Thermal decomposition of Fe(III) nitrate and its aerosol

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The thermal analyses of iron nitrate in stagnant and flowing air using different heating rates were conducted to establish the intermediate phases and reactions during its decomposition. In view of the thermal results, the degree of pyrolysis of the aerosol formed by atomizing ferric nitrate aqueous solution was studied. Hollow spherical particles were obtained and varied from noncrystalline to crystalline materials, depending on the pyrolysis temperature used. The decomposition efficiency of resulting particles increased with the pyrolysis temperature.

I. INTRODUCTION

To produce spherical ultrafine pure particles which can compact to uniform bodies and sinter in a controlled manner, aerosol techniques become valuable routes. In the aerosolization process, an appropriate solution is aerosolized and each droplet acts as a separate reactor in which reactions occur to get the required product. In this study, an aqueous solution of iron nitrate nonahydrate was used as the starting solution of the proposed aerosolization process to produce Fe_2O_3 powders which are required to form ceramic ferrites. Ferrites are used as soft or hard magnetic materials. Unlike metals, these ferrites combine high magnetic permeability with high electrical resistivity. These properties are especially critical in high frequency application since they promote low heat generation and low energy losses during electrical circuit operation.

A series of thermal analyses were conducted using a variety of heating rates, in stagnant and flowing air, to study the thermal behavior of $Fe(NO_3)_3 \cdot 9H_2O$. The thermal results are necessary to understand the reactions occurring during pyrolysis of the aerosol formed from its solution and to assess the products obtained at various temperatures.

II. PREVIOUS WORK

In the thermal behavior of the salt, Wendlandt[1] reported that iron nitrate nonahydrate began to lose its water of hydration at 35 °C in flowing air, when a heating rate of 5.4 °C/min was used. The thermal decomposition proceeded directly to Fe_2O_3, which was obtained at 445 °C. On the other hand, Mu and Perlmutter[2] stated that this salt decomposed to Fe_2O_3 after heating up to 280 °C in flowing nitrogen at a heating rate of 1 °C/min. They reported that anhydrous iron nitrate exists as an intermediate phase during the decomposition.

Pyrolysis of aerosols was reported to give fine spherical particles. This process is known as spray pyrolysis or evaporative decomposition of solution (EDS)[3] technique. O'Holleran *et al.*[3] reported that fine crystals of Fe_2O_3 with particle size 1.8 μm were obtained by decomposing the aerosol of 0.3 M iron nitrate solution at 850 °C. Sproson *et al.*[4] stated that well crystallized Fe_2O_3 having surface area 11.5 m^2/g was produced by evaporative decomposition of 1 M iron nitrate solution at 1000 °C. In both studies the heating rates were not determined.

III. EXPERIMENTAL TECHNIQUES

A. Thermal analysis

A Netzsch Simultaneous Thermal Analyzer, STA 409, which is capable of performing differential thermal analysis (DTA) and thermogravimetric analysis (TG) simultaneously for the same sample, was used to carry out the study of the thermal behavior of $Fe(NO_3)_3 \cdot 9H_2O$ in stagnant and flowing air (10.9 mL/min) using several different heating rates. Calcined kaolin was used as a reference material and alumina crucibles of 99.5% purity were used as sample holders. The starting material was iron nitrate nonahydrate of 98% purity and was purchased from AESAR. The intermediate phases and reactions were concluded from the information of TG, DTA, their first derivatives, and x-ray diffraction.

B. Aerosolization process and product characterization

An iron nitrate aqueous solution was used as the starting solution of the process. The concentration of the solution was confirmed by the Fisher Automatic K-F Titrimeter System. A six-jet atomizer was used to generate the aerosols. Dry, clean, compressed air was passed through a 0.38 mm diam orifice to form a high-velocity jet stream. The pressure drop associated with this jet stream drew the solution up through a narrow tube. The resultant large droplets impinged upon a spherical impactor and returned to the reservoir, while the small droplets failed to make contact and thus

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formed the aerosol. The aerosol was then introduced to a tube furnace which was used to evaporate the solvent and to allow for solid-state reactions in the aerosol droplets. In this study, the aerosol output flow rate was controlled at 7.45 L/min, and the Reynolds number inside the tubular reactor is estimated to be 396 at 20 °C and 34 at 1000 °C (assuming that the flow is mainly air). The operating temperature was varied from 450 °C to 810 °C. The final product was collected on Nucleopore filter membranes with porosity below 1.0 μm.

