Morphologies and properties of NiO particles prepared from NiSO$_4$·6H$_2$O and Ni(NO$_3$)$_2$·6H$_2$O by spray pyrolysis

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Nickel oxide particles were prepared by spray pyrolysis of aqueous solutions of NiSO$_4$·6H$_2$O and Ni(NO$_3$)$_2$·6H$_2$O. In spray pyrolysis reactor hollow salt particles initially formed were collapsed by decomposition to reduce their size. For NiSO$_4$·6H$_2$O less hollowness of the primitive particles and its higher decomposition temperature made the oxide particles highly spherical with very smooth surface. On the other hand the particles prepared from Ni(NO$_3$)$_2$·6H$_2$O were so hollow and fragile with rough surface since they were formed on the liquid pool of the salt melt. The particle size decreased with the furnace set temperature while increased with the initial salt concentration. Single oxide particle was composed of many small nuclei without sintering whose size varied with the rate of decomposition. The crystallinity of the particles increased with both temperature and the initial salt concentration. Preliminary drying in diffusion dryer fixed the size of the oxide particles from NiSO$_4$·6H$_2$O at that of the primitive particles, independent of the temperature. However, by the preliminary drying the particles from Ni(NO$_3$)$_2$·6H$_2$O became more hollow and fragile, whose sizes decreased with the temperature.
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1. Introduction

Nickel oxide particles have been observed as an intermediate in a process of spray pyrolysis of aqueous solution of nickel salt solution [1–4]. They were attractive due to their morphologies quite different from the nickel particles, the ultimate product of the process, which have excellent properties for internal electrode materials of multilayer ceramic capacitors as well as low cost [5]. Nagashima *et al.* [1] prepared hollow and fragile oxide particles with rough surface by spray pyrolysis of Ni(NO$_3$)$_2$·6H$_2$O aqueous solution with 20 vol% H$_2$ in N$_2$ at low H$_2$ flow rates and low temperatures. Che *et al.* [2] prepared nickel oxide particles from the same salt with N$_2$ only, which remained hollow all the way to 1200°C due to the high sintering temperature of the oxide. On the other hand Stovic *et al.* [3] prepared, from NiCl$_2$·6H$_2$O with N$_2$ only between 700 and 900°C, ideally spherical nickel oxide particles having the average diameter larger than theoretically expected one. They discussed the sphericity came from sufficient residence time in the reactor while the size increase was caused by partial coalescence of droplets. However, it has been not clear yet how the differences in the morphologies of the nickel oxide

particles were resulted and how the elementary processes of the spray pyrolysis take place to affect them. In the previous paper [6], we carried out the spray pyrolysis of the aqueous solution of NiCl$_2$·6H$_2$O to show the importance of the elementary processes, such as the drying of salt droplets, removal of crystalline water, precipitation of salt and decomposition of the salt, and empathized the roles of salt solubility in salt precipitation and volume reduction in the salt to oxide transformation.

In this study we have investigated the effect of the precursors or nickel salts such as NiSO$_4$·6H$_2$O and Ni(NO$_3$)$_2$·6H$_2$O on the morphologies and properties of nickel oxide particles as well as the process variables. In addition preliminary drying before spray pyrolysis was inserted, if necessary, to control the morphologies of the particles.

2. Experimentals

The apparatus for preparation of nickel oxide particles by spray pyrolysis, described elsewhere [6], consisting of ultrasonic nebulizer, diffusion dryer, tubular reactor in electrical furnace, filter and acid gas absorber.

Aqueous solution of nickel salts solution with various concentrations (reference concentration was 0.5 M) maintained at 30°C was nebulized indirectly at a rate of 15 ml/h. The nickel salts used were $NiSO_4 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$. The droplets were carried by argon gas (99.99%) at 2500 ml/min (reference value), via diffusion dryer if necessary, to electrically heated tubular reactor 800 mm long with the diameter of 32 mm. The furnace set temperature was obtained only in the middle 1/3 of the furnace length [6]. The diffusion dryer with the dimension described elsewhere [6] was included to study the only effect of drying extracted from main spray pyrolysis. The droplets introduced to the reactor were thus two types, those passing through the diffusion dryer and those directly from the nebulizer. In addition to the mode of drying as well as the nature of nickel salts, the process variables included the initial concentration of the nickel salt and furnace set temperature in order to investigate their effect on the size, morphology, crystallinity and chemical nature of the product particles.

The particles exiting from the reactor were collected by filter. The water vapor and acid formed was finally absorbed in caustic solution before exhausting the waste gas.

