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# THERMAL BEHAVIOUR OF Ni(II) NITRATE HYDRATE AND ITS AEROSOLS

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Fine, hollow, spherical particles with an average size of one micronmeter were formed through pyrolysis of aerosol of nickel nitrate solution. The aerosol product obtained by fast heating to 450°C consisted of tiny crystallites of NiO, hydrated nitrate, and other non-crystalline phase(s). By heating above 480°C, it consisted only of crystalline NiO. To understand the reactions occurring during the aerosolization process, thermal analysis was conducted on nickel nitrate hexahydrate in stagnant and flowing air using different heating rates. The mechanism for the decomposition of nickel(II) nitrate hexahydrate is proposed.

Aerosolization process, also known in literature as Ruthner process, evaporative decomposition of solution (EDS), and spray pyrolysis [1-3], is an attractive route for the preparation of ultrafine pure ceramic powders which have uniform composition, spherical shape, and can be compacted uniformly. The required aerosols in the process can be generated by either evaporation-condensation method or atomization method. The aerosols undergo thermal reaction(s): hydrolysis, decomposition, or pyrolysis, depending on the nature of starting materials. In this study, an aqueous solution of nickel nitrate was the starting material for the aerosolization process to produce NiO powder which is important to ceramic industries. This study was assessed by comparing the thermal analysis of product to those obtained for Ni(II) nitrate hydrate using different heating rates in stagnant and flowing air.

In the thermal analysis of nickel nitrate hexahydrate, several intermediate compounds were reported to develop during decomposition. However, there is no agreement regarding the type of these intermediates. Wendlandt [4] reported that, using a heating rate of 5.4 deg/min in flowing air, nickel nitrate hexahydrate decomposed to NiO at 505° and anhydrous

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$Ni(NO_3)_2$ was formed at 205° as an intermediate compound. Dollimore *et al.* [5, 6] and Criado *et al.* [7] reported that, in stagnant air, basic nickel nitrates appeared as intermediates. In vacuum, Dollimore *et al.* [8] reported that with a heating rate of 0.8 deg/min, the $NO_3^-$ ion started to decompose at about 127° and that above 227°, $Ni(OH)_2$ was observed. On the other hand, Criado *et al.* [7] reported the existence of the anhydrous salt as the vacuum intermediate product.

In a water vapor-air medium, with heating rates of 5-7 deg/min, Kalinichenko and Purtov [9] reported that hexahydrate decomposed to NiO and revealed the following intermediate phases: $Ni(NO_3)_2 \cdot 4H_2O$, $Ni(NO_3)_2 \cdot 3H_2O$, and $xNi(NO_3)_2 \cdot yNi(OH)_2 \cdot zH_2O$, where $y \approx 1.16$, and $x$ and $z$ were unspecified constants. Mu and Perlmutter (10) conducted the thermal analysis in flowing nitrogen (80 $cm^3$/min) with a heating rate of 1 deg/min. They reported the intermediates as $Ni(NO_3)_2 \cdot nH_2O$ where $n$ = 4.5, 3, 1.5 and 0. NiO was obtained at pyrolysis temperatures above 350°.

The objective of this paper is to study the thermal behavior of extremely fast pyrolysis of aerosol droplets and compare the results with normal heating rates used in thermal analysis.

## Experimental techniques

### *Thermal analysis*

The thermal analysis was carried out using a Netzsch Simultaneous Thermal Analyzer, STA 409, which is capable of simultaneously performing differential thermal analysis (DTA) and thermogravimetric analysis (TG) on the same sample. Nickel nitrate hydrate was analyzed in stagnant and flowing (10.9 mL/min) air using 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 nickel nitrate hexahydrate of 99.7% purity purchased from AESAR. The intermediate phases and reactions were concluded from the TG, DTA, their first derivatives, and X-ray diffraction. The results were compared to those obtained by pyrolysis of aerosol.

