Journal of Thermal Analysis, Vol. 33 (1988) 503–509

THERMAL DECOMPOSITIONS OF AMMONIUM AND POTASSIUM ALUMS

R. Wojciechowska, W. Wojciechowski and *J. Kamiński*

INSTITUTE OF INORGANIC CHEMISTRY AND METALLURGY
OF RARE ELEMENTS, POLYTECHNICAL UNIVERSITY OF WROCŁAW,
50–370 WROCŁAW, POLAND

Simultaneous TG, DTG and DTA studies of $NH_4Al(SO_4)_2 . 12H_2O$ and $KAl(SO_4)_2 . 12H_2O$ under nonisothermal conditions were performed with a derivatograph, over the temperature range from 293 K to 1473 K under air and argon atmospheres. Appropriate chemical reactions were attributed to the thermal effects, with consideration to the results of X-ray diffraction and microscopic analyses. From the recorded curves, the activation energies E_a were calculated for all steps of the thermal decomposition reactions.

The various applications of the polymorphic modifications of aluminium oxides, as well as the final product of the phase transformations, i.e. α-Al_2O_3, have aroused great interest in the processes of dehydration of aluminium hydroxides, hydrated aluminium oxides and alums. We earlier carried out studies on the modifications of Al_2O_3 formed on the thermal decomposition of ammonium and potassium alumn synthesized from aluminium melting losses and Turoszów ashes [1]. Thermal, X-ray diffraction and microscopic analyses were performed on how transitory modifications of aluminium oxides are formed in the dehydration processes. The aims of our research were to determine the thermal decomposition products and identify the polymorphic modifications of aluminium oxides formed in the processes of dehydration of the selected alums. The results are presented in this paper.

Experimental

Thermal analysis was carried out under non-isothermal conditions with a Paulik–Paulik–Erdey 3227 T derivatograph with a heating rate programmer. Measurements were carried out at a heating rate of 3.75 deg min^{-1} over the temperature range from 293 to 1473 K, in air and argon atmospheres. The samples weighed 0.500 g each.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

X-ray analysis was performed with a DRON–1 diffractograph, using CuK_α radiation.

A Cambridge Instruments Stereoscan 180 scanning electron microscope was applied in surface studies.

Results and discussion

In the case of the ammonium alum, five endothermic DTA peaks may be observed (Fig. 1), which may be assigned to the following thermal effects:

$$NH_4Al(SO_4)_2 \cdot 12H_2O \xrightarrow{\text{to 500 K}} NH_4Al(SO_4)_2 + 12\,H_2O \qquad (1\text{–}3)$$

$$2\,NH_4Al(SO_4)_2 \xrightarrow{\text{to 870 K}} Al_2(SO_4)_3 + 2\,NH_3 + SO_3 + H_2O \qquad (4)$$

$$Al_2(SO_4)_3 \xrightarrow{\text{to 1170 K}} Al_2O_3 + 3\,SO_3 \qquad (5)$$

Thus, thermal effects associated with the elimination of the crystallization water in three stages (1–3), the dissociation of $(NH_4)_2SO_4$ (4) and the formation of Al_2O_3 (5) may be distinguished.

