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

M. A. A. Elmasry, A. Gaber and E. M. H. Khater***

Metallurgy Department, N. R. C., Atomic Energy Authority, Cairo-Egypt
*Physics Department, Faculty of Science, Assiut Univ., Assiut-Egypt
**National Research Center, Dokki, Giza-Egypt

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Abstract

The thermal decomposition of the ferric and nickel acetate salts has been followed. It was found that the heating rate affects the decomposition steps. For a heating rate of 1 K min^{-1} the product is either Fe_2O_3 or NiO. For a higher heating rate the suboxides are obtained and reoxidized again on further heating. The decomposition of the mixed salt is an overlap of the DTA for the separate salts but the decomposition reactions are shifted to lower temperatures.

Keywords: decomposition, Fe(III) acetate, nickel acetate, nickel ferrite, thermal analysis

Introduction

It has been revealed that during the thermal decomposition of nickel acetate tetrahydrate in air, the salt begins to lose its water of crystallization at about 343 K and the anhydrous material begins to decompose at ~533 K [1]. Below 723 K and in the presence of excess oxygen NiO was found to be formed, but above this temperature the weight of the residue was less than that expected for the oxide. Above 793 K, a gain in weight was observed at the end of the decomposition, implying the oxidation of Ni metal. Dollimore and Pearce [2] have reported that the salt decomposed to give the anhydrous salt in the temperature range 676 to 766 K and NiO first appeared at 896 K when a heating rate of 4 K min^{-1} was used. Other researchers have found that the salt starts to decompose at 368 K and NiO is obtained at a temperature between 433 and 503 K [3].

Basic Fe(III) acetate has been reported to decompose at 423 K to yield α and γ-Fe_2O_3, but above 873 K only α-Fe_2O_3 has been identified [4]. No data are available in the literature on the thermal decomposition of mixed nitrates or mixed acetates. So, it is the aim of the present work to study the thermal decomposition of nickel and Fe(III) acetates and their mixture.

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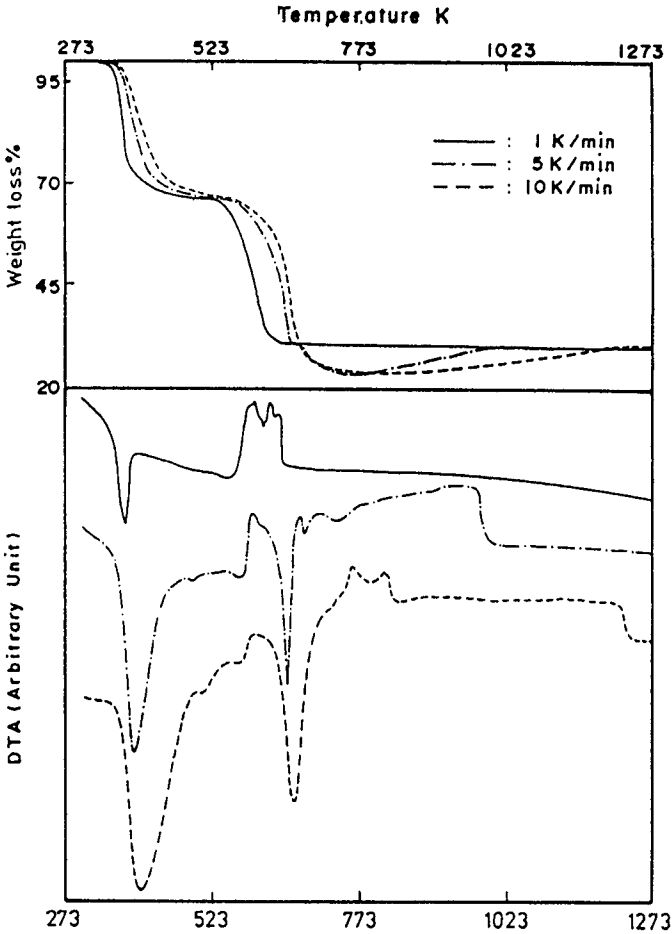

Fig.1 DTA and TG curves of nickel acetate tetrahydrate in static air at different heating rates

Experimental techniques

In the present work, the behaviour of the salts mentioned was studied as a function of the temperature with a Netzsch simultaneous thermal analyzer STA 409. Calcined kaolin was used as a reference material and an alumina crucible (99.5% purity) as a sample holder. Heating rates in the range of 1–20 K min^{-1} were applied while the atmosphere in the furnace was stagnant or flowing air.