2.1. Characterization of particles
Size and shape of the particles prepared were observed with Scanning Electron Microscope (SEM, Philips Co., Philips 515) and Transmission Electron Microscope (TEM, Carl Zeiss-EM912 Omega). Number average diameters of the particles were obtained by measuring at least 100 particles shown in SEM images of each sample. Crystallinity of particles was obtained with X-ray Diffractometer (XRD, Scintag-SDS 2000). Atomic bonds in the particles were analyzed with Fourier Transformed Infrared Spectroscope (FT-IR, Perkin Elmer FT-IR 1615). Energy Dispersive Spectroscope (EDS, Model: Voyager, Noran) was used to analyze chemical composition of the particles. Thermogravimetric-Differential Thermal Analyzer (TG-DTA, MAC Science, TG-DTA 200) was used to see thermal and chemical transformation of reagent nickel salts under environment of argon at a rate of temperature rise of 20°C/min.

2.2. Numerical solution of droplet drying and salt precipitation
Droplet drying and salt precipitation, the initial stage of droplet-to-particle conversion was investigated by numerical simulation in the case of $NiSO_4 \cdot 6H_2O$ only. This is because $Ni(NO_3)_2 \cdot 6H_2O$ remains in the liquid phase even after the completion of drying of its droplet. The detailed procedure on numerical simulation on droplet drying was explained elsewhere [7–9]. System of the ordinary differential equations resulting from material and energy balances of a droplet, and Fick's second law of diffusion within the droplet was solved simultaneously by an ordinary differential

TABLE I Solubilities and densities of particles of nickel salts and oxide

Salt	Solubility in water, g/100 g water		Density, g/cm^3
$NiCl_2 \cdot 6H_2O$	(Cold) 180	(hot) very soluble	–
$NiCl_2$	53.8^0	87.6^{100}	3.544
$NiSO_4 \cdot 6H_2O$	131	281	2.07
$NiSO_4$	27.2^0	76.7^{100}	3.68
$Ni(NO_3)_2 \cdot 6H_2O$	243	Infinite$^{56.7}$	2.05
NiO	Insoluble	Insoluble	7.45

equation solver, IVPAG in IMSL package, as described elsewhere [6].

3. Results and discussion
3.1. Comparisons of properties of nickel salts
Table I shows the aqueous solubilities and the densities of various nickel salts [10]. In the table even though all the salts are highly soluble in water, the solubility of $Ni(NO_3)_2 \cdot 6H_2O$ is extremely high. Furthermore, since $Ni(NO_3)_2 \cdot 6H_2O$ melts at 56.7°C, thermal drying in the furnace will leave liquid droplets of the salt rather than its solid particles. The aqueous solubilities of $NiCl_2 \cdot 6H_2O$ and $NiSO_4 \cdot 6H_2O$ are comparable, and their melting points are known not exactly but higher than at least 900°C, suggesting their decomposition would take place in solid-to-solid conversion. The results of thermogravimetric analysis for the three salts are shown in Fig. 1. From the figure, early loss in the mass of each sample results from the removal of crystalline water, which occurs at different manner depending on the nature of the salts and ended up to about 300°C. Among the nickel salts, the behavior of $Ni(NO_3)_2 \cdot 6H_2O$ is so peculiar in that its crystalline water escapes continuously without multiple steps and its decomposition takes place immediately after the removal of the water. It is therefore highly probable that the decomposition of the nickel nitrate takes place by liquid-to-solid conversion. The salt begins to decompose at 280°C and its decomposition ceases at 310°C implying that among the three salts the rate of
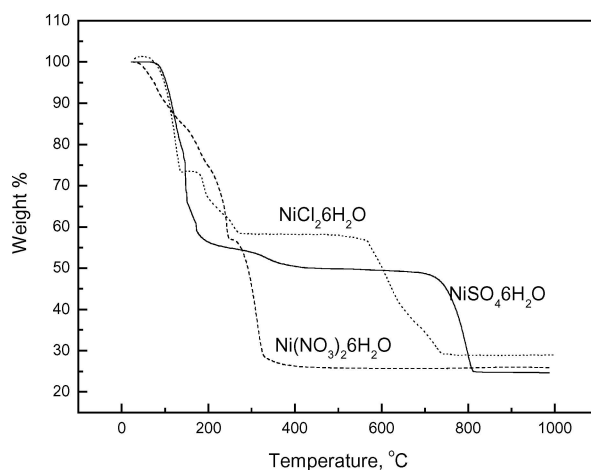