The four endothermic effects appearing in the DTA curve for potassium alum

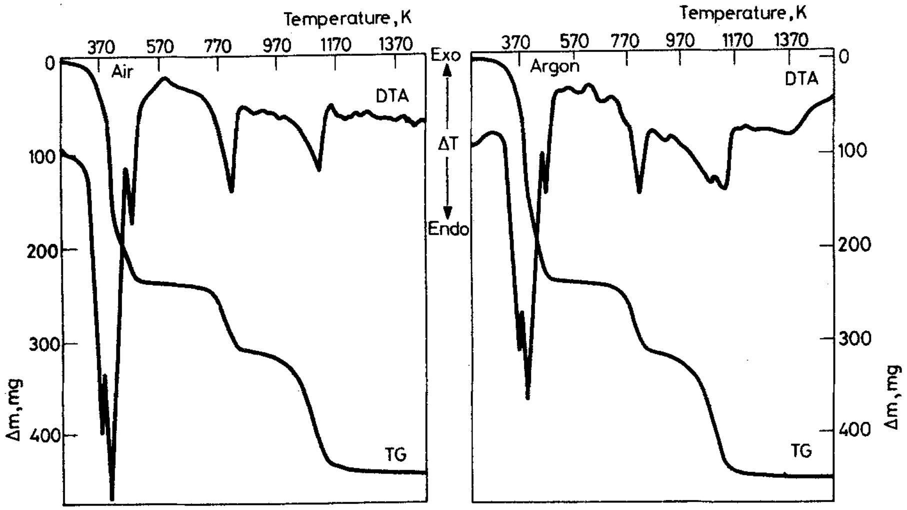

Fig. 1 DTA and TG curves of $NH_4Al(SO_4)_2 . 12H_2O$

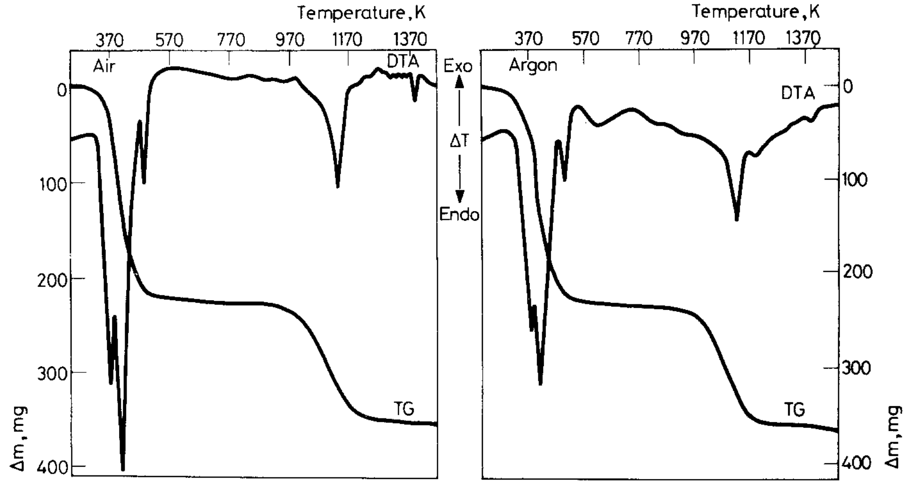

Fig. 2 DTA and TG curves of $KAl(SO_4)_2 . 12H_2O$

(Fig. 2) correspond to the following reactions:

$$KAl(SO_4)_2 \cdot 12H_2O \xrightarrow{\text{to } 510\text{ K}} KAl(SO_4)_2 + 12\,H_2O \qquad (1\text{–}3)$$

$$2\,KAl(SO_4)_2 \xrightarrow{\text{to } 1220\text{ K}} K_2SO_4 \cdot Al_2O_3 + 3\,SO_3 \qquad (4)$$

The first three effects are associated with the elimination of the crystallization water in three stages (1–3) and the fourth effect with the dissociation of $KAl(SO_4)_2$ and the formation of $K_2SO_4 \cdot Al_2O_3$.

The apparent activation energies for the particular stages of thermal decomposition of the investigated compounds were calculated on the basis of a dependence given in [2]:

$$f(\alpha)g(\alpha) = \frac{RT^2}{E_a}\frac{d\alpha}{dT}$$

where $f(\alpha) = (1-\alpha)^{1/2}$, $g(\alpha) = 2[1-(1-\alpha)^{1/2}]$ and α is the degree of reaction.

The results given in Table 1 show that the activation energies for the thermal decomposition of ammonium alum are lower in an oxidizing atmosphere than in an inert one. In the case of potassium alum, these differences are small. It should be mentioned that the activation energies for the thermal peaks associated with the three-stage dissociation of the water molecules were not calculated, as they do not

Table 1 Thermal decomposition of ammonia alum and potash alum in air and argon atmospheres

Compound	Stage	Thermal decomposition temperature, K	Activation energy, kJ/mol air, argon	Phase transformation products
$NH_4Al(SO_4)_2 \cdot 12\,H_2O$	I	748–893 (air) 763–888 (argon)	148.9 159.4	$Al_2(SO_4)_3$, NH_3, SO_3, H_2O
	II	973–1178 (air) 833–1193 (argon)	163.5 179.4	Al_2O_3, SO_3
$KAl(SO_4)_2 \cdot 12\,H_2O$	I	973–1233 (air) 993–1218 (argon)	180.0 172.0	$K_2SO_4 \cdot Al_2O_3$, SO_3

have a significant influence on the phase transformations which lead to the formation of Al_2O_3 modifications.

