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THE HYDROTHERMAL DECOMPOSITION OF ALUMINUM FLUORIDE TRIHYDRATE. KINETICS AND MECHANISM

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SUMMARY

The hydrothermal decomposition of $AlF_3.3H_2O$ in water suspension was investigated by chemical and X-ray analyses at temperatures ranging from 114 to ca. 143°C. It was found that this process runs from a trihydrate to a monohydrate composition according to a zero order rate equation to give subsequently $Al(OH,F)_3.H_2O$ and β -$AlF_3.H_2O$ direct from solution and α -$AlF_3.H_2O$ by conversion of solid trihydrate. Reactions involved in the process are discussed in detail.

INTRODUCTION

In a previous paper [1] concerned with the crystallization of AlF_3 from water solutions in excess of 100°C under steam pressure it was stated that two monohydrates, referred to as the α (cubic) and β (hexagonal) forms, as well as the hydroxyfluoride $Al(OH,F)_3.H_2O$, arising from hydrolysis, may be formed as single phases or as binary, or ternary systems. Whereas the latter two commonly arise together at 115°C, or higher, direct from solution, where $AlF_3.3.5H_2O$ exists, the α -monohydrate is formed by the conversion of $AlF_3.3H_2O$, while in suspension, starting at ca. 125°C. All these phases were found earlier by various authors in other ways [2-4]. As to the hydroxyfluoride, it was found to exist with F/Al atomic ratios extending from the previously known range 1-2 [2] to 2.5 [1]. All the aforementioned processes proceed in the narrow temperature range 110-125°C (1-2.5 at) which was not examined in detail. It was therefore of interest to investigate the AlF_3-H_2O system under isothermic conditions to determine the kinetics and the resulting phases, in order to obtain a closer view into the mechanism involved in the formation of particular solid phases. For this purpose a water suspension of $AlF_3.3H_2O$ was employed.

EXPERIMENTAL

In the experiments, $AlF_3.3H_2O$ crystals of commercial grade were used suspended in water (100 g/l). Taking into account its solubility, which amounts to ca. 18 g AlF_3/l (or 30 g/l as trihydrate), the suspension represented 70 g $AlF_3.3H_2O$/l in equilibrium with the saturated solution.

Experiments were carried out in a steel autoclave (1 l) with external heating, fitted with a manometer, thermometer, agitator (45 rpm) and a needle valve for sampling and discharging. After being placed in the autoclave, the suspension was heated to and then maintained at the desired temperature with an accuracy of ±0.5°C with continuous stirring. The zero time of the measurements was taken at 110°C, the operating temperature being approached in 10-15 min.

The course of the process was followed by analysis of solid samples taken at intervals, which, after drying at 100°C, were analyzed by the EDTA method for Al content, the crystal water being found by difference (100 - 3.11 Al %) or by ignition at 500°C for 1-2 hr. Crystal phases were identified by the X-ray method and their quantity by using calibration curves. For this purpose, the following pure samples were utilized, as described earlier [1]:

- $Al(OH,F)_3.H_2O$ with F/Al = 2.5, obtained by hydrolysis of AlF_3 solution (26 g/l) at ca. 144°C (5 at),
- hexagonal β-$AlF_3.H_2O$, obtained by decomposition of $AlF_3.3.5H_2O$ crystals suspended in acetone and heated in an autoclave to 150°C,
- cubic α-$AlF_3.H_2O$, obtained by decomposition of $AlF_3.3H_2O$ crystals suspended in the AlF_3-saturated water solution, previously acidified to pH ~ 1.8 (H_2SiF_6 10 g/l).

X-ray diffraction patterns for these standards were given previously [1].

Plots in Figure 1 relate to the binary mixtures of $Al(OH,F)_3.H_2O$ with β-$AlF_3.H_2O$, where, for determining the height ratio, the most intense peaks d = 5.7 (7.7°) and d = 6.3 (7°) were selected. For mixtures of β-$AlF_3.H_2O$ and α-$AlF_3.H_2O$ the height ratio of the line d = 6.3 to the common line at d = 3.6 - 3.7 (12°) served for analysis.