### *Aerosolization process and product characterization*

Nickel nitrate hexahydrate was dissolved in deionized water to prepare the starting solution for the process. The concentration of the solution was determined by a Fisher Automatic K-F Titrimeter System. The solution was aerosolized using a six-jet atomizer. Dry, clean compressed air was passed through a 0.38 mm diameter 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, but the small droplets failed to make contact and thus formed the aerosol. The aerosol was introduced to a streamline tubular reactor which evaporated the solvent and induced the decomposition reactions. In the process, the aerosol output flowrate was set at 7.45 L/min, and the Reynold Number inside the tubular reactor was estimated to be 396 at 20° and 34 at 1000° (assuming that the flow was mainly air). The pyrolysis temperature was varied from 450° to 810°. The aerosol product was collected on Nucleopore filter membranes having a pore size of 0.4 $\mu$m. The resultant particles were removed from the filter and then characterized by thermal analysis, X-ray diffraction, and scanning electron microscopy.

## Results and discussion

### *Thermal behavior of $Ni(NO_3)_2 \cdot 6H_2O$*

The thermal curves (DTA & TG) for $Ni(NO_3)_2 \cdot 6H_2O$ obtained in stagnant air using a heating rate of 1 deg/min are given in Fig. 1. Several endothermic peaks accompanied by loss in weight were observed and a constant weight was achieved above 350° after losing 73.33% of the original weight. This constant weight indicated that NiO was achieved. To confirm this conclusion, the salt was heated to 600° and 1500° and the specimens were examined by X-ray diffraction. The X-ray patterns showed the presence of well crystalline NiO and also evidence that high temperature caused rapid crystal growth (based on the broadness of the peaks).

Using the final weight at above 350° to represent NiO, a back calculation indicated that the initial composition of the salt was not $Ni(NO_3)_2 \cdot 6H_2O$ but $Ni(NO_3)_2 \cdot 5.4H_2O$. The discrepancy can be attributed to a partial loss of water of crystallization during transportation and/or storage. This conclusion was based on immediate loss of weight starting at 35° (Fig. 1).

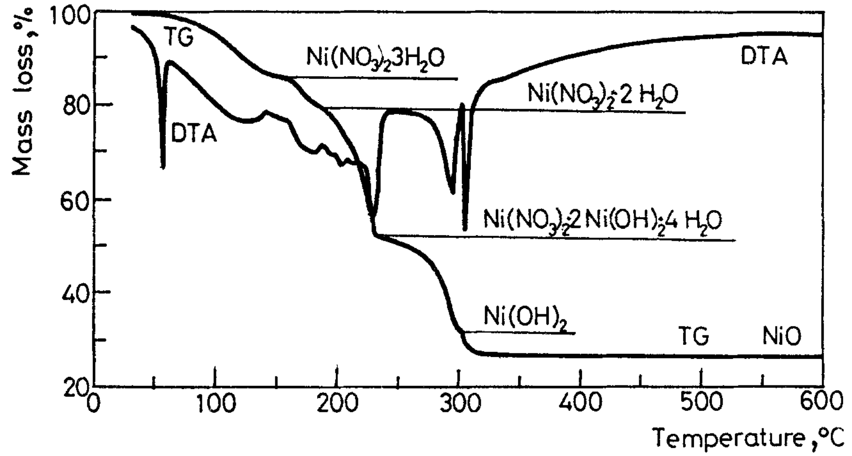

Fig. 1 Thermal analysis of nickel nitrate hexahydrate in stagnant air

In Fig. 1, a sharp endothermic peak started at about 35°. On heating similar sample in a glass container to observe these low temperature changes, the salt seems to decompose giving a liquid phase which dissolves the remaining salt resulting in a clear green solution. Upon further heating, evaporation and gradual precipitation were observed. The precipitation starts when the saturation limit is reached due to loss of water by evaporation. This step appeared on the thermal analysis (Fig. 1) as a gradual loss in weight and endothermic peak with its maximum at about 120°. This endothermic peak corresponds to the latent heat of vaporization. After reaching a composition corresponding to $Ni(NO_3)_2 \cdot 3H_2O$ (on the TG curve), a second progressive loss in weight occurred between 160° and 185° giving a composition corresponding to $Ni(NO_3)_2 \cdot 2H_2O$. The latter decomposed with an accelerated rate between 185° and 233°. At 233° the composition approached that of basic nickel nitrate tetrahydrate, $Ni(NO_3)_2 \cdot 2Ni(OH)_2 \cdot 4H_2O$. Then, it decomposed with an accelerated rate reaching its maximum at 293° until a small plateau on the TG curve was observed at about 303°. This arrest corresponded to the composition of $Ni(OH)_2$ which decomposed to NiO. Above 350°, the weight of the salt approached that corresponding to stoichiometric NiO.