The X-ray diffraction analyses were interpreted by comparing measured interplanar spacings with literature data [3] corresponding to the respective aluminium oxide modifications. These data show that, in the case of ammonium alum, a polyphase system of aluminium oxides (χ, γ, η, and θ) forms at temperatures above 1220 K. Reflections indicating the formation of α-Al_2O_3 also appear. At 1470 K, besides reflections characteristic of high-temperature modificatons ($\varkappa$, δ, and θ), reflections indicating an increase in the amount of α-Al_2O_3 were also observed. In samples heated for 2 h at 1470 K, reflections derived mainly from the α-phase were observed. In the case of potassium alum heated to 1220 K, the structure of the compound is destroyed and $K_2SO_4 \cdot Al_2O_3$ is formed. After

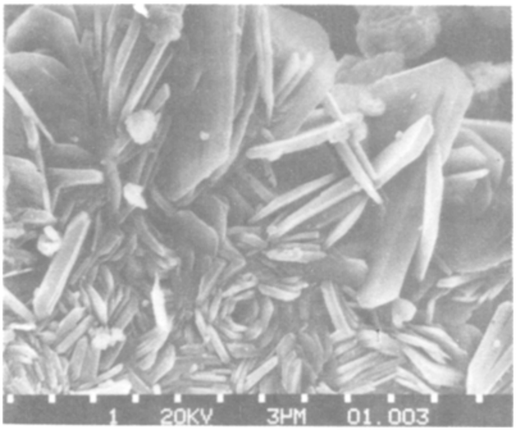

Fig. 3 α-Al_2O_3 crystals with $\varkappa$, Θ—Al_2O_3, obtained from $KAl(SO_4)_2$ at 1470 K. Magn. × 3200

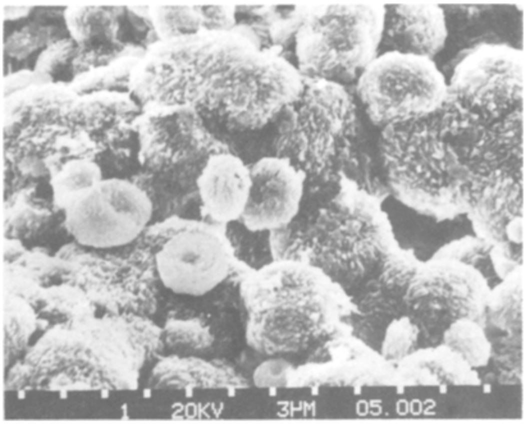

Fig. 4 Mixture of low- and high-temperature γ-, η-, $\varkappa$-, δ-, Θ-Al_2O_3 obtained from $KAl(SO_4)_2$ at 1220 K. Magn. ×3200

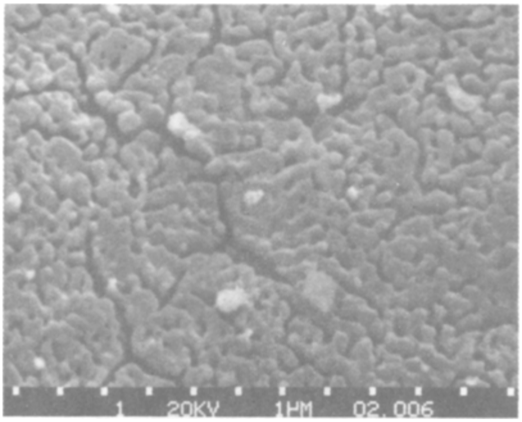

Fig. 5 Fragment of α-Al_2O_3 agglomerate with $\varkappa$-, δ-, Θ-Al_2O_3 obtained from $NH_4Al(SO_4)_2$ at 1470 K. Magn. ×10,000

leaching-out of K_2SO_4 with water, reflections typical of both low-temperature (χ and γ) and high-temperature ($\varkappa$, δ and θ) modificatons of aluminium oxides were observed. At 1470 K, α-Al_2O_3 appears besides the high-temperature modifications. In samples heated for 2 h at 1470 K, the α-phase is the dominant component.

