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Thermal decomposition of basic aluminium ammonium sulphate in an environment of carbon and water vapour

B. Pacewska

Institute of Chemistry, Płock Branch of Warsaw University of Technology, 09-400 Płock (Poland)

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Abstract

By means of the thermogravimetric method, differential thermal analysis, X-ray diffraction phase analysis, infrared spectroscopy, electron microscopy and chemical analyses, stages of decomposition of basic aluminium ammonium sulphate (BAAS) in an environment of carbon and water vapour were studied. It has been found that the addition of carbon and water vapour influences the course of alunite decomposition only in the last stage, i.e. the desulphuration of the compound. This process occurs at a lower temperature than in air. The final product of decomposition of the basic salt at 1223 K is γ-Al_2O_3. The experimental work was preceded by the thermodynamic analysis of the desulphuration process of BAAS in an environment of carbon and water vapour, and the results have been correlated with experimental data.

INTRODUCTION

In previous work [1] the authors presented results of the investigation of the decomposition of basic aluminium ammonium sulphate (BAAS) in air and in a vacuum. The product of dehydration of the basic salt is $3Al_2O_3 \cdot 4SO_3 \cdot (0\text{–}2)H_2O$, which next dissociates into γ-Al_2O_3 and sulphur oxides.

Investigations of the dissociation of BAAS in a hydrogen atmosphere [2] indicate that the reducing environment influences only the desulphuration of the basic salt, causing a decrease in the decomposition temperature.

In this work we present the results of investigations of the process of BAAS decomposition in the presence of carbon and water vapour.

THERMODYNAMIC ANALYSIS OF THE PROCESS

Thermodynamic calculations for the reactions which can make up the thermal decomposition process of a basic salt were conducted with the

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Correspondence to: B. Pacewska, Institute of Chemistry, Płock Branch of Warsaw University of Technology, 09-400 Płock, Poland.

assumption that a decisive influence of the addition of carbon and water vapour is to be expected in the third stage of BAAS decomposition, i.e. on its desulphuration. The addition of carbon and water vapour to the environment of the reaction causes a mixture of C, CO and H_2 to form a reducing agent in the conditions of the process. Moreover, near the higher limit of the temperature range the contribution of gaseous elements is higher.

Thermodynamic calculations were performed for three reductors; they were limited to reactions occurring during decomposition of $Al_2(SO_4)_3$ and secondary reactions which could occur in the gaseous phase.

For the reactions considered, the standard thermodynamic potentials at temperatures of 298, 600, 800 and 1000 K using the standard thermodynamic potentials for reagents $\Delta G_f^\ominus$ have been calculated. Typical standard thermodynamic potentials for forming gaseous reagents were taken from tables [3], and those for solid reagents were calculated on the basic of values of the functions $\Delta H^\ominus_{f298}$, $S^\ominus_{298}$, $S^\ominus_T - S^\ominus_{298}$ and $\Delta H^\ominus_T - \Delta H^\ominus_{298}$ [4]. The results of the calculations are given in Table 1.

These calculations indicate that the desulphuration process of BAAS in

TABLE 1

Standard thermodynamic potentials of reactions occurring during desulphuration process of BAAS in an environment of carbon and water vapour

No.	Reaction	$\Delta G^\ominus$ (kJ mol^{-1})			
		298 K	600 K	800 K	1000 K
1	$Al_2(SO_4)_3 = Al_2O_3 + 3SO_2 + 1.50_2$	614.34	358.04	193.62	33.14
2	$Al_2(SO_4)_3 = Al_2S_3 + 6O_2$	2382.82	2047.32	1829.27	1614.74
3	$Al_2(SO_4)_3 + 1.5C = Al_2O_3 + 3SO_2 + 1.5CO_2$	22.42	−225.80	−395.33	−555.43
4	$Al_2(SO_4)_3 + 6C = Al_2S_3 + 6CO_2$	13.28	−326.65	−546.96	−763.00
5	$Al_2S_3 + 3H_2O = Al_2O_3 + 3H_2S$	−279.18	−270.63	−264.26	−257.98
6	$Al_2(SO_4)_3 + 4.5C = 0.5Al_4C_3 + 3SO_2 + 3CO_2$	911.95	562.55	337.59	117.49
7	$Al_2(SO_4)_3 + 6C = Al_2O_3 + 3COS + 3CO_2$	−166.26	−474.60	−711.25	−927.08
8	$Al_2(SO_4)_3 + 6C = Al_2O_3 + 1.5CS_2 + 4.5CO_2$	−160.44	−491.53	−700.74	−908.69
9	$Al_2(SO_4)_3 + N_2 + 3C = 2AlN + 3SO_2 + 3CO_2$	437.55	148.54	−37.42	−217.96
10	$Al_2(SO_4)_3 + 12CO = Al_2S_3 + 12CO_2$	−706.39	−722.61	−727.97	−731.32
11	$Al_2(SO_4)_3 + 3CO = Al_2O_3 + 3SO_2 + 3CO_2$	−141.20	−334.45	−446.70	−553.37
12	$Al_2(SO_4)_3 + 12CO = Al_2O_3 + 3COS + 9CO_2$	−885.18	−870.05	−895.95	−894.65
13	$Al_2(SO_4)_3 + 12CO = Al_2O_3 + 1.5CS_2 + 10.5CO_2$	−880.24	−884.22	−881.24	−876.25
14	$Al_2(SO_4)_3 + 3H_2 = Al_2O_3 + 3SO_2 + 3H_2O$	−72.49	−285.05	−417.91	−545.58
15	$Al_2(SO_4)_3 + 12H_2 = Al_2S_3 + 12H_2O$	−364.49	−525.01	−616.85	−700.15
16	$SO_2 + C = 0.5S_2 + CO_2$	−95.78	−94.95	−92.01	−107.01
17	$SO_2 + 1.5C = COS + 0.5CO_2$	−64.07	−79.69	−104.96	−121.85
18	$COS = 0.5CO_2 + 0.5CS_2$	1.93	3.69	4.82	6.08
19	$SO_2 + 1.5C = 0.5CS_2 + CO_2$	−60.84	−84.39	−100.06	−115.73
20	$COS + H_2O = H_2S + CO_2$	−33.18	−41.06	−32.14	−31.55
21	$CS_2 + 2H_2O = CO_2 + 2H_2S$	−70.22	−72.70	−74.00	−75.29
22	$SO_2 + 2CO = 0.5S_2 + 2CO_2$	−214.28	−160.85	−122.10	−101.61
23	$SO_2 + 3H_2 = H_2S + 2H_2O$	−190.39	−170.20	−154.40	−137.52
24	$SO_2 + 2H_2 = 0.5S_2 + 2H_2O$	−157.29	−109.57	−103.58	−93.48