The mechanism of decomposition of nickel nitrate hexahydrate under the conditions mentioned above (i. e. stagnant air and 1 deg/min heating rate) can, thus be summarized as

$$Ni(NO_3)_2\cdot 6H_2O \xrightarrow{35-50^{\circ}C} \text{Aqueous Solution} + aH_2O_{(g)} \quad (\text{where } 0 < a < 3) \qquad (1)$$

$$\text{Aqueous Solution} \xrightarrow{160^{\circ}C} Ni(NO_3)_2\cdot 3H_2O_{(s)} + (3\text{-}a)\, H_2O_{(g)} \qquad (2)$$

$$Ni(NO_3)_2\cdot 3H_2O_{(s)} \xrightarrow{160-185^{\circ}C} Ni(NO_3)_2\cdot 2H_2O_{(s)} + H_2O_{(g)} \qquad (3)$$

$$3\{Ni(NO_3)_2\cdot 2H_2O\}_{(s)} \xrightarrow{185-233^{\circ}C} Ni(NO_3)_2\cdot 2Ni(OH)_2\cdot 4H_2O_{(s)} + 2N_2O_{5(g)} \qquad (4)$$

$$Ni(NO_3)_2\cdot 2Ni(OH)_2\cdot 4H_2O_{(s)} \xrightarrow{230-303^{\circ}C} 3Ni(OH)_{2(s)} + 3H_2O_{(g)} + N_2O_{5(g)} \qquad (5)$$

$$Ni(OH)_{2(s)} \xrightarrow{\text{above } 303^{\circ}C} NiO_{(s)} + H_2O_{(g)} \qquad (6)$$

Equations (4) and (5) were written to show the decomposition to $N_2O_5$ for simplicity. Practically brown nitrogen oxide fumes were observed by naked eye upon heating on a sand bath over the indicated temperature ranges. $N_2O_5$ is known to be unstable at those temperatures and dissociated instantly into $NO_2$ (brown) and $O_2$. It is also well established that in this temperature range the following equilibrium exists (11): $2NO_2 = 2NO + O_2$. NO and $O_2$ are colourless gases.

When a stream of air was introduced, all the decomposition reactions occurred at lower temperatures (Fig. 2) due to the enhanced removal of the gaseous by-products by the air stream. Increasing the heating rate caused elevation of the decomposition temperatures and broadening of the DTA peaks (Fig. 3). These were essentially due to increased temperature gradient inside the specimen. A point of interest was that all the curves obtained at heating rates of 5 deg/min and above were similar but were different from