Figure 1 Thermogravimetric analysis of reagent-grade nickel salts with heating rate of 20°C/min under argon atmosphere.

decomposition is the highest for $Ni(NO_3)_2\cdot 6H_2O$. On the other hand, $NiCl_2\cdot 6H_2O$ and $NiSO_4\cdot 6H_2O$ lose their crystalline water in two steps and then their mass loss stops for a while until their decompositions take place between 580 and 730°C, and 730 and 810°C, respectively. Even though $NiSO_4\cdot 6H_2O$ has slightly lower aqueous solubility and its decomposition occurs at higher temperatures in narrower range than $NiCl_2\cdot 6H_2O$, the patterns of all the elementary process involved in the spray pyrolysis are comparable for the two salts. All the three salts have similar densities with and without the crystalline water, respectively. Thus they will experience similar volume contraction during salt-to-oxide conversion.

3.2. Effect of diffusion drying
Jayanthi *et al.* [6] proposed that the particles formed by spray pyrolysis would be formed when salt concentration at droplet surface become critically supersaturated and they would be hollow if the concentration at the center of the droplet is less than the equilibrium solubility at the moment. Since for $NiSO_4\cdot 6H_2O$ there was no information on its critical supersaturation concentration in water, calculation was stopped when the solute concentration at center of the droplet just exceeded the equilibrium solubility. Numerical simulation on thermal drying of $NiSO_4\cdot 6H_2O$ droplet showed that the surface salt concentration reached 1.6 times of the center concentration equal to the equilibrium solubility. Since the ratio was lower than 2 obtained for $NiCl_2\cdot 6H_2O$, the primitive particles from $NiSO_4\cdot 6H_2O$ supposedly became less hollow than those from $NiCl_2\cdot 6H_2O$. On the other hand, the primitive particles by diffusion drying would be solid rather than hollow since the ratio at the end of calculation was only 1.1.

The numerical simulation on thermal drying showed that variation of the initial salt concentration did not affect the radial distribution of the concentration in the droplet and thus the morphology of the primitive particle but did their size, as described for $NiCl_2\cdot 6H_2O$ in the previous paper [5].

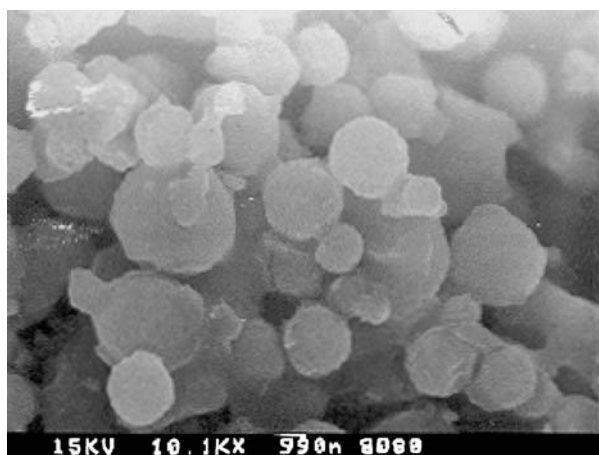Droplets being dried through diffusion dryer, when filtered at its outlet, are shown in Fig. 2. Particulate form

is observed for the sample prepared from $NiSO_4\cdot 6H_2O$, as in the case of $NiCl_2\cdot 6H_2O$ [5]. They are relatively soft and moist with very smooth surface, as expected, while neither hollow nor burst-out particles are observed. However, for $Ni(NO_3)_2\cdot 6H_2O$, the particulate state never appeared even at carrier flow rate as low as 0.3l/min. Instead, thick film of the salt was left in the SEM picture. This indicates that the salt still remained in solution rather than precipitated due to its relatively high solubility.

