Thermochimica Acta, 148 (1989) 311–318
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

APPLICATION OF THERMAL ANALYSIS TO THE INVESTIGATION OF THE REACTION OF AMMONIUM NITRATE MELT WITH SOLID ZINC OXIDE

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ABSTRACT

Metallurgical wastes are often used in the production of fertilizers with zinc as a micro-element. They contain, besides zinc oxide, high concentrations of iron, calcium, magnesium oxides and a large number of other components, which hinder the observation and explanation of the resulting reactions and compounds.

The subject of this paper is the application of thermal and chemical analysis and x-ray powder diffraction in the investigation of the reaction of ammonium nitrate melt with solid zinc oxide and the characterization of the formed compounds.

The results obtained show that oxide reacts with ammonium nitrate forming water-soluble zinc nitrate hexahydrate - $Zn(NO_3)_2.6H_2O$ and les water - soluble compound, which has been characterized as complex zinc nitrate hydroxide hydrate - $Zn_5(NO_3)_2(OH)_8.2H_2O$.

Their content increases with the increase of zinc oxide concentration in the system.

INTRODUCTION

There are no data in the literature on the reaction between solid zinc oxide and ammonium nitrate melt.

It is known that zinc oxide dissolves in acids, and that by the hydrolysis of zinc salt solutions, under definite conditions of pH it redepostits as zinc oxide. Zinc hydroxide is dissolved in ammonia solution, by which process its solubility increases with increase

Thermal Analysis Highlights, 9th ICTA, Jerusalem, Israel, 21–25 August 1988.

in the concentration of ammonia in the system with the formation of complex hydroxide /$Zn(NH_4)_2/(OH)_2$/1,2/.

Zinc nitrate, in water suspension, at a temperature of 2o°C to 7o°C, by the addition of sodium hydroxide forms basic nitrate of the following structure: $Zn_5(OH)_8(NO_3)_2.2H_2O$ /3/. Water suspension of zinc nitrate by the addition of ammonium hydroxide behaves in the same way /3/. More extensive investigations of the system $ZnO-N_2O_5-H_2O$ have bee carried out, which showed that the structure of basic zinc nitrates is changed depending on the conditions used /4/. By introducing ammonia i to the system, as well as basic nitrates, zinc oxide deposit is also s parated /4/. More attention has been paid to the thermal investigatior of basic zinc nitrates /5-7/.
In view of the available data, the heterogeneous reaction of solid zinc oxide with ammonium nitrate melt, required special investigation.

EXPERIMENTAL

The investigations have been carried out with ammonium nitrate melt and solid zinc oxide of p.a. quality. The conditions simulated those in the lime ammonium nitrate industrial production.

Into 95% ammonium nitrate melt, at a temperature of 135°C, zinc oxide, as a powder, in the quantities of o.25; o.5o; o.75; 1.oo; 1.5o; 5.oo; lo.oo and 15.oo% (mass) was added. The content of ammonia over a reaction time of 3o minutes was determined in the gaseous products of the reaction /8/, and the chemical analysis of the residual solid phase was carried out, its thermal changes were studied by differential thermal and differential calorimetric analysis, and its structure by x-ray diffraction of the crystal powder.

RESULTS AND DISCUSSION

The results of the chemical analysis of the investigated samples are shown in the Table 1. The results show that, with increase of zinc oxide concentration in the system from o.25 to 5.o%, the percentage of the decomposed ammonium nitrate, calculated according to the quantity of the evolved ammonia, increases, and practically does not change to a zinc oxide content of 15.o% (mass.).

The content of ammoniacal and total nitrogen, determined according to the Kjeldahl destillation method, shows a tendency of decrease with the increase of zinc concentration in the samples. The difference between the theoretical content of nitrogen, calculated according to the quantity of ammonium nitrate put into the system and the values of the experimental results for the total content of nitrogen as the loss of nitrogen from the system, shows an increase ranging from o.4o to 1.28% (mass).

The zinc content in water soluble form increases from o.23 to 1.o2% (mass) with the increase of zinc oxide concentration in the system from o.25 to 1.5o% and with further increase in zinc oxide to 15.oo%, the content of zinc in water soluble form decreases to o.84% (mass).

The results of the chemical analysis show that the content of zinc in water soluble form is 3 to 14 times higher than expected on the basis of the quantity of the decomposed ammonium nitrate, but lower than expected according to DTA, DSC and x-ray diffraction results.

Table 1 also shows the results of the nitrogen contents determined by DSC, according to the energy of crystal transformation II⟶ I of ammonium nitrate /9/. According to these results the loss of nitrogen in the investigated samples increases from 2.21 to 5.76%. This means that the decomposed quantity of ammonium nitrate during the reaction with solid zinc oxide is higher than the results obtained by chemical analysis. The evolved ammonia remains in the system and probably forms some ammonia zinc complexes.