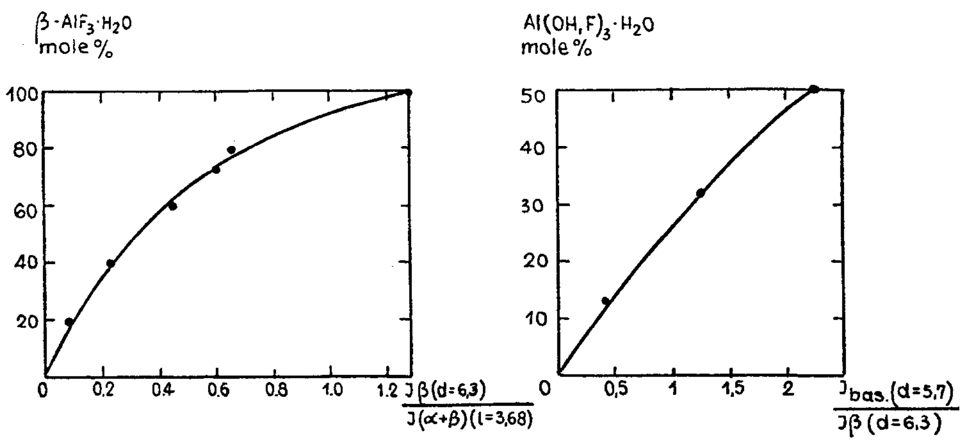

Fig. 1. Calibration curves for (left) β-$AlF_3.H_2O$ determination in admixture with α-$AlF_3.H_2O$ and for (right) $Al(OH,F)_3.H_2O$ in admixture with β-$AlF_3.H_2O$

The $AlF_3.3H_2O$ content (mole %) in mixtures with monohydrates, including hydroxyfluoride, was calculated from the H_2O/AlF_3 molar ratio using the expression:

$$x = 50\,(a - 1) \qquad (1)$$

where x = $AlF_3.3H_2O$ (mole %) and a = the molar ratio of H_2O/AlF_3 in a mixture of monohydrates. The proportions of the monohydrate constituents in the difference (100-x)(mole %) were estimated from the calibration curves given above.

RESULTS AND DISCUSSION

The kinetic data for the hydrothermal decomposition of $AlF_3.3H_2O$ in water suspension, which were obtained at 114, 117, 120, 131 and 143°C over the time ranging from 5 to 8 hrs, are presented in Figure 2.

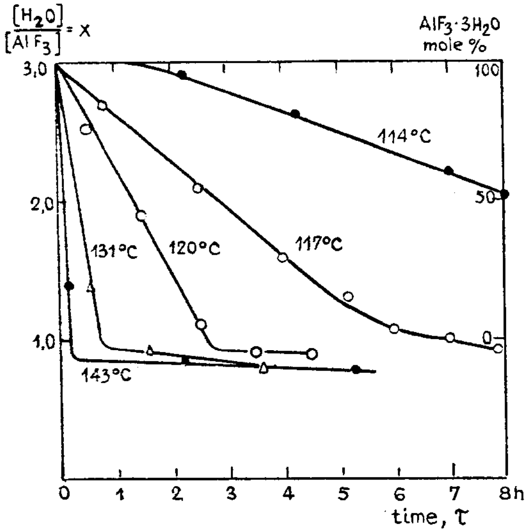

Fig.2. Isotherms for hydrothermal decomposition of $AlF_3.3H_2O$ in water suspension (100 g/l)

The data show both the effect of temperature on the reaction rate, and the paths followed by the reaction at the five temperatures. It is observed that the reaction followed two stages, an initial stage being followed by a second stage after the monohydrate composition had been approached. Rectilinearity of the isotherms obtained indicates that the process runs with a constant rate at a given temperature and conforms to a zero order rate equation:

$$\frac{dx}{d\tau} = k \qquad\qquad x = k\,.\tau \tag{2}$$

where: k = the rate constant for the reaction, $x = H_2O/AlF_3$ - the decrease in content of $AlF_3.3H_2O$ after time τ .

Rates of the process (moles H_2O/hr) calculated from the slopes of particular straight lines in Fig. 2, are plotted in Figure 3. Curve 1 represents the function k = f(t) and the plot 2 the relation lg k = f (1/T). Extrapolation of curve 1 shows the lowest temperature for hydrothermal decomposition of $AlF_3.3H_2O$ to lie at ca. 110°C.