In order to confirm the results of thermal analysis, the powder obtained after completing a DTA run was tested by X-ray diffraction to identify the developed phases and to determine the degree or crystallinity of both raw materials and their intermediates.

Results and discussion

Thermal decomposition of nickel acetate tetrahydrate

Figure 1 shows the DTA and TG curves of nickel acetate tetrahydrate at different heating rates in stagnant air. At a heating rate of 1 K min^{-1} the salt started to lose mass at 338 K, and at 398 K about 30% of the original mass was lost, associated with a sharp endothermic peak in the DTA curve, which represents the release and vaporization of the water of crystallization. Above 398 K the rate of mass loss decreased and the composition approached (1-Y) $Ni(CH_3COO)_2 \cdot YNi(OH)_2$, with a value of Y of 0.116 at 523 K. A second rapid mass loss accompanied by an exothermic effect was detected between 533 K and 648 K. From the shape of this exothermic peak it can be concluded that it is due to several overlapping reactions with a net exothermic effect. This exothermic effect is due to the oxidation of H_2 and CO resulting from the dissociation as it is confirmed when a specimen was heated in a muffle furnace. Above 673 K no peaks appeared in the DTA curve and the mass remained constant. The product of decomposition is NiO as confirmed by X-ray diffraction. The thermal decomposition is suggested to proceed as follows:

$$Ni(CH_3COO)_2 \cdot 4H_2O \rightarrow (1-Y)Ni(CH_3COO)_2 \cdot YNi(OH)_2 \rightarrow NiO$$

At heating rates of 5 and 10 K min^{-1}, the curves (from room temperature up to 673 K) were similar to that obtained at 1 K min^{-1}. Above 673 K the material continued to lose mass. At 756 K, a slight gain in mass was observed. The quenched material between 723 and 823 K was black and exhibited a magnetic character. The quenched material was analysed by means of X-ray diffraction method and NiO and Ni metal were identified. It seems that the gas evolved during decomposition built a reducing atmosphere with an oxygen pressure low enough to reduce the material to metallic Ni. At heating rates of 5 K min^{-1} and/or higher the oxidation of the formed Ni by oxygen in the atmosphere was retarded. At a heating rate of 10 K min^{-1} it may be observed from (Fig. 1) that longer time and higher temperature were needed to complete the oxidation of Ni to NiO. The decomposition steps suggested for a heating rate of 5 K min^{-1} and above are:

$$Ni(CH_3COO)_2 \cdot 4H_2O \rightarrow (1-Y)Ni(CH_3COO)_2 \cdot YNi(OH)_2 \rightarrow NiO + Ni \rightarrow NiO$$

Thermal decomposition of basic Fe(III) acetate

The thermal curves for heating rates of 1, 5 and 10 K min^{-1} are shown in Fig. 2. At a heating rate of 1 K min^{-1} the salt begins to lose mass at 303 K. A rapid mass loss occurs below 573 K and some exothermic and endothermic peaks are observed in the DTA curve. Above 573 K, the composition approached that of Fe_2O_3 as confirmed by X-ray diffraction. At heating rates of 5

