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THERMAL DECOMPOSITION OF Ni(II) AND Fe(III) NITRATES AND THEIR MIXTURE

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Abstract

The thermal decompositions of nickel(II) nitrate hexahydrate and iron(III) nitrate nonahydrate were followed. It was found that the final decomposition products were NiO at 623 K and Fe_2O_3 at 523 K, respectively. The two salts exhibited only endothermic peaks and a loss in mass until constant mass was attained. The decomposition reactions and the compounds corresponding to each reaction were established. A heating rate of 1 K min^{-1} revealed several intermediates; higher heating rates shifted the peaks to higher temperatures. The use of an air flow during decomposition shifted the reactions to lower temperatures.

The DTA for the mixed salts was found to be an overlap and the TG a summation of the results for the two individual salts. At 773 K, the decomposition products were composed of three phases: NiO, Fe_2O_3 and $NiFe_2O_4$. When these products were heated to 1773 K, only $NiFe_2O_4$ was identified by X-ray diffraction.

Keywords: Fe(III) nitrate, nickel ferrite, nickel nitrate, thermal decomposition

Introduction

Results have been published on the thermal decompositions of nickel(II) nitrate hexahydrate and iron(III) nitrate nonahydrate [1]. Several intermediate compounds were reported to appear during the thermal decomposition of nickel nitrate hexahydrate, but there is no agreement regarding the type of these intermediates. At a linear heating rate of 5.4 min^{-1} in flowing air, the salt was stated to lose water of hydration at 323 K. At 478 K, anhydrous $Ni(NO_3)_2$ was obtained; at 778 K, the end-product was NiO. On the other hand, in stationary air, basic nickel nitrate was reported as the only intermediate [2–4]. In a water vapour – air atmosphere at heating rates of 5–7 K min^{-1}, the following steps were suggested [5]:

$$Ni(NO_3)_2{\cdot}6H_2O \longrightarrow Ni(NO_3)_2{\cdot}4H_2O \longrightarrow Ni(NO_3)_2{\cdot}3H_2O \longrightarrow$$

$$xNi(NO_3)_2{\cdot}yNi(OH)_2{\cdot}zH_2O \longrightarrow NiO$$

where y ~1.16, x and z unspecified constants.

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Wendlandt [1] reported that in flowing air at a heating rate of 5.4 K min^{-1}, iron(III) nitrate nonahydrate loses its water of hydration at 307 K. At 718 K, Fe_2O_3 was obtained. On the other hand, in flowing nitrogen and at 553 K, Fe_2O_3 was obtained while anhydrous iron nitrate was reported to exist as an intermediate [6]. No experimental work has been reported on the thermal decomposition of mixed Ni(II) and Fe(III) nitrates. Thus, it was the aim of the present work to study the thermal decomposition of the mixed salt as concerns the production of pure $NiFe_2O_4$, which is a very important material as a magnetic ceramic used in the electronics industry [7].

Experimental techniques

In the present study, the behaviour of these salts was followed as a function of temperature. A Netzsch STA 409 simultaneous thermal analyser was used. Calcined kaolin was used as reference material and an alumina crucible (99.5% purity) as sample holder. Heating rates in the range 1–20 K min^{-1} were applied, while the atmosphere in the furnace was either stationary or flowing air [8].

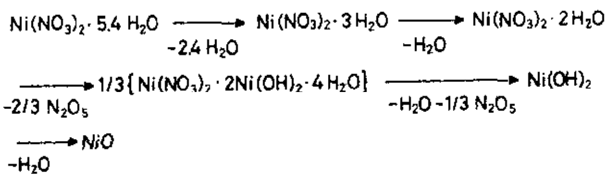
In order to confirm the thermal analysis results, the powder resulting from the DTA was X-rayed to identify the developed phases and to establish the degree of crystallinity of both the starting materials and their intermediates.