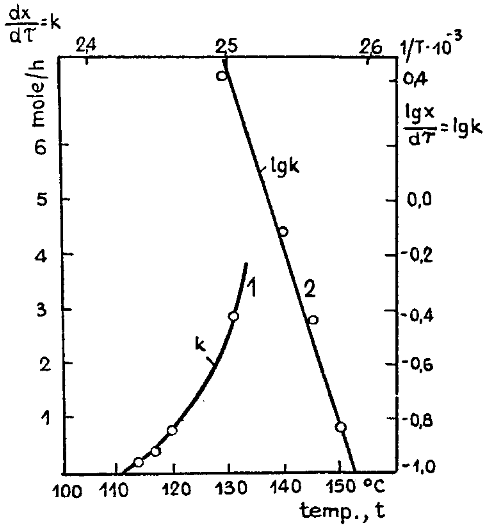

Fig.3. Dehydration rate of $AlF_3.3H_2O$ (moles/hr) versus temperature

1 - k=f(t); 2 - lg k=f(1/T)

The straight line 2 can be expressed by the Arrhenius equation:

$$\lg k = - \frac{12300}{T} + 31.0 \qquad (3)$$

Hence, the activation energy amounts to E = 4.575 . 12300 = 56.3 $kcal.mole^{-1}.deg\ K^{-1}$.

X-ray analyses of the samples taken during experiments provide additional information on the kinetics and chemistry of the processes investigated. The progressive variations in phase composition with time at different temperatures are presented in Figure 4.

The process is rather complex in nature. At the lowest temperature used, viz. 114°C, Al basic fluorides is the sole product, at least up to 50 mole % of its content in the solid mixture with $AlF_3.3H_2O$. This process is attended by decrease in pH from ca. 3 to 1.6.

At higher temperatures, 117 and 120°C, $Al(OH,F)_3.H_2O$ is not the only product, although initially the dominating one, attaining maximum content of 40-50 mole % at the conclusion of the trihydrate decomposition. Slightly later other solid

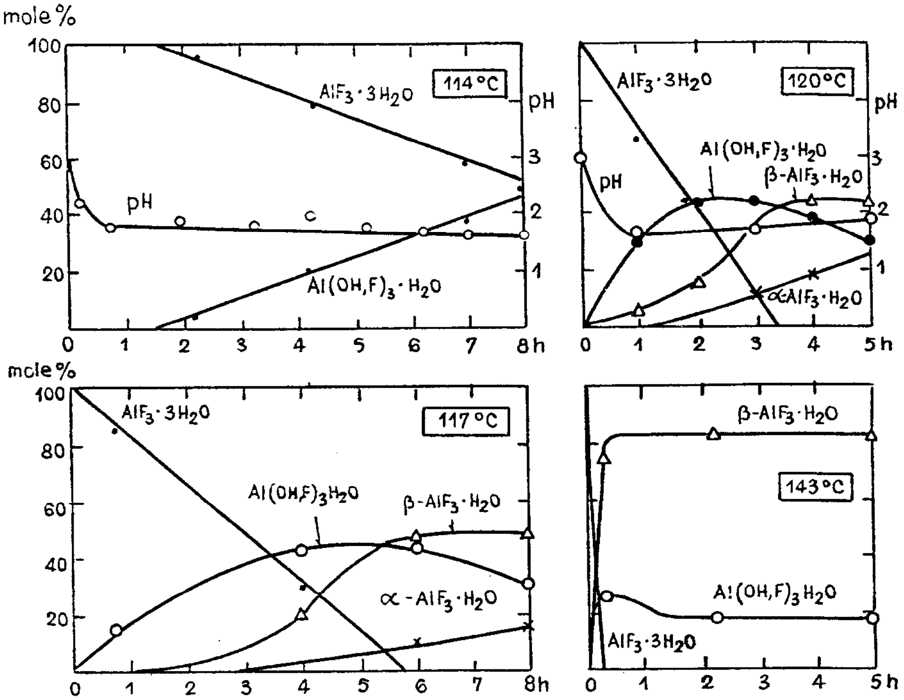

Fig. 4. Variations in phase composition (mole %) of solids during hydrothermal decomposition of $AlF_3.3H_2O$ at different temperatures.

phases appear, initially β -$AlF_3.H_2O$ and then α-$AlF_3.H_2O$; the latter increases at the expense of basic fluoride when $AlF_3.3H_2O$ is no longer present, while β -$AlF_3.H_2O$ remains at a constant level. This phenomenon fall into line with the second and slower stage of the hydrothermal decomposition, which occurs below the monohydrate composition. The final product at 120°C, after 5 hr (Fig. 4), has the composition 52% β -$AlF_3.H_2O$, 24% α -$AlF_3.H_2O$ and 24% $Al(OH,F)_3.H_2O$.