To study the effect of operating conditions on the resultant particles, the aerosol product was characterized by thermal analysis, x-ray diffraction, and scanning electron microscopy.

IV. RESULTS AND DISCUSSION

A. Thermal behavior of $Fe(NO_3)_3 \cdot 9H_2O$

Figures 1 and 2 summarize the thermal curves obtained in the present work for $Fe(NO_3)_3 \cdot 9H_2O$. A flow of air or lower heating rates shifted the decomposition temperatures to lower values. The TG curves indicate that the weight remained constant at temperatures

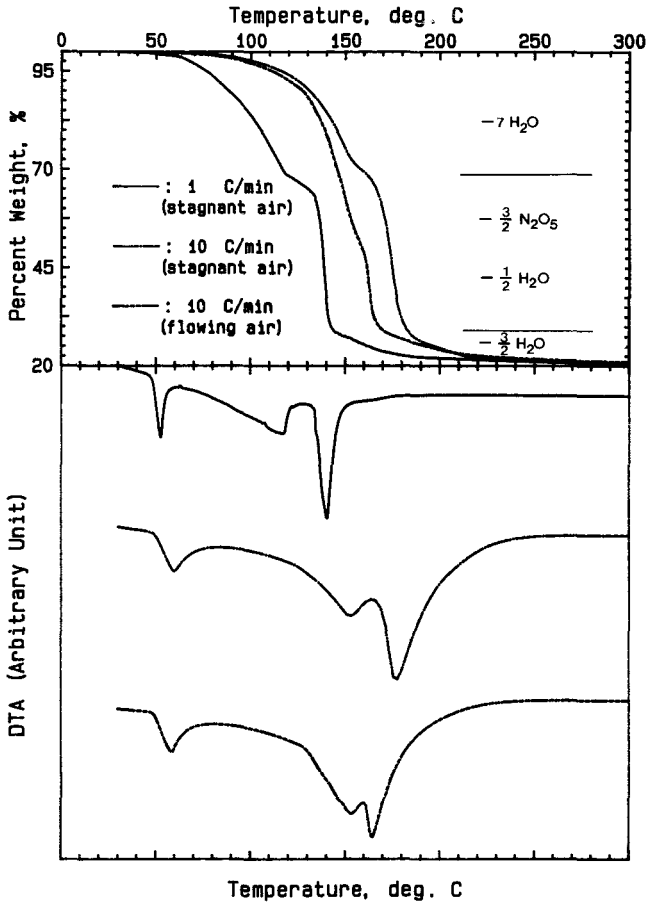

FIG. 1. Thermal curves of iron nitrate nonahydrate.