an environment of carbon and water vapour can proceed at a lower temperature in comparison with its course in air.

Assuming that the desulphuration of basic salt resolves into the capture of O^{2-} by the Al^{3+} cation [2]

$3SO_4^{2-} \rightarrow SO_3 + 3O^{2-}$

$3O^{2-} + 2Al^{3+} \rightarrow Al_2O_3$

and subsequent decomposition of SO_3

$SO_3 \rightleftharpoons SO_2 + 0.5O_2$

the treatment with reducing agents refers mainly to the reduction of SO_3 formed as the original product of decomposition, which can be especially important near the lower limit of the temperature range of this stage, for which the equilibrium of the reaction $SO_3 \rightleftharpoons SO_2 + 0.5O_2$ is shifted towards SO_3 [1].

In solid products of the decomposition of BAAS in an environment of carbon and water vapour, the presence of aluminium oxide should be expected, with a mixture of SO_2, H_2S and elementary sulphur in the gaseous products.

EXPERIMENTAL

The subject of the studies was the basic aluminium ammonium sulphate isomorphous with alunite, which has composition Al_2O_3 35.2%, NH_3 3.5%, SO_3 42%, H_2O 19.3%. The grain composition of the starting material is presented in Fig. 1, and a photomicrograph is shown in Fig. 2.

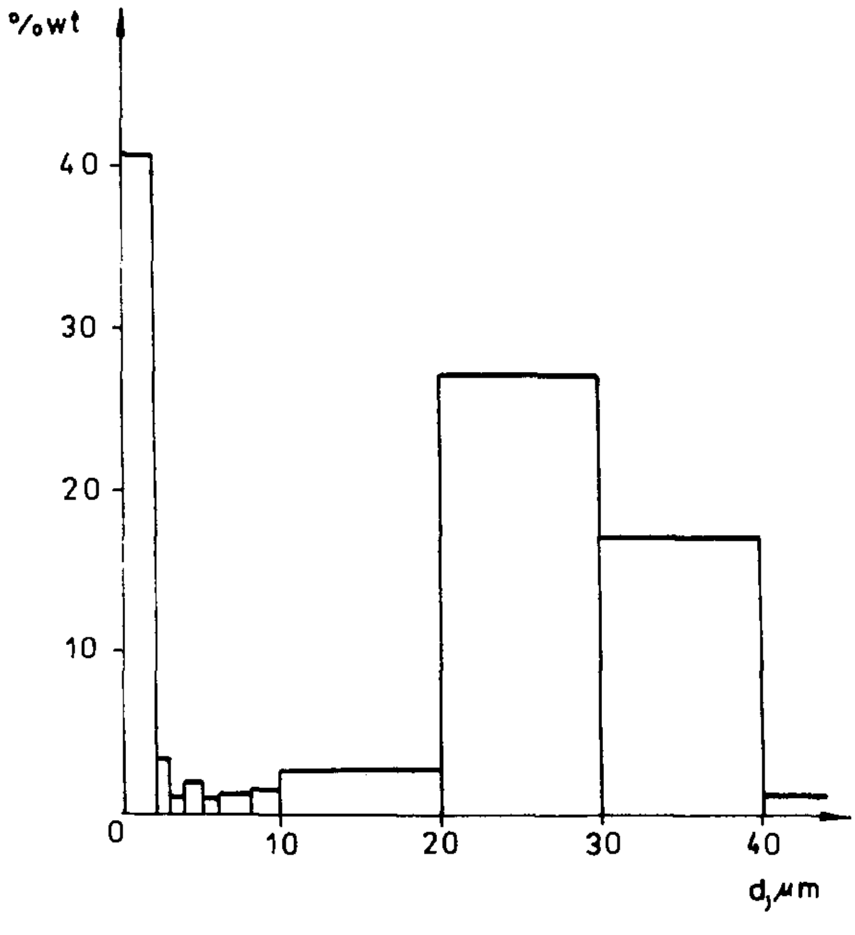

Fig. 1. Grain composition of starting material.