TABLE 1. THE RESULTS OF THE CHEMICAL ANALYSIS OF THE INVESTIGATION SAMPLES

Content of ZnO in the sample %(mass.)	o.oo	o.25	o.5o	o.75	1.oo	1.5o	5.oo	1o.oo	15.oo
Decomposed NH_4NO_3 % (mass.)	o.o1	o.o8	o.11	o.13	o.14	o.12	o.2o	o.17	o.17
Zn in water soluble form % (mass.)	-	o.23	o.36	o.43	o.79	1.o2	o.94	o.81	o.84
Nitrogen % (mass.)									
Total+	34,54	34.49	34.42	34.31	34.35	34.o7	32.71	3o.66	28.47
Ammoniacal+	17.o4	17.22	17.19	17.17	17.12	16.97	16.45	15.46	14.61
Theoretical	35.oo	34.91	34.82	34.74	34.65	34.47	33.25	31.49	29.75
Loss of nitrogen % (mass.)	o.46	o.42	o.4o	o.43	o.79	1.o2	o.94	o.81	o.84
Nitrogen determined by DSC, %(mass.)	32.79	32.14	31.92	3o.85	31.64	32.34	29.68	26.42	23.99
Loss of nitrogen % (mass.)	2.21	2.77	2.9o	3.89	3.o1	2.13	3.57	5.o9	5.76

The content of zinc is determined in water soluble form. In water solution, in the presence of ammonium ion, zinc nitrate probably forms basic nitrate or perhaps oxide.

The Fig.1 presents the DSC curves of ammonium nitrate samples with different zinc oxide contents. The DSC curves show the presence of trigonal into cubic ammonium nitrate transformation /II⟶ I/ and its melting and with the increase in th contents of zinc oxide also the tra nsformation of rhombic into trigona /IV⟶II/ crystal form of ammonium n trate and three small peaks at 5o° 57°C, about 75°C and 89°C

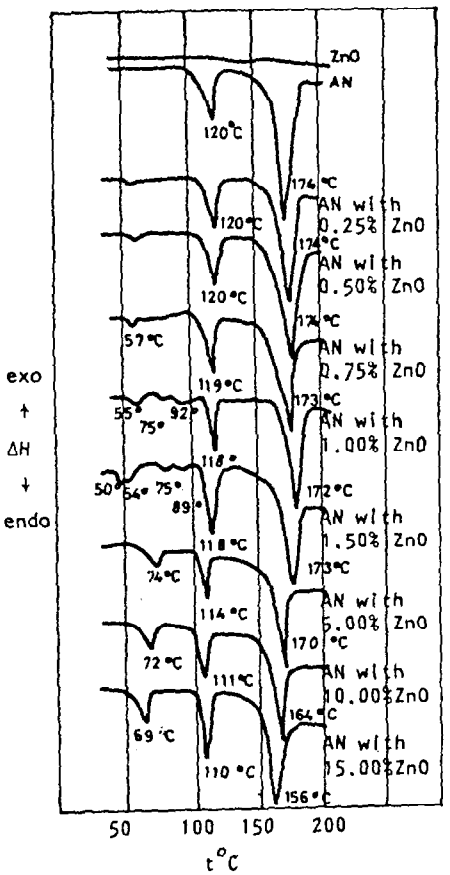

Fig.1 DSC curves of the samples of ammonium nitrate (AN) with the different zinc oxide content

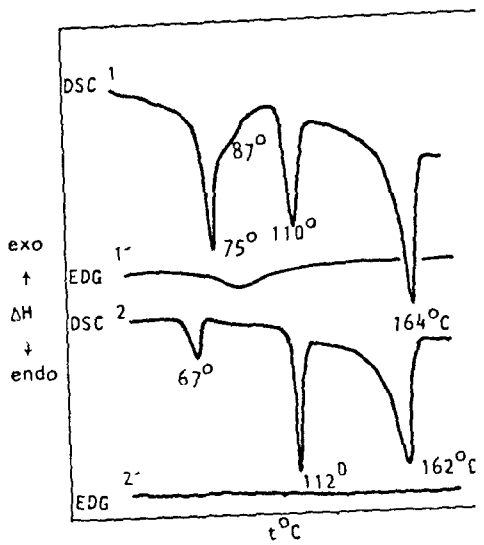

Fig.2 DSC and EGD curves of the samples of ammonium nitrate with lo.o% of zinc oxide before (curve 1 and 1') and after heating the s me sample at 17o°C (curves 2 and

to 92°C which cannot be ascribed to ammonium nitrate changes.
Fig.2 presents the DSC and EGD curves of the samples of ammonium nitrate with 1o.o% of zinc oxide before and after treatment at 17o°C. The DSC and EGD curves before treatment show the peaks between 75°C and 9c which represents dehydration of some crystal hydrate present.
Fig.3 presents the DSC and EGD curves of the insoluble part in the wat of the sample of ammonium nitrate with 1o.o% of zinc oxide, before anc after treatment at 17o°C. The peaks at 125°C and 155°C can be ascribec to the dehydration and destruction of the basic zinc nitrate $Zn_5(NO_3)_2(OH)_8.2H_2O$. The peak at 33o°C corresponds to the destruction of zinc nitrate.