3.3. Effects of salts and preliminary drying
Fig. 3 shows SEM pictures of the particles prepared by spray pyrolysis of aqueous solution of $NiSO_4\cdot 6H_2O$ with and without diffusion drying. Most particles from $NiSO_4\cdot 6H_2O$ were highly spherical with very smooth surface, which, in general, were much better than those from $NiCl_2\cdot 6H_2O$ under the same conditions. Inclusion of the diffusion drying did not show any significant difference in the morphology of the particles. Such characteristics would be resulted from two reasons. One is less hollowness of the primitive $NiSO_4\cdot 6H_2O$ particles prepared by thermal drying, as described before. It reduces substantial collapse of the shape during de-
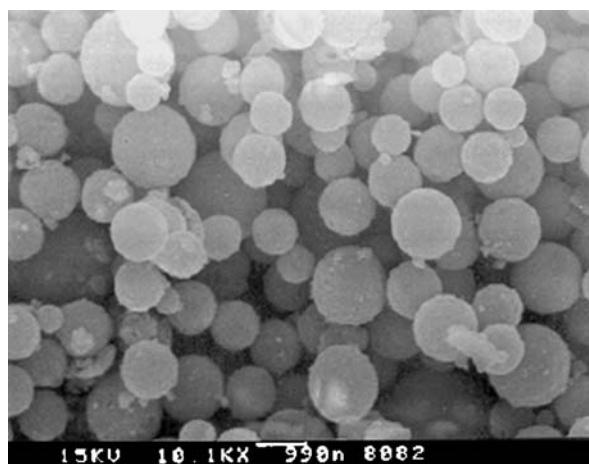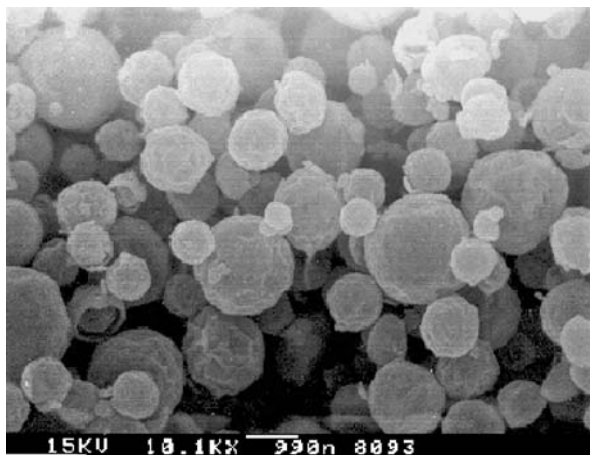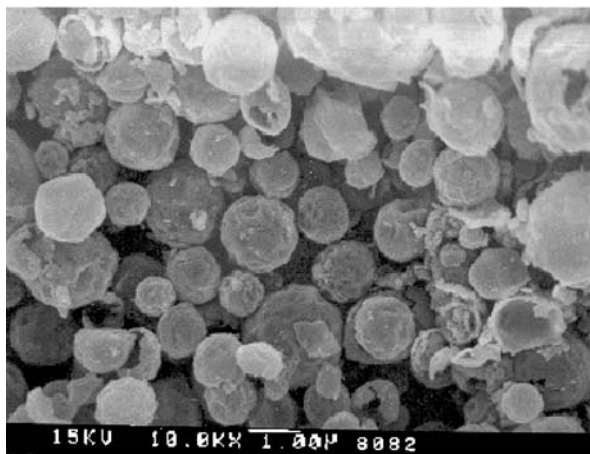

(a)
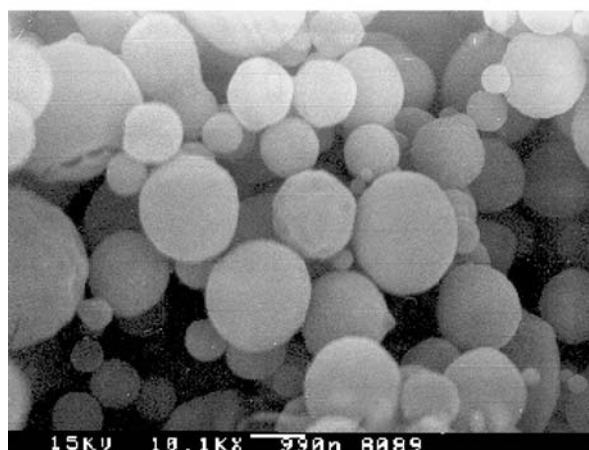
(b)

Figure 3 SEM pictures of particles prepared from $NiSO_4\cdot 6H_2O$ droplets with (a) thermal drying and (b) diffusion+thermal drying under reference condition.

Figure 2 SEM pictures of droplets passing through diffusion dryer under reference condition.

composition thus to keep the original spherical shape of the primitive particles. The other is higher decomposition temperature of the salt, as shown in Fig. 1, which would extend the life of the salt particles such that the particles took time to age, again reducing the substantial collapse during decomposition.