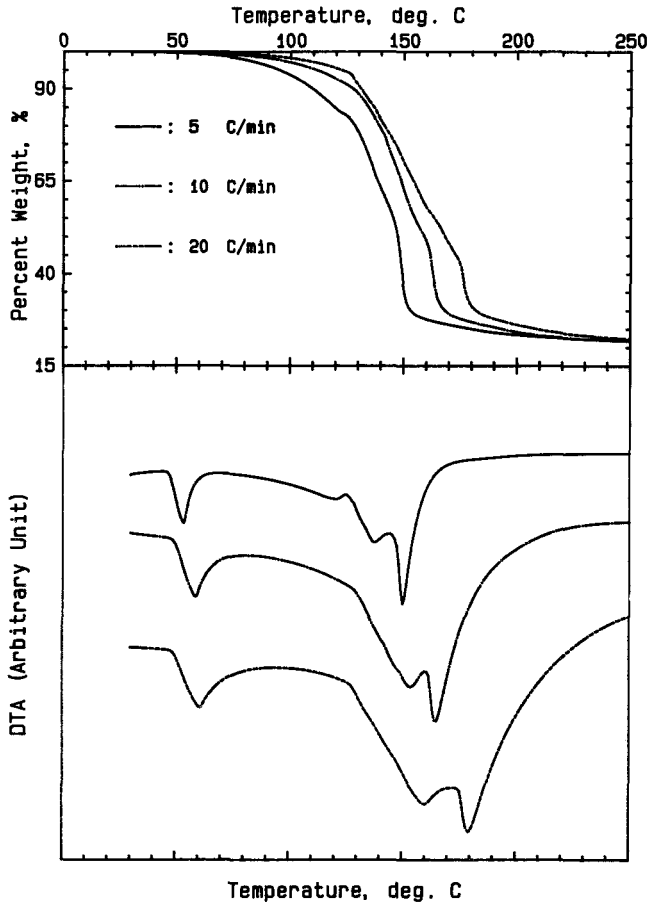

FIG. 2. Effect of heating rate on the decomposition of iron nitrate nonahydrate in flowing air (10.9 mL/min).

above 250 °C and corresponded to Fe_2O_3, as proved by x-ray analyses at 600 °C and 1100 °C. Using the weight obtained at 500 °C to correspond to stoichiometric Fe_2O_3, a back calculation indicated that the initial composition was not $Fe(NO_3)_3 \cdot 9H_2O$ but $Fe(NO_3)_3 \cdot 8.7H_2O$. This discrepancy can be attributed to a partial loss of water of hydration during transportation and/or storage, as is evident from the TG curve which indicated that loss in weight began at 50 °C.

It is to be noted that thermal analysis was interrupted at the break points of the TG curves and the specimens were quenched, followed by x-ray diffraction to determine the intermediate phases. Unfortunately, the x-ray patterns showed the hydrated phases were not well crystallized. Based on the intermediate compositions achieved on the TG curves, the following mechanism was suggested. In Figs. 1 and 2, all the DTA curves revealed an endothermic peak starting at about 50 °C corresponding to partial decomposition of the hydrate, giving liquid water. As 1 °C/min heating rate was used (see solid curves in Fig. 1), the decomposed water was lost with an accelerated rate until a break corre-

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sponding to the composition of iron nitrate dihydrate, $Fe(NO_3)_3 \cdot 2H_2O$, was reached. The dihydrate decomposed with another accelerated rate (appearing as a nearly vertical step on the TG curve). The end of this step corresponded to the composition of $Fe_2O_3 \cdot 3H_2O$ and was accompanied by an endothermic peak (on the DTA curve). This peak was due to a combined loss of nitrogen oxides and water vapor. Increasing the temperature caused the gradual dehydration of $Fe_2O_3 \cdot 3H_2O$ and then the formation of anhydrous Fe_2O_3, causing the TG curves to level to a constant weight. No evidence for the existence of an anhydrous iron nitrate, as intermediate, was found in this study. Accordingly, iron nitrate nonahydrate in stagnant air using 1 °C/min heating rate follows the following endothermic steps:

$$Fe(NO_3)_3 \cdot 9H_2O \longrightarrow Fe(NO_3)_3 \cdot 2H_2O + 7H_2O_{(l)} \quad (1)$$

$$H_2O_{(l)} \longrightarrow H_2O_{(v)} \quad (2)$$

$$2Fe(NO_3)_3 \cdot 2H_2O \longrightarrow Fe_2O_3 \cdot 3H_2O + 3N_2O_5 + H_2O_{(v)} \quad (3)$$