Results and discussion

Thermal decomposition of nickel nitrate hexahydrate

In stationary air

The DTA and TG curves of nickel nitrate hexahydrate at a heating rate of 1 K min^{-1} in stationary air were recorded in the temperature range 300–873 K (Fig. 1). The thermograms reveal several endothermic peaks accompanied by a loss in mass; constant mass was achieved above 623 K, after the loss of 73.33% of the original mass, which indicates that NiO is the final product. To confirm this result, the salt was heated up to 873 and 1773 K and the final products were X-rayed. The results indicated the presence of a well-crystalline NiO; the average crystal size was much smaller in the case of heating to 873 K than to 1773 K, as revealed by calculation on X-ray charts [9]. Back-calculations based on these results indicated that the formula of the original salt was $Ni(NO_3)_2 \cdot 5.4H_2O$ rather than $Ni(NO_3)_2 \cdot 6H_2O$. The resulting loss may have occurred during transportation and/or storage of the salt. Accordingly, at a heating rate of 1 K min^{-1} in stationary air, according to the TG curve in Fig. 1, the following decomposition mechanism is postulated:



$$\mathrm{Ni(NO_3)_2\cdot 5.4\,H_2O} \xrightarrow[-2.4\,\mathrm{H_2O}]{} \mathrm{Ni(NO_3)_2\cdot 3H_2O} \xrightarrow[-\mathrm{H_2O}]{} \mathrm{Ni(NO_3)_2\cdot 2H_2O} \xrightarrow[-2/3\,\mathrm{N_2O_5}]{} 1/3\{\mathrm{Ni(NO_3)_2\cdot 2Ni(OH)_2\cdot 4H_2O}\} \xrightarrow[-\mathrm{H_2O}-1/3\,\mathrm{N_2O_5}]{} \mathrm{Ni(OH)_2} \xrightarrow[-\mathrm{H_2O}]{} \mathrm{NiO}$$

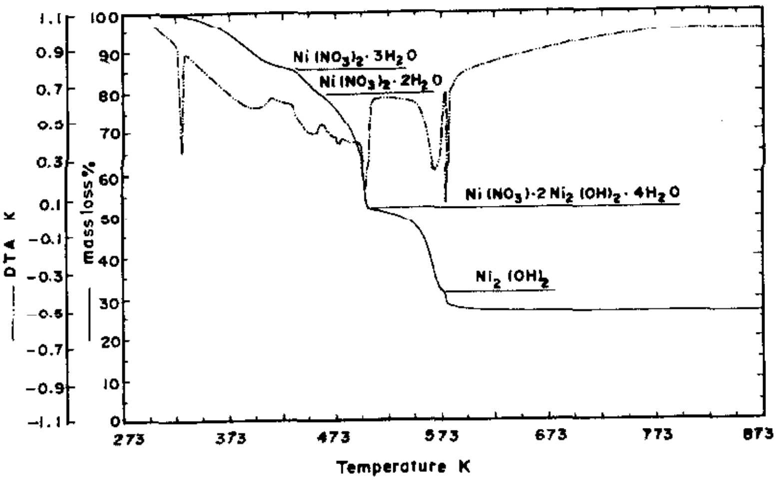


Fig. 1 DTA and TG curves of nickel nitrate hexahydrate in stagnant air, 1 K min^{-1}

In flowing air

The effects of flowing air and the heating rate on the thermal decomposition of nickel nitrate hexahydrate were investigated. DTA and TG curves were recorded for nickel nitrate hexahydrate at heating rates of 5, 10 and 20 K min^{-1} in air and at 10 K min^{-1} in air flowing at 10.9 ml min^{-1}. In flowing air, all the decomposition reactions occurred at lower temperatures, due to the enhanced removal of the gaseous products by the air stream. A similar effect was observed at lower heating rates. It was also interesting that all the curves obtained at heating rates of 5 K min^{-1} and above were similar, but the decomposition reactions were shifted towards higher temperatures for higher heating rates. A heating rate of 1 K min^{-1} revealed several intermediates, while higher rates caused the overlap of the corresponding decomposition reactions, revealing only the anhydrous basic nitrate, which was not detected at the lowest rate investigated.

Thermal decomposition of iron(III) nitrate nonahydrate

DTA and TG curves were recorded for iron(III) nitrate nonahydrate at heating rates of 1, 5, 10 and 20 K min^{-1} in stationary air and at 10 K min^{-1} in flowing air

(10.9 ml min^{-1}). From the results, it was obvious that a flow of air or lower heating rates shifted the decomposition temperatures to lower values. The composition achieved above 523 K corresponded to Fe_2O_3, as identified by X-ray analyses at 873 and 1337 K. Back-calculation from the mass obtained at 773 K indicated that the initial composition was $Fe(NO_3)_3 \cdot 8.7H_2O$, and not $Fe(NO_3)_3 \cdot 9H_2O$. The difference may be due to a loss of crystallization water during transportation and/or storage. All the DTA curves indicated an endothermic peak starting at 323 K. Above this temperature, water was rapidly lost until a break corresponding to iron(III) nitrate dihydrate was reached. $Fe(NO_3)_3 \cdot 2H_2O$ decomposed rapidly to $Fe(OH)_3$. Gradual decomposition of the latter compound occurred on increase of the temperature, and finally Fe_2O_3 was formed, the TG curves indicating a constant mass. From these results, the decomposition of the salt proceeds in the following steps:

$$Fe(NO_3)_3 \cdot 8.7\,H_2O \xrightarrow[-6.7\,H_2O]{} Fe(NO_3)_3 \cdot 2H_2O \xrightarrow[-0.5\,H_2O-3(NO_3)]{}$$

$$Fe(OH)_3 \xrightarrow[-1.5\,H_2O]{} Fe_2O_3$$

On heating from 573 up to 1773 K, a small endothermic peak was obtained between 1645 and 1673 K. This is due to the decomposition of Fe_2O_3 to $Fe_3O_{4.09}$. This result is supported by the phase diagram of $FeO-Fe_2O_3$ [10], which indicates that in air Fe_2O_3 decomposes to a non-stoichiometric magnetite rich in oxygen.

Thermal decomposition of mixed nitrates

Results of the thermal analyses of a mixture of Ni(II) and Fe(III) nitrates, prepared in a ratio corresponding to $NiFe_2O_4$, carried out in stationary air at different heating rates, are shown in Fig. 2. On heating the mixture up to 773 K in a muffle furnace, a total mass loss of 78% was observed, a value close to the theoretical loss of 78.27% for the formation of $NiFe_2O_4$. From the thermal decompositions of the individual salts and the thermal decomposition of the mixed salt (Fig. 2) at a heating rate of 1 K min^{-1}, it was concluded that the DTA curve for the mixed salt is an overlap of those for the individual salts. The first double peak, between 303 and 330 K (Fig. 2) reflects the decomposition of the two hydrates, giving liquid water. In the temperature range from 330 to 387 K, an accelerated mass loss, giving an endothermic peak, was observed. In the temperature range 388–433 K, the nitrate began to decompose, giving nitrogen oxides. This decomposition was accompanied by a sharp endothermic peak in the DTA curve and a rapid mass loss in the TG curve. Above 648 K, no mass loss was observed, and at 773 K the material had a weak magnetic character, as indicated by a Gouy magnetic balance. The X-ray diffraction pattern of the product (Fig. 3) indicated the presence of Fe_2O_3 and $NiFe_2O_4$. The $NiFe_2O_4$ peaks were very broad, including

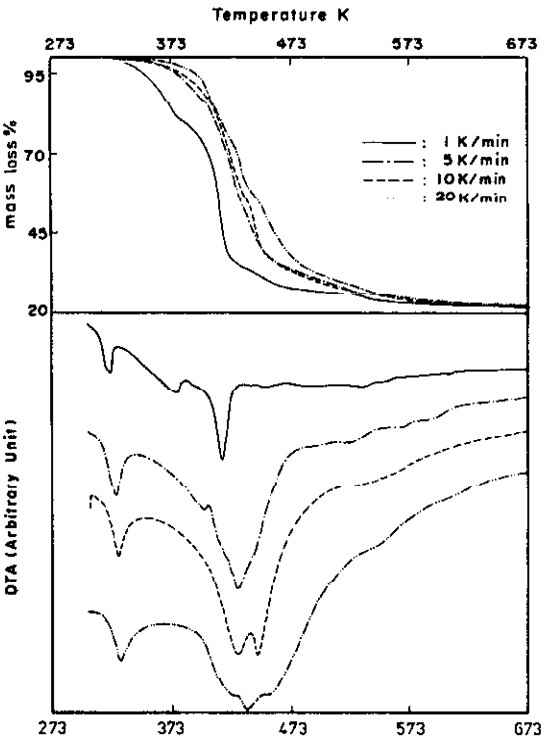


Fig. 2 Effect of heating rate on the thermal behaviour of the mixed Ni(II) and Fe(III) nitrates in stagnant air