Microscopic studies of alums heated at 1470 K for 2 h and at 1220 K for 2 h show distinct differences in the shapes and structures of the grains. This is especially prominent in the case of ammonium alum.

Potassium alum heated at 1470 K for 2 h forms crystalline α-Al_2O_3 (Fig. 3), exhibiting a crystal texture. Admixtures of $\varkappa$ and θ-Al_2O_3 are also visible. On the

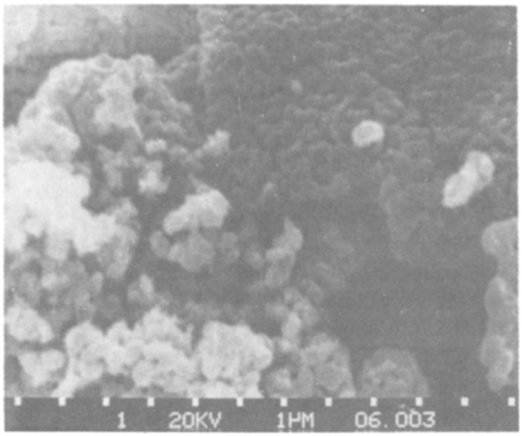

Fig. 6 Fragment of $\varkappa$-, γ-, η-, Θ-, α-Al_2O_3 agglomerate, obtained from $NH_4Al(SO_4)_2$ at 1220 K. Magn. × 10,000

other hand, when heated at 1220 K for 2 h, this compound forms a mixture of low- and high-temperature modifications of fine-grained aluminium oxide (Fig. 4). The aluminium oxides formed from ammonium alum exhibit different grain shapes (Figs 5 and 6). A fragment of an α-Al_2O_3 agglomerate with $\varkappa$, δ and θ-Al_2O_3 admixtures, having a distinctly crystalline structure (1470 K for 2 h), is illustrated in Fig. 5. An agglomerate comparising a mixture of poorly crystallized low- and high-temperature (1220 K for 2 h) modifications of aluminium oxides is shown in Fig. 6.

Microscopic studies and specific surface area measurements have shown differences in the crystal structures, the shapes and sizes of the grains, and the specific surface areas of aluminium oxides obtained from the two investigated alums at 1470 K. The aluminium oxides derived from potassium alum exhibit a crystalline structure with grain sizes of 1–10 μm and specific surface areas of 1–2 m^2/g, whereas aluminium oxides derived from ammonium alum display a fine-grained structure, an agglomerate-forming capacity, and a much larger specific surface area, of 37 m^2/g.

References

1 J. Kamiński and R. Wojciechowska, Materials Science, 3 (1980) 79.

2 A. B. Phadnis and V. V. Deshpande, Thermochim. Acta, 62 (1983) 362.

3 B. C. Lippens, Physical and Chemical Aspects of Adsorbents and Catalysts, Acad. Press, London–New York 1970.

Zusammenfassung — Simultane TG—DTG—DTA-Untersuchungen von $NH_4Al(SO_4)_2 \cdot 12H_2O$ und $KAl(SO_4)_2 \cdot 12H_2O$ wurden unter nicht-isothermen Bedingungen mit einem Derivatographen von 293—1473 K an Luft und unter Argon durchgeführt. Den thermischen Effekten werden chemische Reaktionen zugordnet, wobei Röntgenbeugungs- und mikroskopische Ergebnisse berücksichtigt werden. Aus den thermoanalytischen Messkurven werden Aktivierungsenergien der Zersetzungsreaktionen berechnet.

Резюме — С помощью дериватографа проведены совмещенные ТГ, ДТГ и ДТА исследования $NH_4Al(SO_4)_2 \cdot 12H_2O$ и $KAl(SO_4)_2 \cdot 12H_2O$ в неизотермических условиях в атмосфере воздуха и аргона в интервале температур 293—1473 К. На основе рентгенофазового и микроскопического анализа, происходящие химические реакции были отнесены к соответствующим термическим эффектам. На основании измеренных кривых были вычислены энергии активации E_a для всех стадий термического разложения.