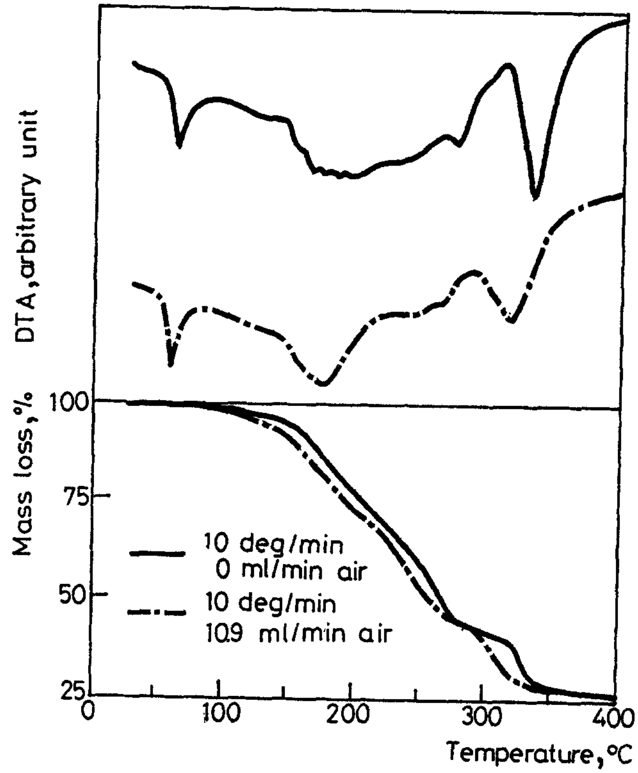

Fig. 2 Effect of flowing air on the decomposition of nickel nitrate hexahydrate

that obtained with a heating rate of 1 deg/min. Faster rates showed initial acceleration of weight loss which did not slow down at about 135° as shown in Fig. 1 for the low heating rate. No indication for the complete loss of water, formation of $Ni(NO_3)_2 \cdot 3H_2O$, or its decomposition at 160°, was observed at the faster heating rates. With faster heating rates, the loss of liquid water at 60-70° was accelerated by heating and at 150° a faster drop in weight was observed and the rate continued to accelerate. A new endothermic peak appeared at 150°. The elevation in boiling point (above 100°) indicates that the nitrate dissolves in the water formed by the decomposition. The distinct breaks, discussed at 1 deg/min, which corresponded to $Ni(NO_3)_2 \cdot 3H_2O$, $Ni(NO_3)_2 \cdot 2H_2O$, $Ni(NO_3)_2 \cdot 2Ni(OH)_2 \cdot 4H_2O$ were not detected at higher heating rates. The nearly horizontal line observed in Figs 2 and 3 corresponds to $Ni(NO_3)_2 \cdot 2Ni(OH)_2$. This anhydrous basic nitrate decomposed directly to NiO except for the heating rate of 5 deg/min. The peak at 250° obtained at 5 deg/min may correspond to the decomposition of $Ni(NO_3)_2 \cdot 2Ni(OH)_2 \cdot 4H_2O$ to $Ni(NO_3)_2 \cdot 2Ni(OH)_2$. However, at higher heating rates, this peak broadened and became difficult to distinguish (Fig. 3). It seems that the heating rate of 1 deg/min revealed several intermediate products and 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.

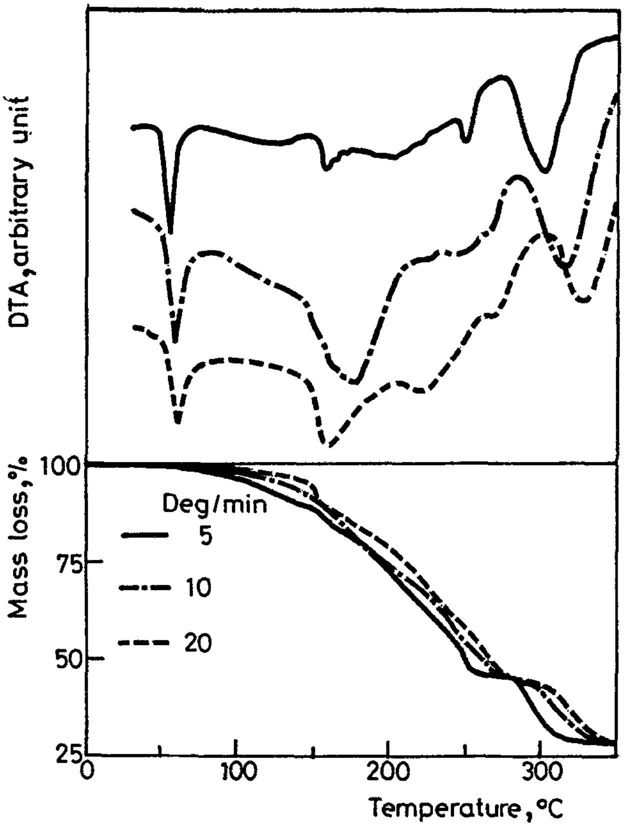

Fig. 3 Effect of heating rate on the decomposition of nickel nitrate hexahydrate in flowing air (10.9 mL/min)

*Characterization of aerosol product*

A 22 wt% nickel nitrate aqueous solution was prepared and was used as starting solution for the aerosolization process. The corresponding aerosols were then subjected to six different heat treatments. The temperature profile inside the tube furnace indicated that the droplets were heated to 450°, 480°, 570°, 660°, 740° or 810° in 2 seconds and kept at these temperatures for 0.3 seconds, followed by cooling to about 100° in 0.7 seconds.