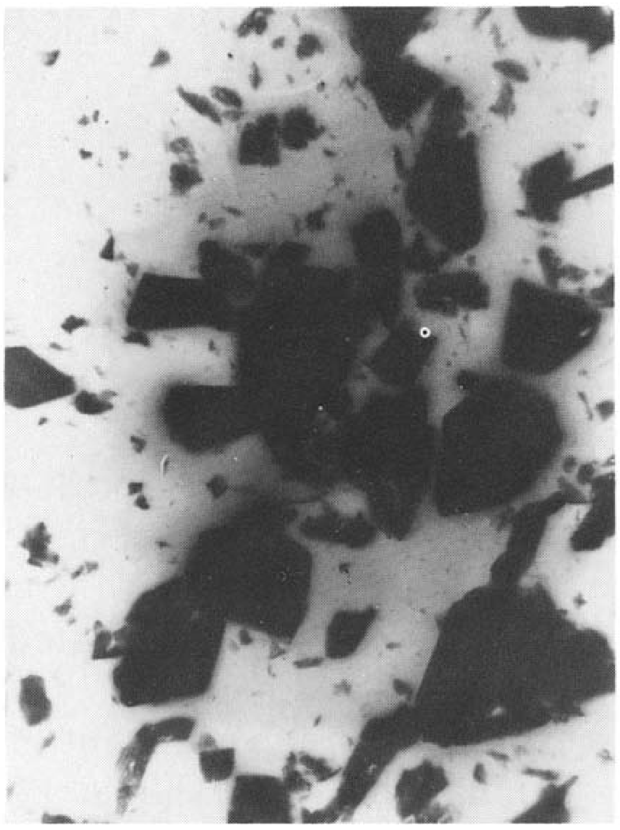

Fig. 2. Uncalcined particles of BAAS. Original magnification 4000×.

The BET specific surface of BAAS, determined on the basis of adsorption of benzene vapour is equal to 6 $m^2 g^{-1}$.

The process of reductive decomposition of the basic salt was carried out for samples containing 94% of BAAS and 6% of the soot VULCAN 6. The amount of added soot was determined in previous investigations [5].

The process was performed in an inert (nitrogen) atmosphere with the addition of water vapour (45 vol%). In Fig. 3 the thermogram of BAAS with carbon as additive in the presence of water vapour and the thermogram of this compound in a nitrogen atmosphere are presented. Both thermograms were recorded with a model C derivatograph for 150 mg samples of BAAS at a heating rate of 10 K min^{-1}.

In another experimental series the BAAS samples, with carbon and water vapour, were heated up to a given temperature with a heating rate of 20 K min^{-1}. At this temperature the samples were calcined for 2 h. The isothermal calcination temperature of the samples was determined on the basis of the BAAS thermogram with carbon and water vapour present (Fig. 3). The results are given in Fig. 4.

In parallel with thermogravimetric investigations, the samples of the basic salt with carbon as additive were heated isothermally in a tube reactor in a stream of nitrogen and water vapour at the following temperatures, for 2 h each: 773 K, 973 K, 1123 K, and 1223 K.

By means of X-ray phase analysis, infrared spectroscopy and chemical analyses, the solid products formed as intermediates of dissociation were determined. Observations of the investigated samples by scanning electron microscopy were also performed.