$$Fe_2O_3 \cdot 3H_2O \longrightarrow Fe_2O_3 + 3H_2O_{(v)} \quad (4)$$

If the salt is heated further up to 1500 °C, a small endothermic peak can be detected on the DTA curve in the temperature range 1372°–1400 °C. This endothermic reaction is accompanied with a weight loss corresponding to the decomposition of Fe_2O_3 to magnetite, as proved by x-ray diffraction. On cooling, the magnetite oxidized reversibly to Fe_2O_3 with an exothermic peak in the DTA curve. This weight loss indicates that the magnetite is not stoichiometric and has the formula Fe_3O_{4+x}. The phase diagram published for $FeO–Fe_2O_3^5$ indicates beyond any doubt that the decomposition of Fe_2O_3 in air occurs to a nonstoichiometric magnetite which is rich in oxygen and has a composition about $Fe_3O_{4.09}$ at 1400 °C.

B. Characterization of aerosol product

A 23 wt.% iron nitrate aqueous solution was prepared as the starting solution for the aerosolization process. The corresponding aerosols were then subjected to six different heat treatments. The temperature profile inside the furnace indicated that the aerosol was suddenly heated up to 450°, 480°, 570°, 660°, 740°, or 810 °C in 2 s, followed by isothermal heating at these temperatures for 0.3 s, and then cooling to about 100 °C in 0.7 s. Figure 3 shows the TG curves for the aerosol products obtained in stagnant air using a heating rate of 5 °C/min. The TG curves showed that the aerosol products prepared by using higher pyrolysis temperatures had less volatiles. These thermal curves revealed the efficiency of decomposition of iron nitrate hydrates through the aerosolization process. Based on the assumption that the aerosol products are free from any moisture and comparing the TG curves for the aerosol products to those for iron nitrate nonahydrate at the same analyzing condition, the efficiency of decomposition can be calculated. Increasing the pyrolysis temperature increased the decomposition efficiency of iron nitrate hydrates from 79% at 450 °C to 93% at 570 °C. Above 570 °C decomposition efficiency increased slightly and crystallization started at about 740 °C. The material obtained by pyrolysis at 740 °C or 810 °C gave broad x-ray peaks corresponding to tiny crystallites of hematite, Fe_2O_3.

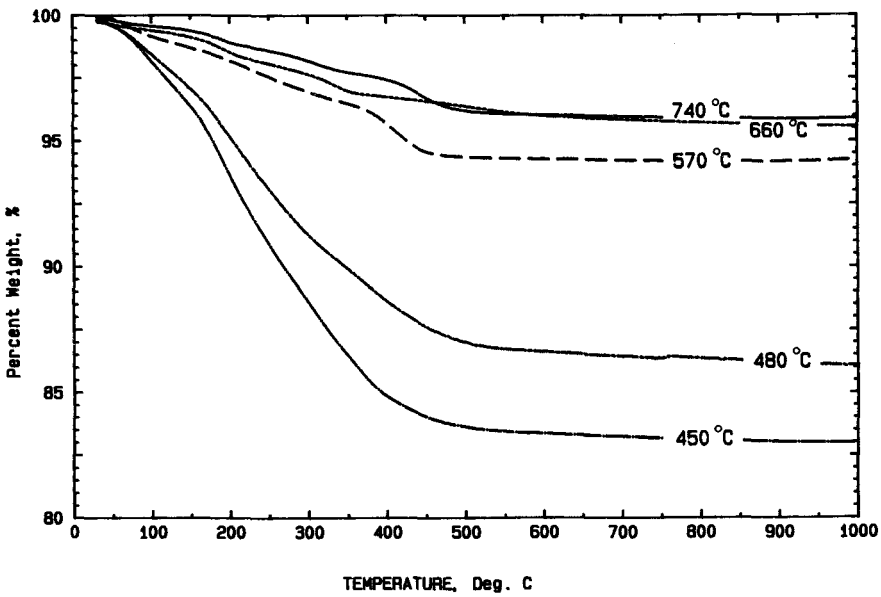

FIG. 3. TG curves of the aerosol products using hydrated ferric nitrate solution.