Fig. 4 shows SEM image of the oxide particles prepared from $Ni(NO_3)_2 \cdot 6H_2O$, whose morphologies are quite different from those from other salts. They look hollow and thus fragile enough to easily fragment into small pieces while their surfaces were rough and composed of layer by layer. In according to Jain *et al.* [11], when salt in melt rather than in solid was transformed to the solid oxide, hollow structure was obtained if the theoretical volume of the oxide particle was below 0.16 times that of the salt-melt droplet. By the criterion, the oxide particles derived from $Ni(NO_3)_2 \cdot 6H_2O$ would be hollow. As a matter of fact, the solid oxide nuclei would be formed from the surface of the salt-melt droplet in crust shells layer-by-layer. However, the shells were hardly sinterable and would be thus unstable on the surface of liquid pool of $Ni(NO_3)_2 \cdot 6H_2O$ to form such a morphology. The situation was quite different for $NiCl_2 \cdot 6H_2O$ and $NiSO_4 \cdot 6H_2O$ since the oxide nuclei are stably formed on the surface of pre-solidified salt without such unrest. The figure shows that inclusion of

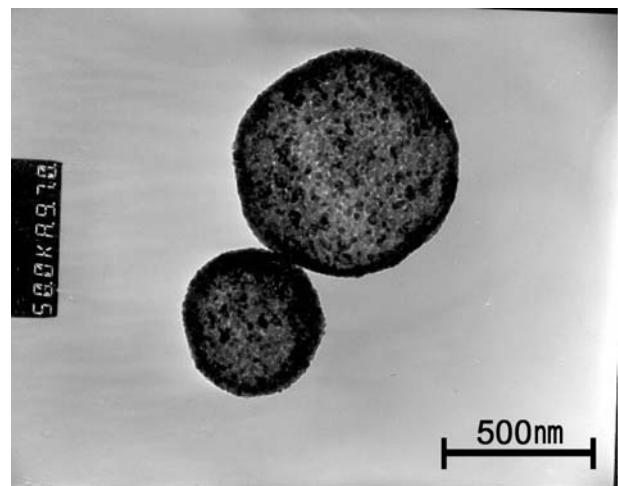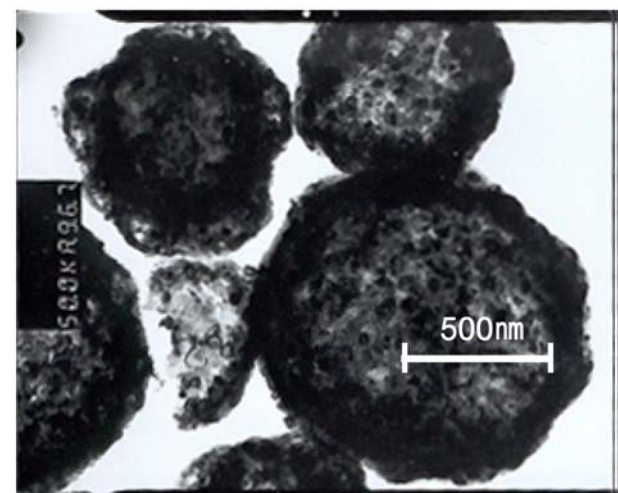diffusion drying increased the size of the particles as well as their hollowness the former of which is similar for either $NiCl_2 \cdot 6H_2O$ or $NiSO_4 \cdot 6H_2O$ while the latter is not. For $Ni(NO_3)_2 \cdot 6H_2O$ since the primitive salt droplets via diffusion dryer would have water content distributed throughout, their decomposition occurs in the process as described before to result in hollow and fragile particles. However, those directly dried in the furnace, due to the water confined inside the droplet, would shrink during the decomposition by at least partially filling the void which escaping water left.

TEM images of the particles prepared from $NiSO_4 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ by direct pyrolysis are shown in Fig. 5. However, the figure clearly supports the difference in the morphology between the two salts, as already described. It is noted in the Figure all the oxide particles, irrespective the nature of the salt, are composed of very small nuclei generated during salt-to-oxide conversion, without sintering. In addition, the oxide nuclei from $NiSO_4 \cdot 6H_2O$ are smaller and packed more densely and regularly. On the other hand those from $Ni(NO_3)_2 \cdot 6H_2O$ were coarser and irregularly packed. As discussed before, Due to

(a)

(b)

Figure 4 SEM pictures of particles prepared from $Ni(NO_3)_2 \cdot 6H_2O$ droplets (a) by direct spray pyrolysis and (b) via diffusion dryer under reference condition.

(a)

(b)

Figure 5 TEM pictures of particles prepared from (a) $NiSO_4 \cdot 6H_2O$ and (b) $Ni(NO_3)_2 \cdot 6H_2O$ droplets with thermal drying only, otherwise under reference condition.

the higher rate of decomposition of $Ni(NO_3)_2·6H_2O$ than the counterpart, there would appear smaller nuclei of the oxide with much more number, in turn to grow more actively to larger size, which will explain the difference in the TEM images.