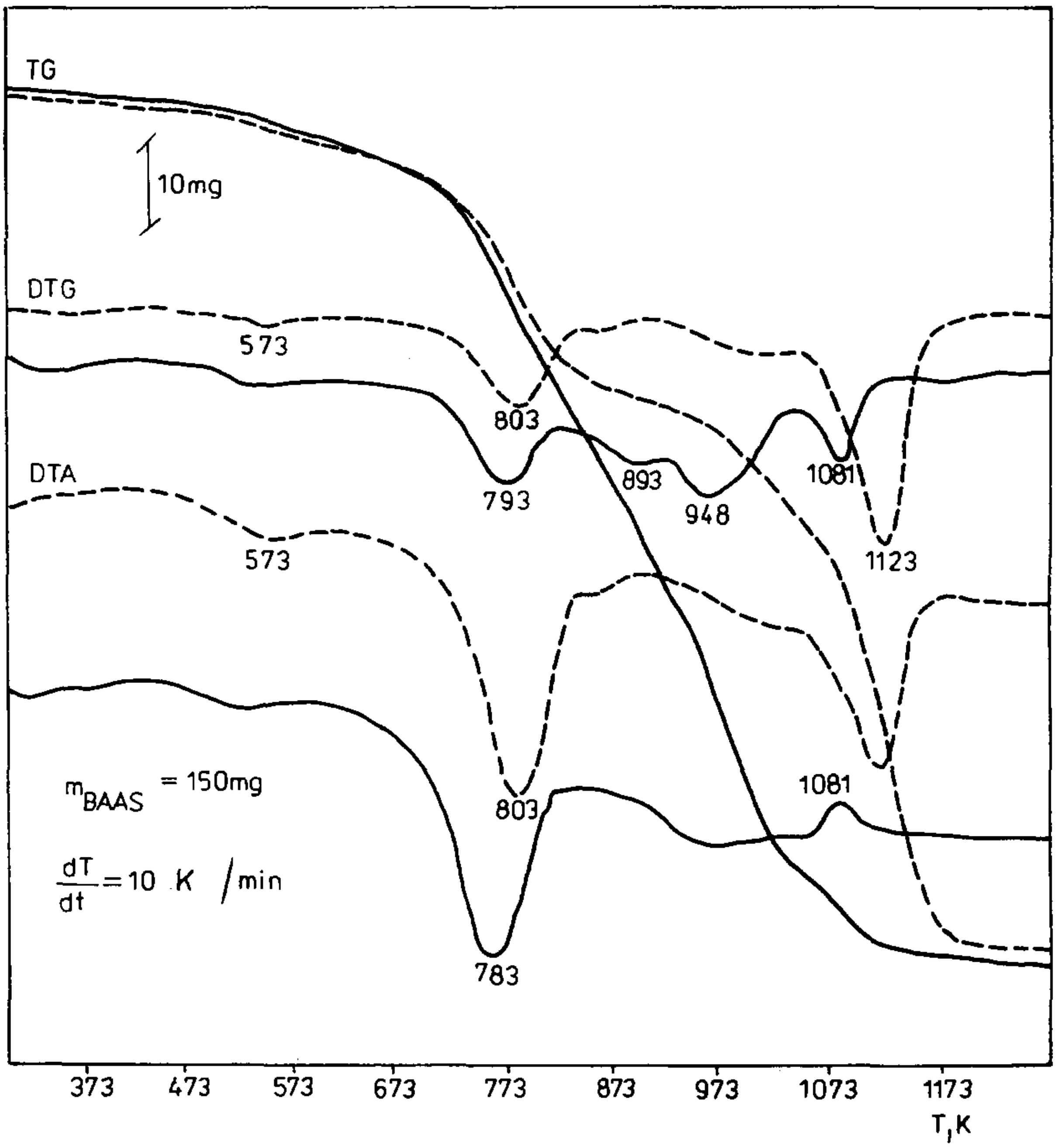

Fig. 3. Thermograms of BAAS samples: --------, in nitrogen atmosphere; ——, in an environment of carbon and water vapour.

X-ray phase analysis of partially decomposed BAAS samples was carried out in a model HZG-4C diffractometer made in Germany, using Co Kα radiation, and the results are presented in Table 2 and Fig. 5.

The infrared spectra were recorded with a Specord spectrometer (Carl Zeiss, Jena) within the wavenumber interval 4000–400 cm^{-1}. The samples were compressed into the form of tablets with KBr. The infrared absorption spectra of BAAS and of the products of its partial and complete decomposition are presented in Fig. 6.

Figure 7 shows the scanning electron micrograph of particles of the starting material and that calcined at 973 K for 2 h in an environment of carbon and water vapour. In the solid products, S^{2-} was determined semi-quantitatively with sodium nitroprusside. The content of sulphates as SO_4^{2-} was also determined gravimetrically (precipitation with barium sulphate).