The process at 143°C is entirely different. Formation of β -$AlF_3.H_2O$ is here the fastest reaction. It is attended by precipitation of $Al(OH,F)_3.H_2O$ but not by α-$AlF_3.H_2O$. This leads to the conclusion that $AlF_3.3H_2O$ apparently dissolves faster than it is transformed into the α-monohydrate. The nature of the final product with ca. 20% $Al(OH,F)_3.H_2O$ and 80% β-$AlF_3.H_2O$ does not vary with time. This product composition is the same as that obtained from a supersaturated solution of AlF_3 of a comparable concentration 60 g/l [1].

The results presented above indicate clearly that hydrothermal decomposition of $AlF_3.3H_2O$ crystals is a convolution of numerous processes involving:

a) dissolution of $AlF_3.3H_2O$ crystals in water to give saturated solutions of $AlF_3.3.5H_2O$,

b) hydrolysis of AlF_3 in solution with formation of Al basic fluoride and hydrogen fluoride:

$$AlF_3 + (1+x)H_2O \longrightarrow Al(OH)_xF_{(3-x)}.H_2O + x\ HF \qquad (4)$$

This reaction, initially very rapid, decreases with time and goes to an equilibrium between AlF_3 and HF at a given temperature. Simultaneously, increasing amounts of HF cause the pH to drop from an initial value of ca. 3 to 1.6, due to the dissociation.

c) decomposition of $AlF_3.3.5H_2O$ in solution to form β-monohydrate:

$$AlF_3.3.5H_2O \longrightarrow \beta\text{-}AlF_3.H_2O + 2.5\ H_2O \qquad (5)$$

This reaction, not observable at 114°C, is apparent at 117°C and above. It appears subsequent to hydrolysis, and occurs increasingly until $AlF_3.3H_2O$ disappears.

d) decomposition of $AlF_3.3H_2O$ in the suspension to afford α-monohydrate:

$$AlF_3.3H_2O \longrightarrow \alpha\text{-}AlF_3.H_2O + 2\ H_2O \qquad (6)$$

This reaction appears in the third step and apparently requires the highest temperature of all the three reactions (4) - (6).

e) possible variations in composition within the range of Al basic fluoride phase existence:

$$2\ Al(OH)_2F.H_2O + 3\ HF \longrightarrow 2\ Al(OH)_{0.5}F_{2.5}.H_2O + 3\ H_2O \qquad (7)$$

f) the establishement of an equilibrium between Al basic fluoride and α-monohydrate:

$$2\ Al(OH)_{0.5}F_{2.5}.H_2O + HF \longrightarrow 2\ \alpha\text{-}AlF_3.H_2O + H_2O \qquad (8)$$

g) the reduction in water content of the monohydrate phases:

$$AlF_3.H_2O \longrightarrow AlF_3.(1-y)H_2O + y\ H_2O \qquad (9)$$

The two latter reactions, (8) and (9), take place after the complete disappearance of $AlF_3.3H_2O$.

The reactions (7) and (8) could be responsible for the observed increase in pH values during the run at 120°C (see Fig. 4).

It should be emphasized that in processes being run at 114-120°C equilibria among the solid phases were not attained within the time used and a further decrease in the basic fluoride content (parallel to an increase in α-phase) would be expected, probably to a value below 20%, as was observed at 143°C.

It is notable that, despite the high complexity of the overall reaction, the temperature effects on the decomposition rate of $AlF_3.3H_2O$ could be expressed by an extremely simple kinetics equation (2).

It is not easy to determine which of the component processes may be regarded as controlling the whole kinetics. This might be the dissolution of $AlF_3.3H_2O$ crystals, or the formation of two solid phases, $Al(OH,F)_3.H_2O$ and β-$AlF_3.H_2O$.

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