3.4. Effect of temperature

For $NiSO_4·6H_2O$, the particles prepared at 700°C had rough surface with bumps in their SEM image, which is not shown. However, at higher temperatures all the particles had their inherent sphericity and surface smoothness, as described before, irrespective of the modes of drying. All the particles obtained from $Ni(NO_3)_2·6H_2O$ became smaller but less fragile, probably by decreasing the hollowness with the temperature. Fig. 6 shows the XRD patterns of the particles prepared by direct pyrolysis of the two salts at different furnace set temperatures. In the case of $NiSO_4·6H_2O$ shown in Fig. 6a, pure nickel oxide was identified for the particles prepared at 800°C and up, while those prepared at 700°C were, however, just the sulfate, all of which also hold for the particles via diffusion dryer. This is compared to the case of $NiCl_2·6H_2O$ in which the nickel oxide formed from 700°C but nickel chloride remained
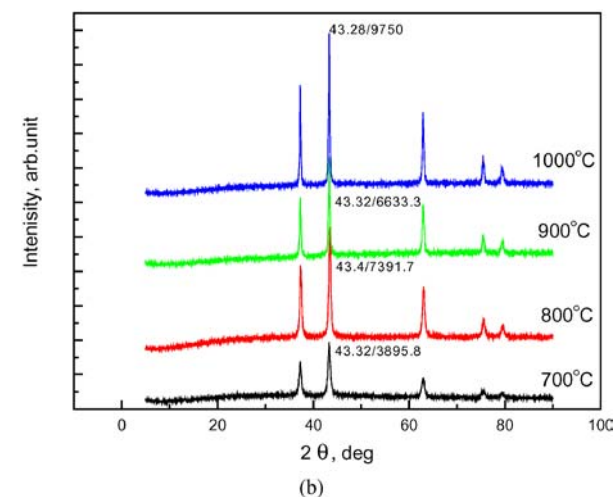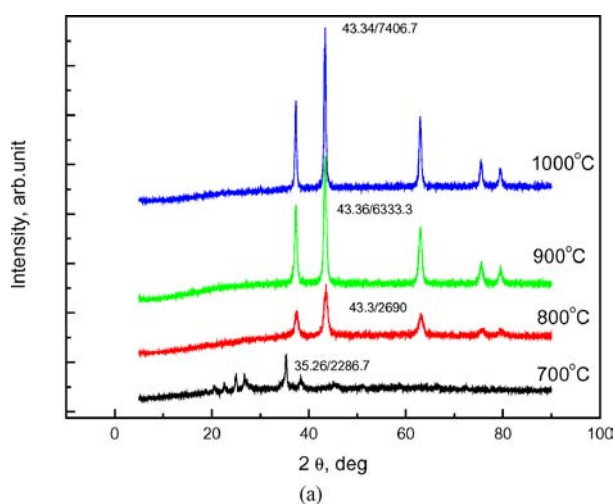
all the way up to 1000°C even though its concentration reduced. The heights of the nickel peaks increase with the temperature, which implies the size of crystallites still increase with it, even though decomposition was completed at 800°C. On the other hand, Fig. 6b shows that the decomposition of $Ni(NO_3)_2·6H_2O$ were already completed below 700°C, reflecting its high rate of decomposition, as described before. In this case the crystalline growth of the oxide particles proceeds further at given temperature since the peak heights of the nickel oxide in Fig. 6b are always higher than those corresponding to Fig. 6a.

Fig. 7 shows the effect of furnace set temperature on number average diameter of the oxide particles prepared via two modes of drying. For $NiSO_4·6H_2O$ shown in Fig. 7a, the particles prepared via diffusion dryer keep their average size close to those of the precursor salt particles, independent of the temperature. However, the size of the directly pyrolyzed particles decreases with the temperature at the expense of the hollowness of the primitive particles. These were similar to the case of $NiCl_2·6H_2O$ [5]. For $Ni(NO_3)_2·6H_2O$ shown in Fig. 7b it is noted that the average diameters of all the particles, independent of modes of drying, de-