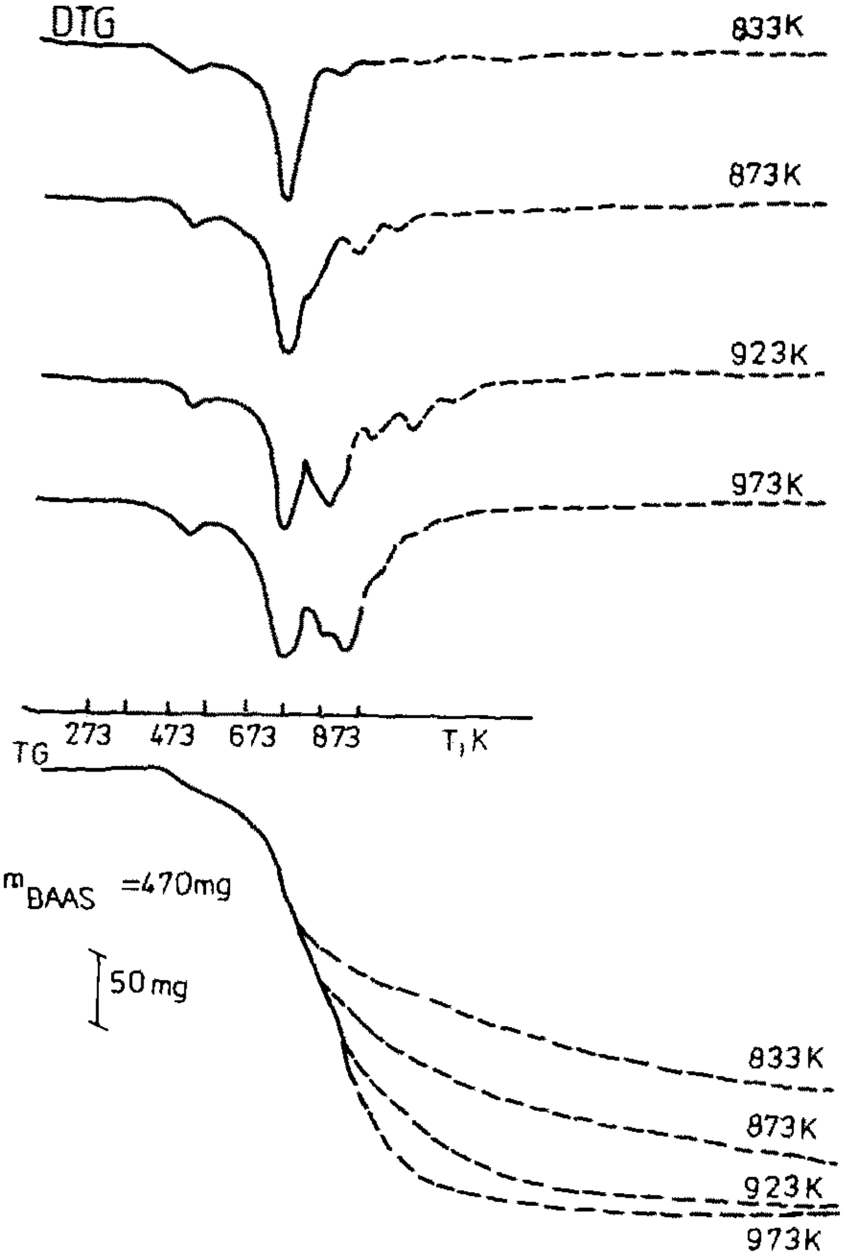

Fig. 4. Thermal decomposition of BAAS samples in environment of carbon and water vapour at the conditions indicated: ——, $T \neq$ const., $dT/dt = 20\ \mathrm{K\ min^{-1}}$; --------, $T =$ const.

TABLE 2

X-ray diffraction analyses of intermediate and final products of decomposition of BAAS in environment of carbon and water vapour

γ-Al_2O_3					$3Al_2O_3 \cdot 4SO_3 \cdot (0\text{–}2)H_2O$		
Standard (Mirkin)		Sample 973 K 2 h	Sample 1123 K 2 h	Sample 1223 K 2 h	Standard (ASTM)		Sample 773 K 2 h
d (nm)	*I*	*d* (nm)	*d* (nm)	*d* (nm)	*d* (nm)	*I*	*d* (nm)
—	—	0.299	0.299	—	—	—	—
—	—	0.288	0.289	—	—	—	—
0.239	19	0.238	0.239	0.239	0.453	10	—
0.228	13	0.228	0.228	0.227	0.349	30	0.348
0.198	72	0.198	0.198	0.197	0.309	100	0.312
0.152	6	0.152	0.152	0.152	0.247	15	—
0.139	100	0.139	0.139	0.139	0.220	10	—