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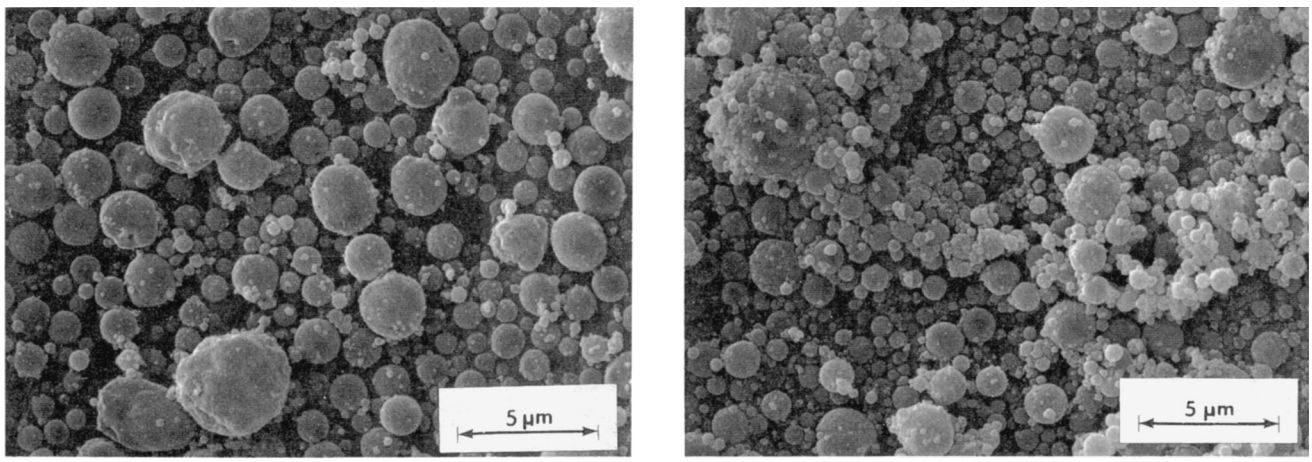

(a) (b)

FIG. 4. SEM photomicrographs for the aerosol products at (a) 480 °C and (b) 810 °C.

Figure 4 shows the SEM photomicrographs of the resultant particles obtained at pyrolysis temperatures of 480° and 810 °C, respectively. The powder density was less than half that of Fe_2O_3 and was difficult to determine, indicating that they consist of hollow spheres. Slight compression followed by examining with SEM revealed beyond any doubt that the particles consisted of hollow spheres. It is evident that increasing the pyrolysis temperature gave a wide size distribution of particles. Due to the variation of density of the particles, the size distribution could not be determined using sedimentation techniques. The photomicrographs also show limited agglomeration and sintering occurring in the aerosol products. The tiny particles tended to agglomerate and sinter, resulting in larger particles in order to reduce surface energy.

According to the results obtained, the process can be divided into the following steps: (1) evaporation of water from the aerosol droplets; (2) precipitation of solute at the surface of the droplets; (3) formation of a spherical, solid, porous crust; (4) decomposition of salt, diffusion of gaseous products, and sealing of pores to form impermeable skins; and (5) agglomeration and sintering of the formed hollow spheres. Modeling of these steps is under investigation in order to understand the relations between the resulting particles' characteristics and operating conditions.

V. CONCLUSIONS

The thermal decomposition of iron nitrate nonahydrate was affected by the ambient atmosphere and heating rate used. When a flow of gas was introduced during the decomposition, all decomposition reactions occurred at lower temperatures due to the enhanced removal of the gaseous by-products by the stream. On the other hand, the increase of heating rate caused the elevation of decomposing temperatures and the broadness of the peaks on the DTA curves, which were essentially due to the less homogeneity of temperatures inside the material. By increasing the heating rate, the salt tended to decompose directly to anhydrous hematite.

In the aerosolization process, fine, spherical, hollow particles with a micron average size were obtained. The aerosol products varied from noncrystalline to crystalline materials, depending on the pyrolysis temperature used. Limited agglomeration and sintering were observed on the resulting particles at all pyrolysis temperatures investigated.

ACKNOWLEDGMENTS

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