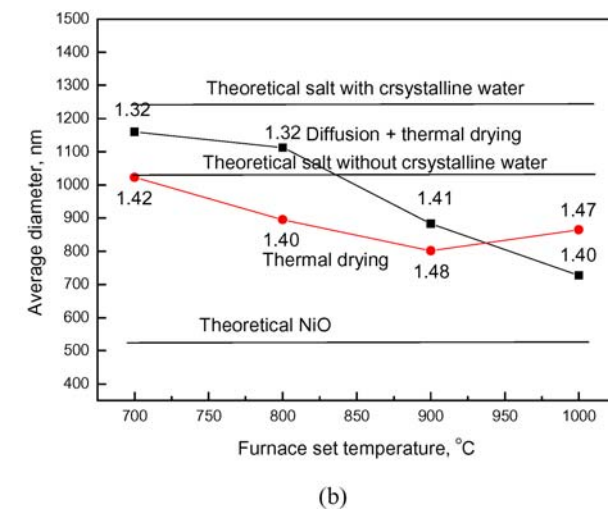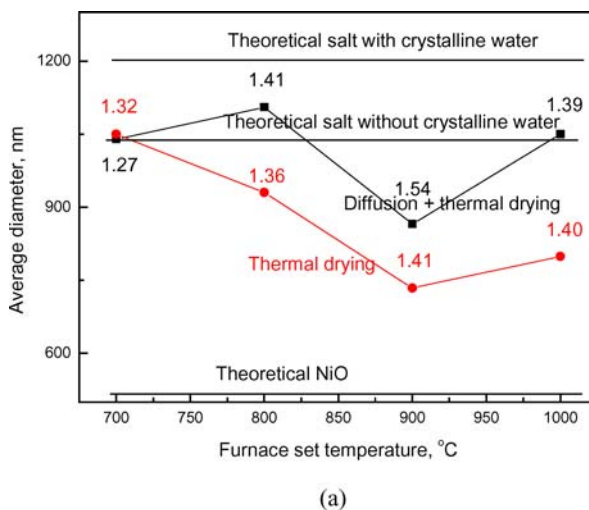*Figure 6* XRD patterns of particles prepared from (a) $NiSO_4·6H_2O$ and (b) $Ni(NO_3)_2·6H_2O$ droplets with thermal drying only at different furnace set temperatures, otherwise under reference condition.

Figure 7 Effects of furnace set temperature on diameter of particles prepared from (a) $NiSO_4·6H_2O$ and (b) $(NO_3)_2·6H_2O$ droplets, respectively, otherwise under reference condition. (Geometric standard deviations are shown in numbers.).

crease with the furnace set temperature. In general, at low temperature since the decomposition was initiated at the surface and then propagate into inside, the size of the oxide particles would be fixed at the initiation. However, as the temperature was raised, the decomposition took place in depth further from the surface of the particles, resulting in either porosity increase or size reduction. For $NiSO_4 \cdot 6H_2O$ as the temperature was raised, the particles via diffusion dryer would be formed by the increase in the porosity without size reduction due to the solidness of the precursor salt particles while the directly pyrolyzed particles by the size reduction due to their hollowness. For $Ni(NO_3)_2 \cdot 6H_2O$, all the particles shrink with the temperature since they were formed on the liquid pool, irrespective of the drying modes, whose volume was easily contractible, as discussed before. From the Figure, the directly pyrolyzed particles were always smaller due to the void which confined water seized than those via diffusion dryer, as described before.

3.5. Effect of initial salt concentration

No significant changes such as hollowness and surface smoothness were observed by the increase in the ini-

tial salt concentration. Fig. 8 shows the variation in the average diameter of the direct pyrolyzed particles prepared with respect to the initial salt concentration. The theoretical diameters of both the salts and oxide particles calculated [5] are also shown in the figure. The size of the particles, irrespective of the nature of the salts, increases with the concentration, as described elsewhere [5], while all the oxide particles prepared are larger than theoretical oxide particles. As shown in the Figure, it is noted that the sizes of the directly pyrolyzed particles locate apparently in the same relative positions between the sizes of theoretical salt and nickel oxide particles. This confirms that the particles prepared have the same morphology at the given temperature irrespective of the initial salt concentrations.

The XRD patterns of the particles prepared, not shown, indicate that the heights of nickel oxide peaks increased with the concentration, reflecting that the size of crystallites increased with the concentration at a given temperature due to the increase in the crystalline sources.
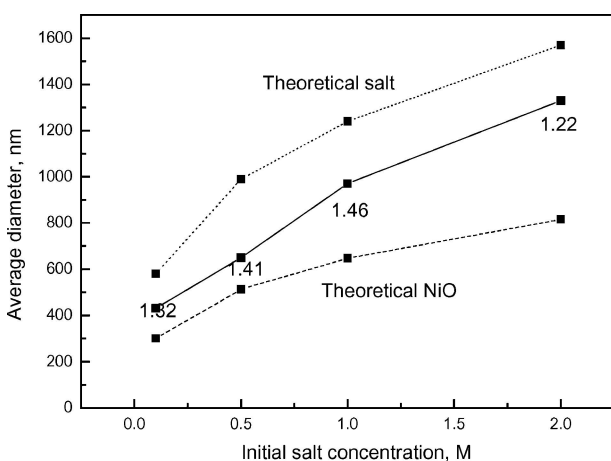
4. Conclusions

