neutral behaviour obtained using NaF, $Na_3AlF_6$ and LiF, confirm the thermodynamic analysis and the conclusion based on the results shown in Fig. 3.

X-ray analysis shows a slightly deformed crystal lattice of $\alpha$-$Al_2O_3$ as a result of the addition of fluorides, which decreases the temperature of formation. With the addition

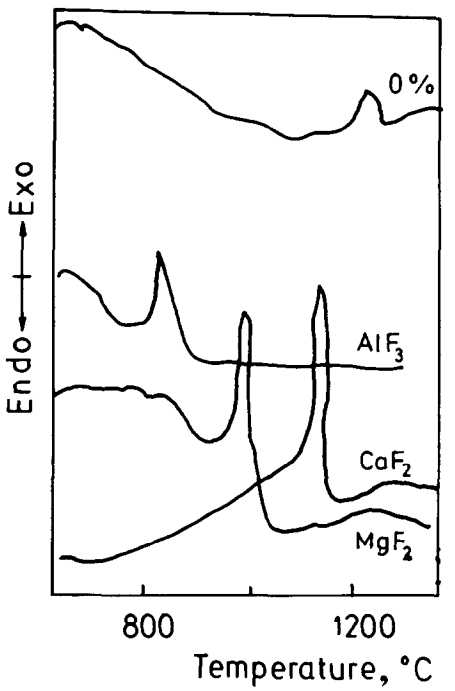


Fig. 4. DTA curves for $\gamma$-$Al_2O_3$ with 2%F added in the form of different fluorides; heating rate 10°C $min^{-1}$.

of NaF, $Na_3AlF_6$ and LiF, which do not affect this temperature, no changes in the lattice parameters for $\alpha$-$Al_2O_3$ are found.

The IR spectra for alumina calcinated by the addition of different fluorides, after the exothermic DTA peak, are shown in Fig. 5. For samples with added $AlF_3$, $MgF_2$ and $CaF_2$, spectra showing poorly crystallized $\alpha$-$Al_2O_3$ are obtained. For samples with added NaF, $Na_3AlF_6$ and LiF annealed up to 1250°C, the spectra show similar degrees of $\alpha$-$Al_2O_3$ crystallization.

Deformation vibrations of $AlO_4$ tetrahedra in the 400–500 $cm^{-1}$ range can be seen on spectra 2, 3 and 4. The 500–680 $cm^{-1}$ range contains vibrations for $AlO_4$ octahedra. The interval 750–900 $cm^{-1}$ displays the bands of the asymmetric valence vibrations of $AlO_4$ tetrahedra, while the band at 1030 $cm^{-1}$ corresponds to the vibration of the –O–Al–O– group. These results and the results of scanning electron microscopy (Fig. 6) show the presence of fluorides ($MgF_2$ and $CaF_2$) in the crystal lattice of $\alpha$-$Al_2O_3$ in the surface layer of the particles.

The data obtained show that fluoride is completely incorporated in the surface of the very active $\gamma$-$Al_2O_3$ by forming bridges between two cations (one from the fluoride and

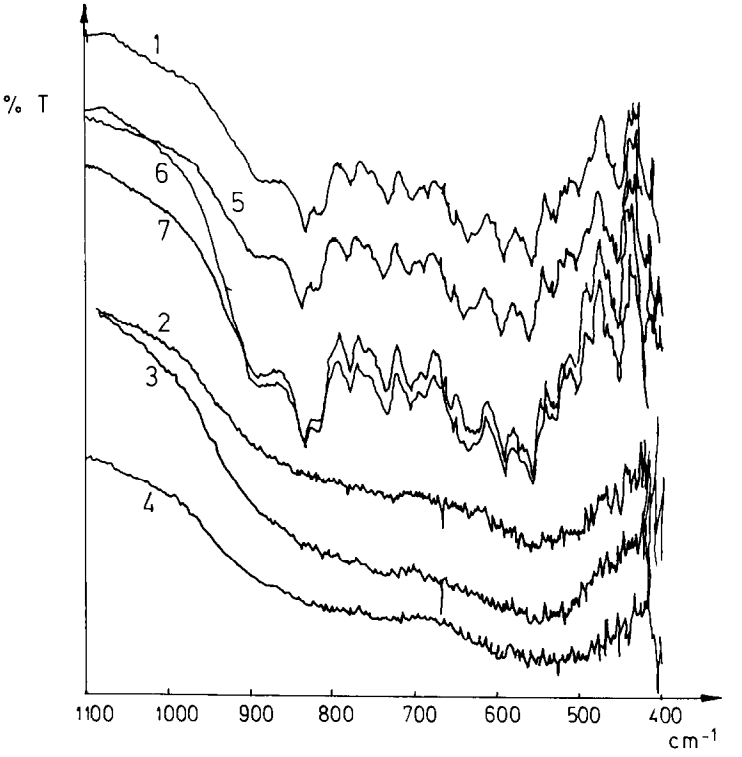


Fig. 5. IR spectra for $\alpha$-$Al_2O_3$ with the addition of different fluorides: 1, no fluoride; 2, $AlF_3$; 3, $MgF_2$; 4, $CaF_2$; 5, NaF; 6, $Na_3AlF_6$; 7, LiF.