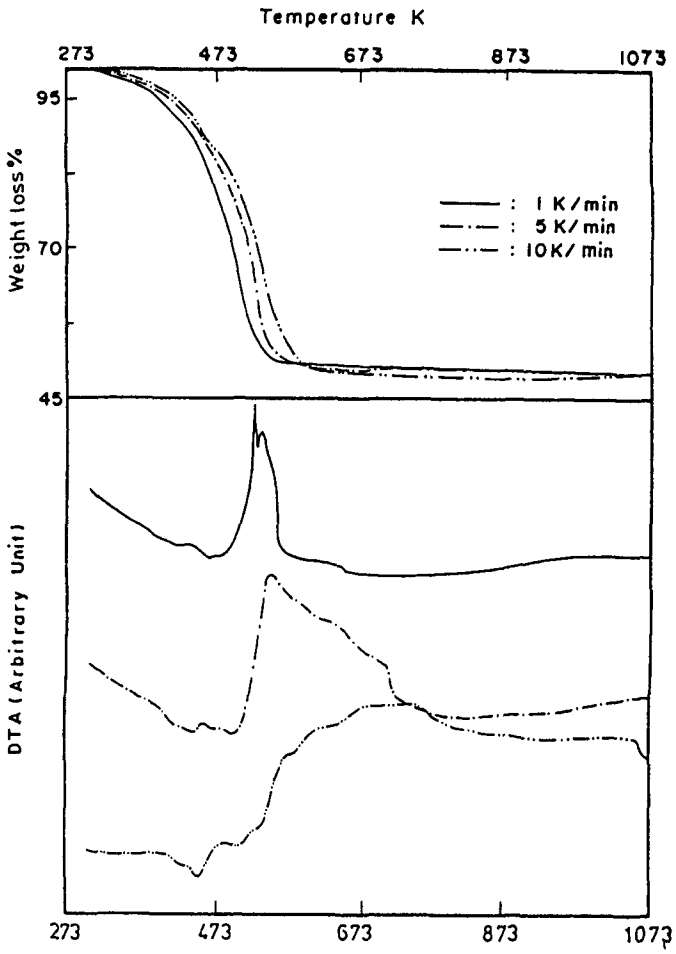

Fig. 2 Thermal analysis of basic Fe(III) acetate in static air

and 10 K min^{-1} these thermal curves were shifted to higher temperatures and the salt decomposed to Fe_2O_3 with some iron existing in a valency state less than three. On further heating the material was completely oxidised to Fe_2O_3. X-ray diffraction analysis of the quenched material confirmed the presence of magnetite. So, at higher heating rates, higher temperatures are required to fully oxidize the iron to Fe_2O_3. The decomposition steps for this salt in air can be:

$$Fe(OH)(CH_3COO)_2 \rightarrow Fe_2O_3 \qquad \text{[for a heating rate of 1 K min}^{-1}\text{]}.$$

$$Fe(OH)(CH_3COO)_2 \rightarrow Fe_2O_3 + Fe_3O_4 \rightarrow Fe_2O_3$$

[for a heating rate of 5 K min^{-1} and above].

Thermal decomposition of mixed Ni(II) and Fe(III) acetates

Nickel acetate tetrahydrate and basic Fe(III) acetate were mixed in a molar ratio of 1:2 to give $NiFe_2O_4$ after thermal decomposition. Thermal analyses of the mixed acetates were carried out in stagnant air at heating rates of 5 and 20 K min^{-1}, and the results are shown graphically in Fig. 3. The first endothermic peak at 338 K corresponds to the decomposition of the nickel acetate tetrahydrate and evaporation of the water of crystallization. This peak is followed by several endothermic and exothermic overlapping peaks due to the decomposition of the acetate salts and the burning of H_2 and CO (decomposition gases