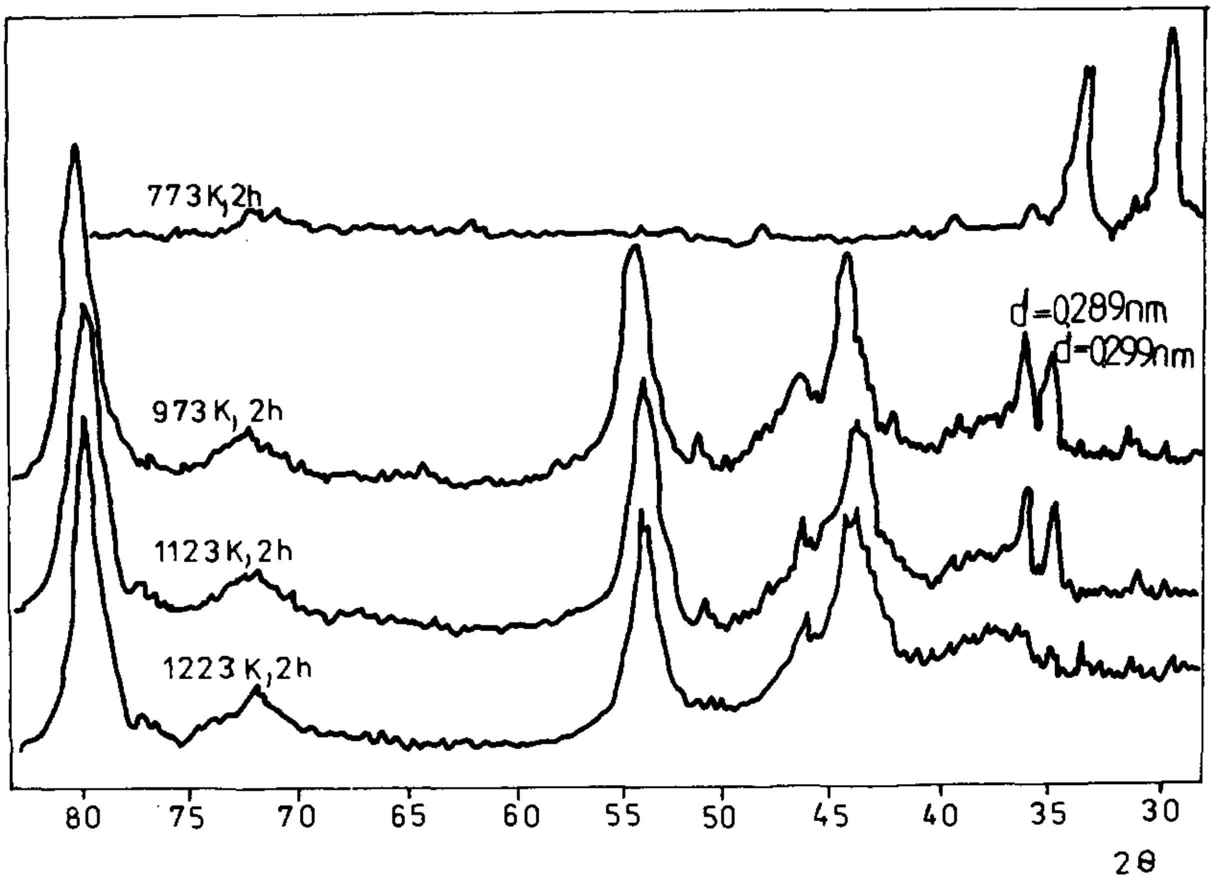

Fig. 5. X-ray diffraction analyses of intermediate and final products of decomposition of BAAS in environment of carbon and water vapour at the indicated temperatures and times.

Gaseous products released during decomposition of the compound were absorbed in 30% NaOH and determined by the Wiele method [6] in the form of the contents of the ions S^{2-} and SO_3^{2-}.

RESULTS

The dehydration of BAAS in an environment of carbon and water vapour and in a nitrogen atmosphere (Fig. 3) takes place similarly. In the temperature range 298–823 K the loss in weight of both samples is about 20%, and is connected with the release of water (except for 1 mol) and ammonia from BAAS.

The onset of desulphuration in this temperature region observed by other authors studying the decomposition of compounds of alunite [7, 8] cannot be excluded.

By means of X-ray diffraction, $3Al_2O_3 \cdot 4SO_3 \cdot yH_2O$ (where y is in the range 0–2) was identified as the intermediate solid product of calcination of BAAS at 773 K for 2 h in an environment of carbon and water vapour (Table 2 and Fig. 5).

The presence of water in the product of dehydration of the basic salt is also confirmed by the characteristic absorption band at 3500 cm^{-1} in the infrared spectrum (Fig. 6). The band at 1430 cm^{-1} characteristic of ammonium ion is not observed.