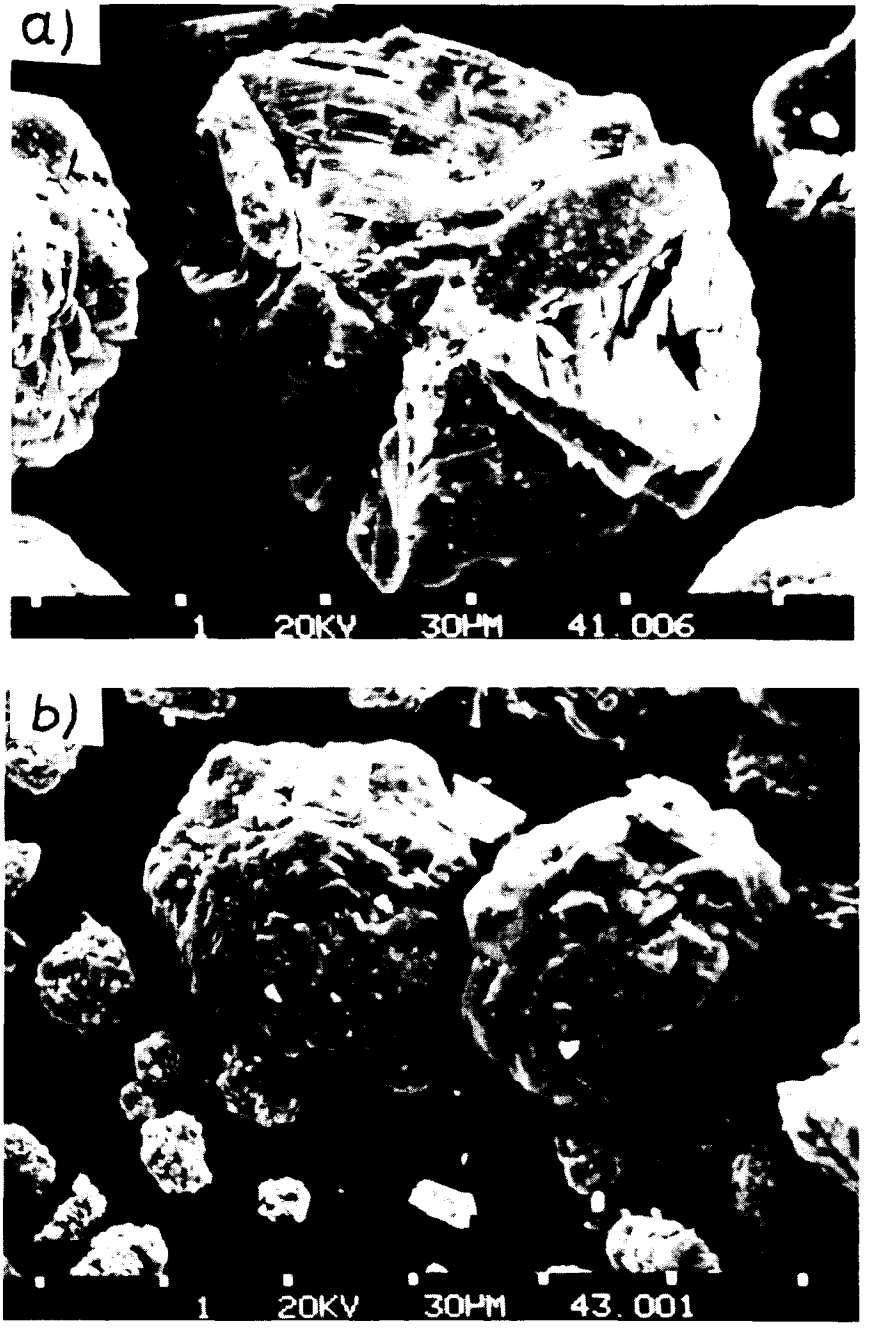


Fig. 6. SEM micrograph of $Al_2O_3$, × 3000: (a), addition of 1% $CaF_2$; (b), addition of 1% $MgF_2$.

one from the $\gamma$-$Al_2O_3$ lattice). The decrease in the polymorphous transformation of $\alpha$-$Al_2O_3$ formation with up to 2% F added in the form of the fluoride, for constant granulometric composition of the initial $Al(OH)_3$, shows that when this amount of fluorine is added, all the free places on the $\gamma$-$Al_2O_3$ surface are occupied in bridge formation of the type $Me^{2+}$–F–$Al^{3+}$ ($Me^{2+}$ is $Al^{3+}$, $Mg^{2+}$, $Ca^{2+}$, the cation of the added fluoride).

## References

[1] Ž.D. Živković, Thermochim. Acta, 21 (1979) 391.
[2] Ž.D. Živkovic, N. Pacović and M. Filipović, Thermochim. Acta, 32 (1979) 181.
[3] O.V. Bulgakov, A.V. Uvarov and T.V. Antipina, Zh. Phys. Khim., 43 (1969) 681 (in Russian).
[4] L.A. Paskevic, G.H. Gopinenko and G.A. Zavarickaja, Tsvetn. Metall., 2 (1971) 37.
[5] R. Odegard, S. Rolseth, S. Ronning and J. Thonstad, Trav. ISCOBA, 13 (1983) 471.
[6] M. Frankel, A. Glasner and S. Sarig, J. Phys. Chem., 84 (1980) 507.
[7] S.R. Stojković, Ž.D. Živković, N.D. Štrbać and I.S.G. Stojković, Spectrosc. Lett., 27(9) (1994) 1135.