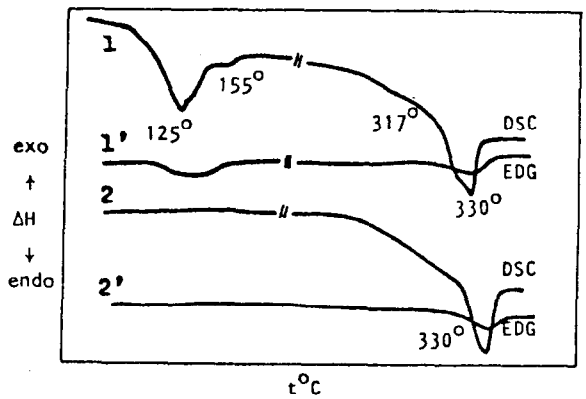

Fig.3. DSC and EGD curves the insoluble part in the water of the sample of ammonium nitrate with 1o.o% of zinc oxide before (curves 1 and 1') and after heating at 17o°C (curves 2 and 2')

The x-ray powder diffraction shows the presence of zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$, basic zinc nitrate - zinc nitrate hydroxide hydrate $Zn_5(NO_3)_2(OH)_8.2H_2O$ /1o/, zinc oxide and ammonium nitrate.
The contents of zinc nitrate hexahydrate and basic zinc nitrate increase with the increase of zinc oxide contents in the sample. The dehydration of basic zinc nitrate at 125°C and its conversion to zinc nitrate at 155°C /Fig.4 and Fig.5/.

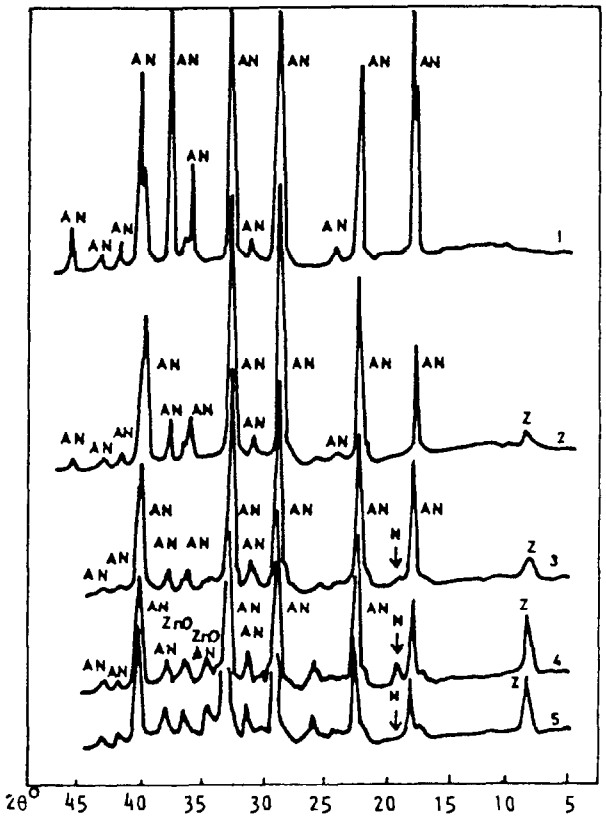

Fig.4 The results of the x-ray powder diffraction the samples of ammonium n trate:

1. without ZnO;
2. with 1.o% ZnO;
3. with 5.o% ZnO;
4. with 1o.o% ZnO;
5. sample with 1o.o% ZnO after heating at 65°C;

AN - ammonium nitrate

Z - basic zinc nitrate $Zn_5(NO_3)_2(OH)_8.2H_2O$

N - zinc nitrate hexahydr $Zn(NO_3)_2.6H_2O$

Fig.5 The results of the x-ray powder diffraction:t insoluble part in water of the sample of ammonium nit rate with 1o.o% ZnO (1) an the same sample after heat ing at 15o°C (2)

AN - ammonium nitrate

Z - basic zinc nitrate $Zn_5(NO_3)_2(OH)_8.2H_2O$

CONCLUSIONS

The investigations of the reaction of ammonium nitrate melt with solid zinc oxide, according to the results of chemical analysis, DTA, DSC and x-ray diffraction, show that the components react forming water soluble zinc nitrate $Zn(NO_3)_2.6H_2O$, and less water soluble basic zinc nitrate $Zn_5(NO_3)_2(OH)_8.2H_2O$, the contents of which increased with the increase of zinc oxide content. and probably some ammonia zinc complexes which could not be found in the system with the methods use

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