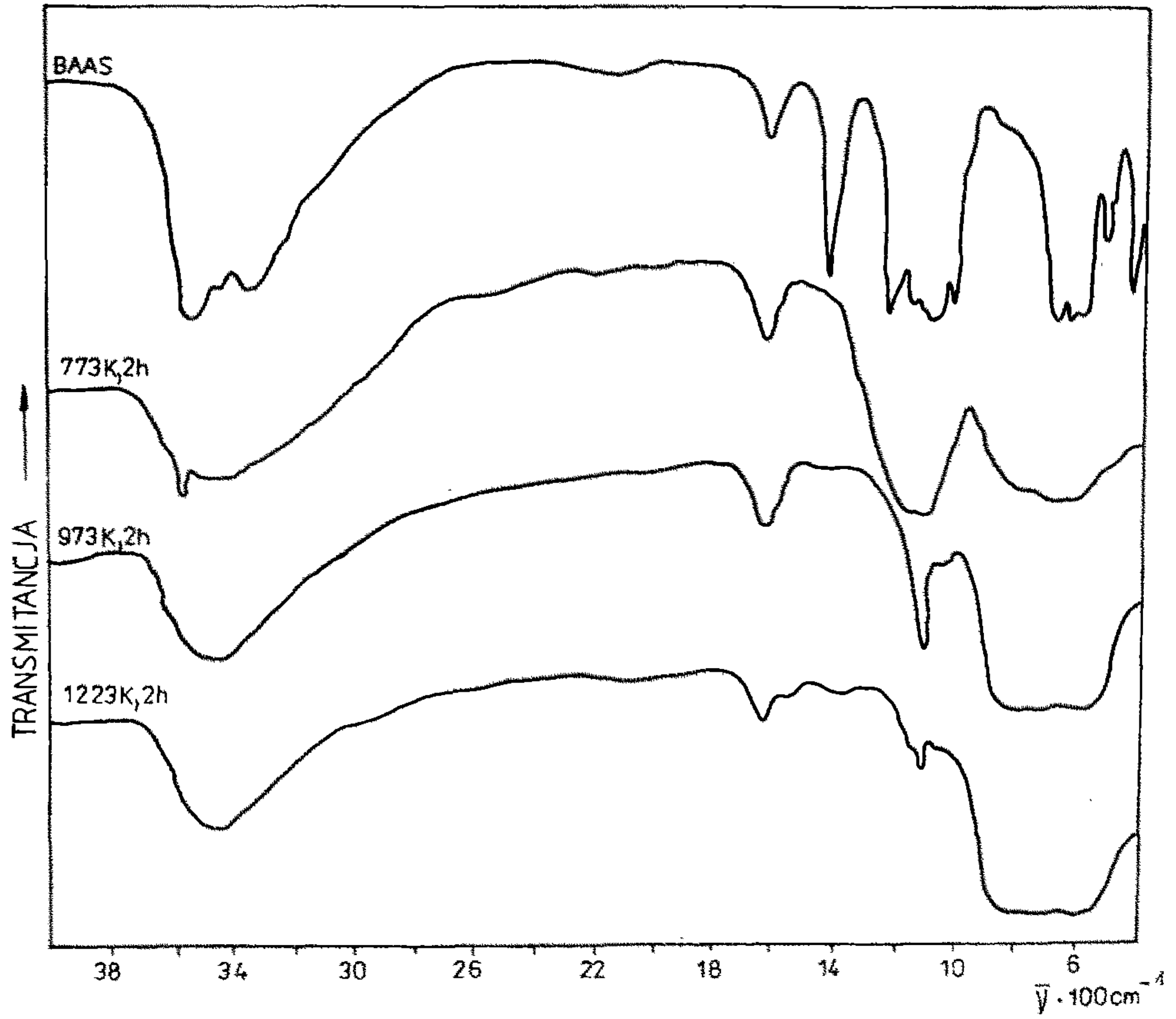

Fig. 6. Infrared spectra of starting material and of partly and completely decomposed samples of BAAS in environment of carbon and water vapour at indicated temperatures and times.

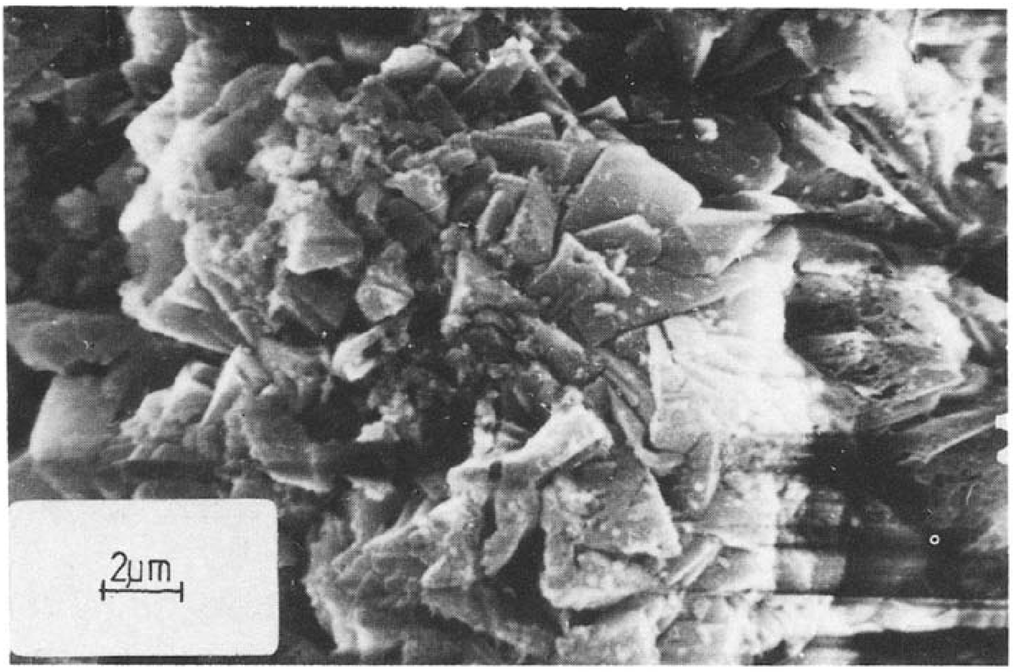

Fig. 7. Scanning electron micrograph of BAAS samples decomposed at 973 K for 2 h in environment of carbon and water vapour.

Similar results were obtained during the thermal decomposition of BAAS in a vacuum [1].