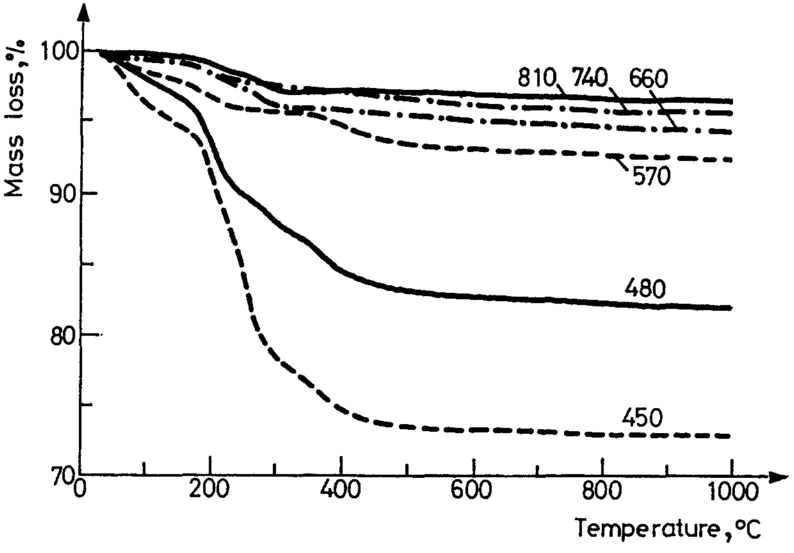

Fig. 4 TG curves of the aerosol products using hydrated nickel nitrate solution

Figure 4 shows the TG curves obtained by heating the resultant particles from this process in stagnant air at a rate of 5 deg/min. These TG curves and their first derivatives indicate that fast pyrolysis even at high temperatures did not allow complete decomposition. The X-ray diffraction pattern obtained for the product at the lowest pyrolysis temperature (450°) indicates the presence of tiny crystallites of NiO, nickel nitrate hydroxide hydrates with the chemical formula of $Ni_2(NO_3)_2(OH)_2 \cdot 2H_2O$, and another non-crystalline phase. In view of the endothermic peak at 50° observed on the DTA curve for the product of pyrolysis, this noncrystalline phase is undecomposed hydrate. On the other hand, the patterns obtained for the products at pyrolysis temperature of 570° and above show only the existence of crystalline NiO (Fig. 5). The crystal size was found to increase with temperature as expected. Comparing the TG curves for the aerosol products to that for nickel nitrate hexahydrate under the same analyzing condition, the efficiency of decomposition was calculated. Increasing the pyrolysis temperature increased the decomposition efficiency of the salt from 63% at 450° to 90% at 570°. Above 570°, the decomposition efficiency increased slightly and 96% was achieved at 810°.

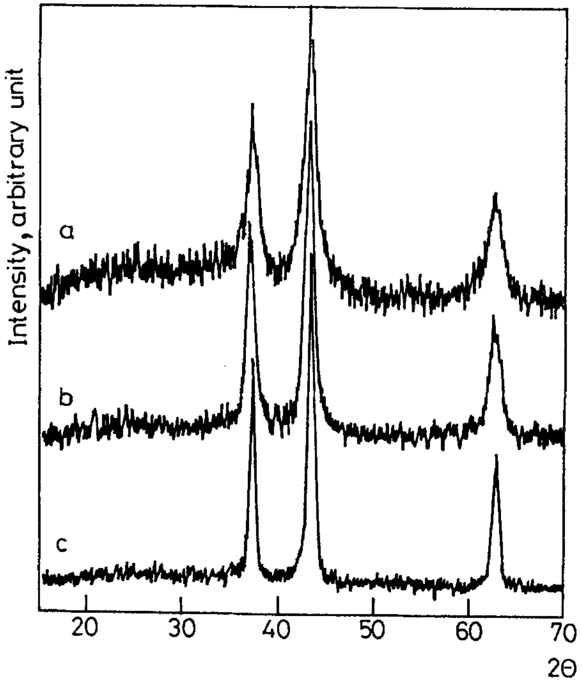

Fig. 5 X-ray pattern for the aerosol product using hydrated nickel nitrate solution, (a) 480°C, (b) 570°C, and (c) 740°C