Nickel oxide particles were prepared by spray pyrolysis of aqueous solutions of $NiSO_4 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$, respectively. The oxide particles obtained from $NiSO_4 \cdot 6H_2O$ were highly spherical with very smooth surface due to the less hollowness of the primitive salt particles and its inherent high decomposition temperature. On the other hand $Ni(NO_3)_2 \cdot 6H_2O$ converted to hollow and fragile oxide particles having rough surfaces by liquid-to-solid conversion immediately after removal of crystalline water. Direct pyrolysis, in general, reduced the size of the hollow salt particles (or droplets) by collapse. The size of the oxide particles decreased with the temperature of spray pyrolysis but increases with the initial concentration of the salts. For $NiSO_4 \cdot 6H_2O$, inclusion of diffusion drying fixed the oxide particles at the size of the primitive salt particles, independent of the temperature. However, the preliminary drying made the oxide particles from $Ni(NO_3)_2 \cdot 6H_2O$ more hollow and fragile, and reduced their size with the temperature. The oxide particles were made of many isolated nuclei without sintering. The crystallinity of the oxide particles increased with temperature as well as the initial salt concentration.

(a)

(b)

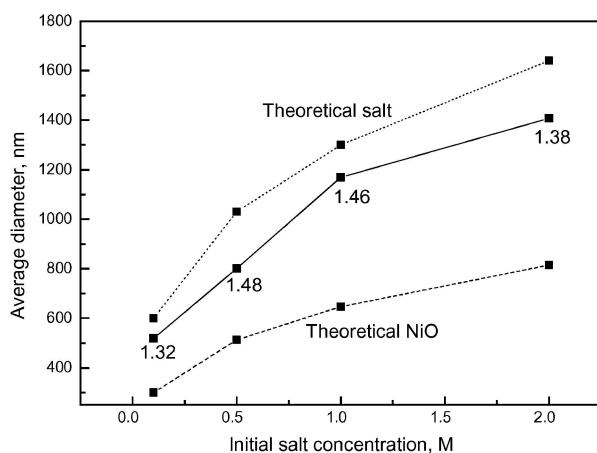*Figure 8* Effects of initial salt concentration on diameter of particles prepared from (a) $NiSO_4 \cdot 6H_2O$ and (b) $Ni(NO_3)_2 \cdot 6H_2O$ droplets, otherwise under reference condition. (Geometric standard deviations are shown in numbers.).

References

1. K. NAGASHIMA, M. WADA and A. KATO, *J. Mater. Res.* **5** (1990) 2828.
2. S. STOVIC, I. ILIC and D. USKOKOVIC, *Mater. Lett.* **24** (1995) 369.
3. S. L. CHE, K. TAKADA, K. TAKASHIMA, O. SAKURAI, K. SHINOZAKI and N. MIZUTANI *J. Mater. Sci.* **34** (1999) 1313.

4. W.-N. WANG, Y. ITOH I. W. LEGGORO and K. OKUYAMA, *Mater. Sci. Engng. B* **111** (2004) 69.
5. T. ADDONA, P. AUGER, C. CELIK and G. CHEN, *Pass. Comp. Ind.* (1999) Nov./Dec., 14.
6. D. J. KANG, H. S. KIM and S. G. KIM, *J. Mater. Sci.* (2003) Submitted.
7. G. V. JAYANTHI, S. C. ZHANG and G. L. MESSING, *Aerosol Sci. Technol.* **19** (1993) 478.
8. H.-F. YU and W.-H. LIAO, *Int. J. Heat Mass. Transf.* **41** (1998) 993.
9. I. W. LENGGORO, T. HATA, F. ISKANDAR, M. M. LUNDEN and K. OKUYAMA, *J. Mater. Res.* **15** (2000) 733.
10. R. H. PERRY and D. W. GREEN, in "Perry's Chemical Engineer's Handbook", 7th edn. (McGraw-Hill, 1997).
11. S. JAIN, D. J. SKAMSER and T. T. KODAS, *Aerosol Sci. Technol.* **27** (1997) 575, *J. Mater. Sci.* **34** (1999) 1313.