The desulphuration process of BAAS in an environment of carbon and water vapour proceeds at a lower temperature in comparison with its course in nitrogen (Fig. 3). One can observe a broad peak with extrema at 893, 948 and 1081 K on the DTG curve (Fig. 3). Up to 993 K the compound loses about 38% of its weight, which means the release of 3.5 mol of SO_3 and all of the remaining water. The effect observed at 1081 K on the DTG curve corresponds to the evolution of 0.5 mol of SO_3 (curve TG). The one broad flattened endothermic feature in the DTA curve (Fig. 3) accompanies the desulphuration process of BAAS, and an exothermic effect at 1081 K corresponds to γ-Al_2P_3 formed from the amorphous phase.

Another course of the BAAS desulphuration process was observed under isothermal conditions; the calcination of the sample at 973 K for 2 h with addition of carbon and water vapour led to the production of γ-Al_2O_3 (X-ray diffraction patterns in Fig. 5, infrared spectra in Fig. 6 and DTG curve in Fig. 4).

An absorption band centred at $\approx 1120\ \mathrm{cm}^{-1}$ in the infrared spectra of BAAS decomposed in reducing conditions at 973 and 1223 K for 2 h (Fig. 5) indicates a small content of residual sulphate groups in the alumina, probably present as a solid solution. This is consistent with the result of gravimetric analysis, which indicates a trace of sulphates in the sample heated at 973 K for 2 h. This also agrees with previous observations of the persistence of sulphate in alumina to temperatures above 1373 K [9, 10].

The X-ray diffraction patterns do not permit identification of all the intermediate solid products of BAAS samples partially decomposed by reduction at temperatures in the range 773–973 K. X-ray diffraction analyses indicate insufficiently developed structures of the investigated samples.

In the sample of BAAS heated at 773 K for 2 h only $AlH(SO_4)_2$ was determined unequivocally by the XRD method. One cannot exclude the presence of alumoxane sulphate as intermediate, particularly in view of the character of infrared spectra of BAAS sample heated at 773 K for 2 h, which contain weak absorption bands in the range $800–700\ \mathrm{cm}^{-1}$ [11] overlapping the broad absorption bands of aluminium oxide.

Two peaks at $d = 0.289$ nm and 0.299 nm in the XRD pattern (Fig. 5 and Table 2) were not identified.

Further heating of BAAS samples at 1123 and 1223 K for 2 h did not change the crystallographic form of aluminium oxide (Figs. 5 and 6). In the intermediate and final solid products of BAAS decomposition, no sulphide anions were detected. In the gaseous phase SO_2 and H_2S were found. Elementary sulphur was observed in the form of a yellow bloom accumulating in the cooler parts of the apparatus.

CONCLUSIONS

The unified interpretation of the presented results makes it possible to propose the following probable scheme for the desulphuration of BAAS in an environment of carbon and water vapour.

With carbon as reducing agent

$2AlH(SO_4)_2 + 0.5C = Al_2(SO_4)_3 + SO_2 + 0.5CO_2 + H_2O$
$Al_2(SO_4)_3 + 1.5C = Al_2O_3 + 3SO_2 + 1.5CO_2$
$2AlH(SO_4)_2 + C = Al_2O(SO_4)_2 + 2SO_2 + CO_2 + H_2O$
$Al_2O(SO_4)_2 + C = Al_2O_3 + 2SO_2 + CO_2$

With CO as reducing agent

$2AlH(SO_4)_2 + CO = Al_2(SO_4)_3 + SO_2 + CO_2 + H_2O$
$Al_2(SO_4)_3 + 3CO = Al_2O_3 + 3SO_2 + 3CO_2$
$2AlH(SO_4)_2 + 2CO = Al_2O(SO_4)_2 + 2SO_2 + H_2O + 2CO_2$
$Al_2O(SO_4)_2 + 2CO = Al_2O_3 + 2SO_2 + 2CO_2$

With H_2 as reducing agent

$2AlH(SO_4)_2 + H_2 = Al_2(SO_4)_3 + SO_2 + 2H_2O$
$Al_2(SO_4)_3 + 3H_2 = Al_2O_3 + 3SO_2 + 3H_2O$
$2AlH(SO_4)_2 + 2H_2 = Al_2O(SO_4)_2 + 2SO_2 + 3H_2O$
$Al_2O(SO_4)_2 + 2H_2 = Al_2O_3 + 2SO_2 + 2H_2O$

One may conclude that the smaller contribution to the BAAS desulphuration process is made by reactions occurring in solids, because of difficulties of contact between the phases. One can assume that the reduction of SO_3 in the gaseous phase causes the release of the primary reaction product, which facilitates the formation of solid products and causes lowering of the temperature of the process. Under isothermal conditions, the decomposition of BAAS in an environment of carbon and water vapour is given by

$$\text{BAAS} \xrightarrow[2\,h]{773\,K} AlH(SO_4)_2 \xrightarrow[2\,h]{973\,K} \gamma\text{-}Al_2O_3 \xrightarrow[2\,h]{1123\,K} \gamma\text{-}Al_2O_3 \xrightarrow[2\,h]{1223\,K} \gamma\text{-}Al_2O_3$$

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