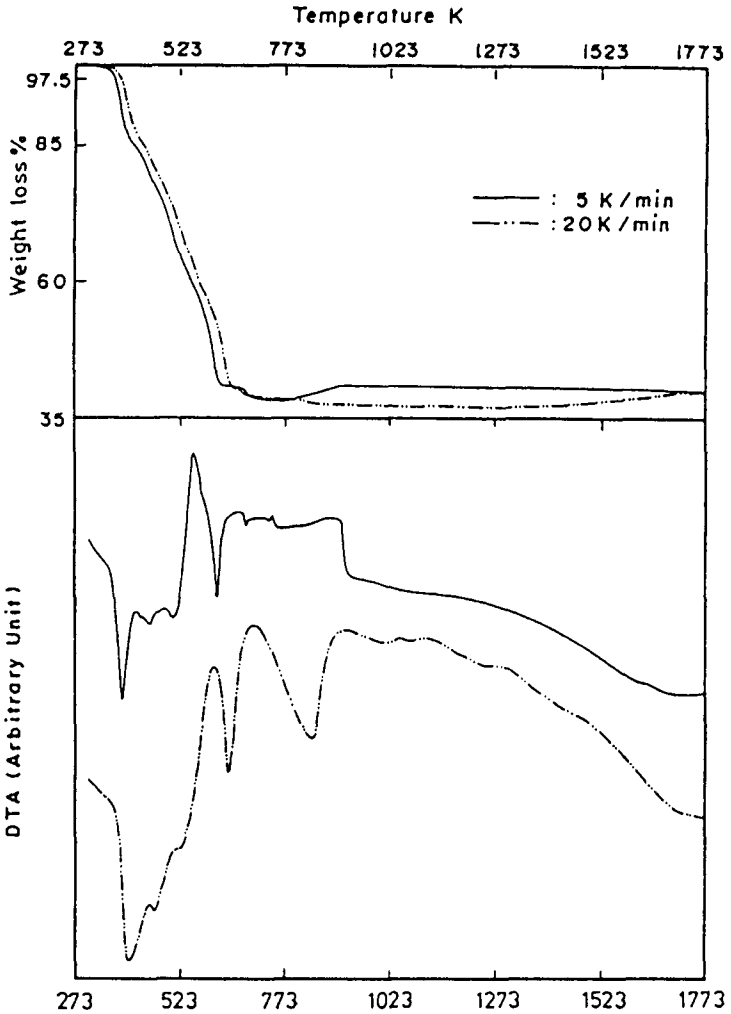

Fig. 3 Thermal analysis of a mixture of Ni(II) and Fe(III) acetates in static air

evolving). It is clear that a rapid mass loss occurs between room temperature and 673 K which is due to the evolution of water vapour and decomposition of acetate ion to gases. At 673 K, about 59.8% mass loss was obtained and above that a slight mass loss occurred. The curvature on the TG curve between 673 and 923 K is mainly due to the reduction of NiO to Ni metal and then the oxidation of Ni to NiO. The effect of the heating rate on the TG and DTA curves is the same as those observed before for the separate acetate salts, i.e., the high heating rate causes an elevation of the decomposition temperatures and the broadening of the peaks.

Conclusions

The present study permits the following conclusions;

1. For a heating rate of 1 K min^{-1}:

a) The decomposition of nickel acetate tetrahydrate begins at 338 K. The release and evaporation of water are accompanied by an endothermic peak.

b) Between 533 and 648 K a rapid mass loss and an exothermic peak were observed for nickel acetate tetrahydrate.

2. For heating rates of 5 and 10 K min^{-1}:

a) The thermal decomposition of nickel acetate tetrahydrate follows the same route as for 1 K min^{-1} up to 673 K.

b) The quenched material from the thermal decomposition between 723 and 823 K is a mixture of Ni and NiO which is due to the partial reduction of the oxide by the evolving gases.

3. For the thermal decomposition of basic ferric acetate:

a) For a heating rate of 1 K min^{-1} the decomposition begins at 303 K and above 573 K Fe_2O_3 is obtained.

b) The use of higher heating rates shifts the decomposition to higher temperatures with the formation of some iron in a valency state less than three.

4. The thermal decomposition curves of the mixed acetate salts is a combination of the curves of the separate salts.

5. At higher heating rates the decomposition reactions are shifted towards higher temperatures and the product oxides are partially reduced.

6. Further heating leads to reoxidation of the product to stoichiometric composition.

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