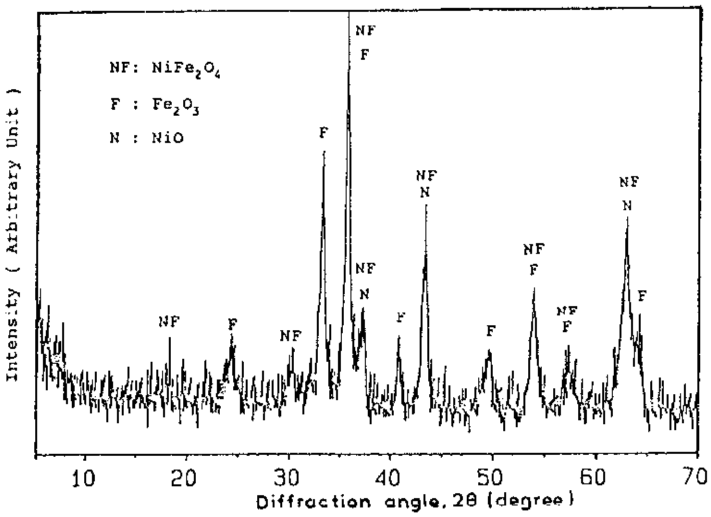


Fig. 3 An X-ray pattern for fired mixed Ni(II) and Fe(III) nitrates, (heated up to 773 K at a rate of 1 K min^{-1}

those for NiO. The X-ray diffraction pattern of the mixed nitrates after heating up to 1773 K at a heating rate of 10 K min^{-1} (Fig. 4) gave sharp peaks for well-crystalline $NiFe_2O_4$ only. No peaks that correspond to the formation of $NiFe_2O_4$ were detected in the DTA curve.

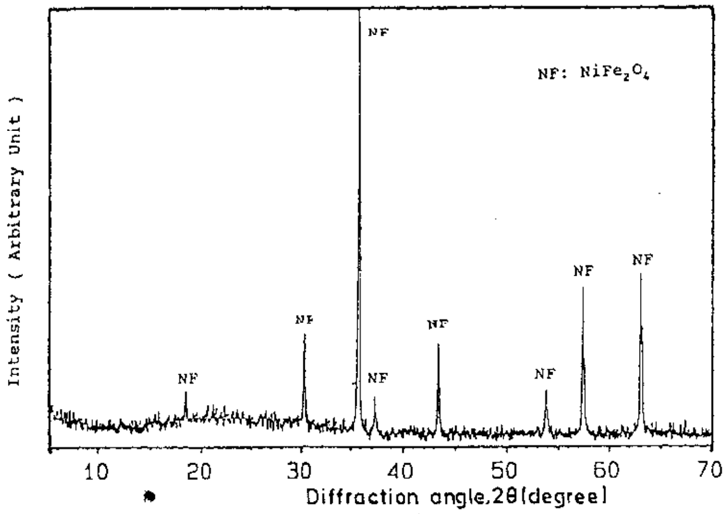


Fig. 4 An X-ray pattern for fired mixed Ni(II) and Fe(III) nitrates (heated up to 1773 K at a heating rate of 10 K min^{-1})

To confirm the conclusion that the behaviour of the mixed nitrates is an overlap of the mass losses of the individual components, the values of the losses in mass at different temperatures were calculated for the individual salts, added together and compared with those for the mixed salts. It was concluded that the mixed nitrates tend to decompose earlier than the individual nitrates. This phenomenon indicates a fine particle size for the intermediates obtained from the mixture. When the analysis was carried with a 20 K min^{-1} heating rate in flowing air (10.9 ml min^{-1}), better agreement was obtained between the calculated and experimental results.

Conclusions

From the present study, it can be concluded that:

1. NiO is the final product of thermal decomposition of nickel(II) nitrate hexahydrate above 623 K.

2. FeO is the final product of thermal decomposition of iron(III) nitrate nonahydrate above 523 K.

3. The initial composition of the nickel nitrate hexahydrate was $Ni(NO_3)_2\cdot 5.4H_2O$ and not $Ni(NO_3)_2\cdot 6H_2O$.

4. The initial composition of the iron(III) nitrate nonahydrate was $Fe(NO_3)_3\cdot8.7H_2O$ and not $Fe(NO_3)_3\cdot9H_2O$.

5. A heating rate of 1 K min^{-1} revealed several intermediates; higher rates caused an overlap of the peaks and shifted them to higher temperatures.

6. The DTA curve of the mixed salt is an overlap of those of the two individual salts, and the TG curve is the summation of the two curves.

7. The decomposition of the mixed salt is completed at 648 K, since no mass loss was observed above that temperature.

8. No peaks in the DTA curve correspond to the formation of $NiFe_2O_4$.

9. The decomposition products of the mixed salt at 773 K were Fe_2O_3, $NiFe_2O_4$ and NiO, as detected by X-ray diffraction.

10. A single phase of NiFeO was formed when the decomposition products were heated up to 1773 K, as $NiFe_2O_4$ confirmed by X-ray diffraction.

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