Comparing the TG curves obtained for the aerosol products (Fig. 4) with those for the hydrated nitrate, it is obvious that the products, unlike the mother crystals, have their decomposition curves shifted to higher temperatures and show a slight decrease in weight on further heating above 400°. This observation can be explained in view of the type of product obtained which will be discussed later. Attempts to measure the density of the particles gave unexpectedly low values and were not reproducible. This was attributed to the presence of hollow particles. Cracking or breaking part of these particles increased the density to different degrees. To confirm that hollow spheres were obtained, the products were slightly crushed and examined by SEM. Figure 6 shows the photomicrographs for the aerosol products obtained at 480°, 660° and 810°, respectively. Indeed, the particles consisted of hollow spheres and had a wide size distribution. Limited agglomeration and sintering were also observed in the aerosol products at all pyrolysis temperatures investigated. Because of the thermal coagulation (due to Brownain motion) and/or kinematic coagulation (due to external forces) of aerosol particles, the tiny particles tended to agglomerate and further sinter resulting in larger particles. This reduces the surface energy of particles.

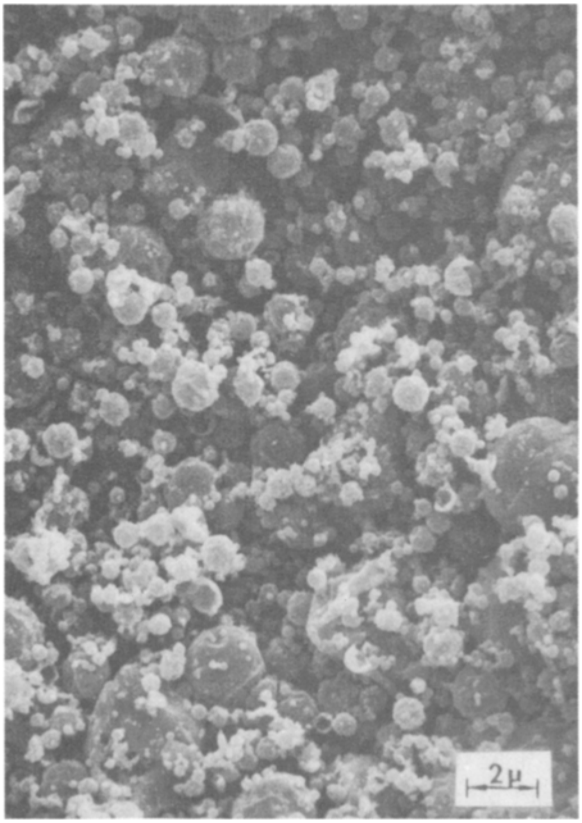

**Fig. 6a** SEM photomicrographs – Aerosol products at (a) 480°C

According to the results obtained here and from our previous study [12], the following mechanism can be suggested: (1) evaporation of water from the surface of droplet, resulting in contracting the droplets, (2) precipitation of solute at the surface of the droplet, (3) formation of spherical solid crust, (4) pyrolysis of salt, and (5) agglomeration and sintering of the hollow particles formed.

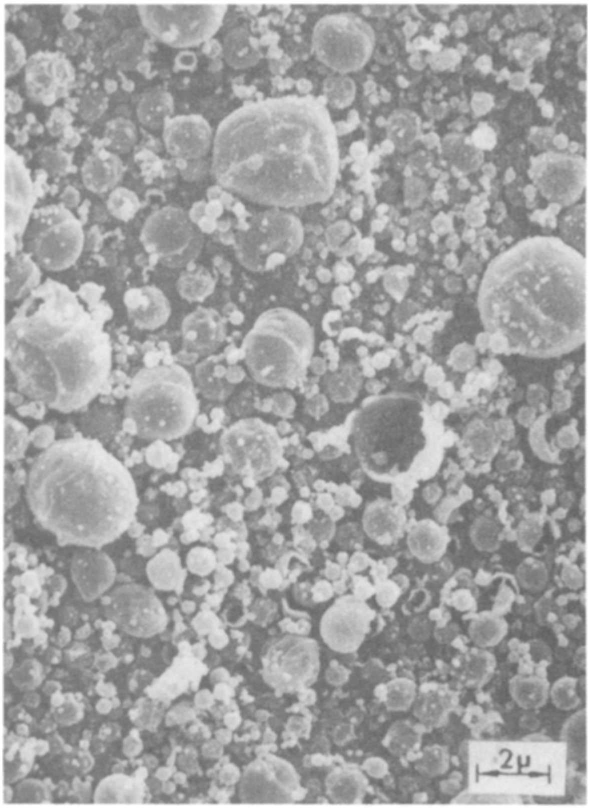

**Fig. 6b** SEM photomicrographs – Aerosol products at (b) 660°C

The mechanism postulated for the formation of hollow spheres can explain the behavior of the TG curves. Water vapor and nitrogen oxides were evolved during heating and were retained inside the spheres after building a thin impermeable skin. The evolved gases increased the pressure within the spheres and retarded further decomposition causing the curves to be shifted to higher temperatures. Complete elimination of the gases is difficult and the gases left diffuse slowly at high temperatures causing the continuous decrease in weight observed.

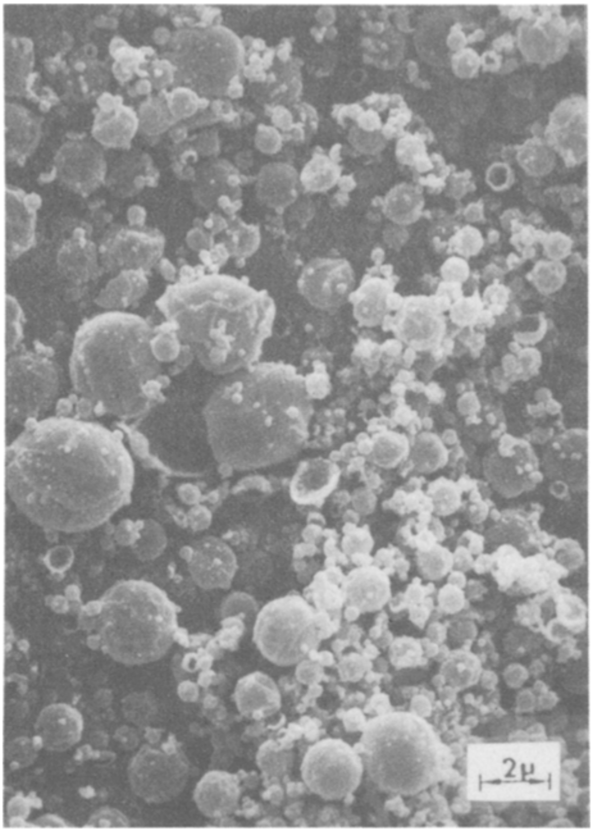

**Fig. 6c** SEM photomicrographs – Aerosol products at (c) 810°C

## Conclusion

The ambient atmosphere and heating rate affected the decomposition of nickel nitrate hexahydrate. Introducing a slow stream of air or using lower heating rate caused the decomposition temperatures of the salt to occur at lower temperatures. At high heating rates, nickel nitrate hexahydrate decomposed to NiO revealing only the anhydrous basic nickel nitrate as an intermediate.

Fine, spherical, hollow particles with an average size of one micronmeter were formed from the aerosolization process. The increase of pyrolysis temperature increased the broadness of particle size distribution. Also, limited agglomeration and sintering were observed on the resulting particles at all pyrolysis temperatures investigated. To minimize the degree of agglomeration and sintering of aerosol particles, the factor of number concentration of aerosols will be considered in the future studies.

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**Zusammenfassung** — Durch Pyrolyse eines Aerosols von Nickelnitratlösung werden feinkörnige, hole, kugelförmige Partikel mit einer durchschnittlichen Größe von einem Mikrometer gebildet. Das durch schnelles Erhitzen auf 450°C erhaltene Aerosolprodukt bestand aus winzigen NiO-Kristallen, aus hydratiertem Nitrat und aus anderen nichtkristallinen Phasen. Durch Erhitzen über 480°C erhält man ausschließlich kristallines NiO. Zum Verständnis der während des Aerosolierungsvorganges ablaufenden Reaktionen wurde in ruhender und dynamischer Luftatmosphäre sowie bei verschiedenen Aufheizgeschwindigkeiten eine Thermoanalyse von Nickelnitrat-Hexahydrat durchgeführt. Im Ergebnis konnte ein Mechanismus für die Zersetzung von Nickel(II)-nitrat-Hexahydrat entwickelt werden.