

## Reductive crystallization of each metal in composite particles spray-pyrolyzed from silver/nickel mixed nitrates

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**Abstract**—Composite particles prepared by spray pyrolysis of aqueous solution of AgNO<sub>3</sub> and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O with 10 vol% H<sub>2</sub>-N<sub>2</sub> were characterized and compared with the particles similarly prepared from their pure nitrates. The composite particles were composed of metallic silver, nickel oxide or metallic nickel, depending on the condition, with no trace of alloy. The existence of nickel ions dispersed throughout the particles did not affect the rate of reduction to the highly reducible silver but retarded its subsequent crystal growth. On the other hand, both the reduction to nickel and its crystal growth were all retarded due to the existence of the more reducible silver ions. In addition to these, the incompatibility also increased the size of the composite particles from the corresponding single component particles and kept it almost constant with respect to the preparation temperature.

Key words: Silver/nickel, Composite particles, Spray pyrolysis, Intraparticle properties, Reduction, Crystallization, Incompatibility

### INTRODUCTION

As phase-pure silver and nickel particles are widely used in conducting pastes for integrated circuits and other electronic devices, silver/nickel composite particles also have been applied to electrical contacts and switches due to their fine electrical conductivity tuning and anti-melting capability [1].

There have been many studies on spray pyrolysis for preparing pure silver particles from their corresponding salts [2,3] and nickel [4,5]. They could be obtained above 500 °C with a residence time around 25 s and initial salt concentration of 0.5 M. The silver particles were easily prepared in the environments of nitrogen gas and even air without any reducing agent, while the nickel particles required hydrogen and other reducing agents. In addition, the former were formed to highly dense spheres with smooth surfaces on being reduced from its salt, while the latter demanded increased furnace temperature and/or the extended residence time, otherwise their surfaces were found bumpy and porous. On the other hand, the two metals are immiscible from the point of the view of equilibrium thermodynamics [1,6,7]. Metastable alloy particles from the mixed precursors [1,7] were formed under an extreme condition such as laser irradiation. In the previous study [8], we pointed out the immiscibility between the two metals in the particles prepared by spray pyrolysis via EDX mapping. However, more experimental evidences are necessary to prove their incompatibility.

In this study we prepared composite particles of silver and nickel by spray pyrolysis from aqueous solution of mixed silver and nickel nitrates. The size and morphology of the particles, and the alloying, reduction and crystallite growth of the metal constituent were by varying the gas environment, furnace set temperature, residence time in the reactor and initial molar ratio of the salts. Then the characteristics were compared with those of single component

particles prepared otherwise under the same condition.

### EXPERIMENTAL

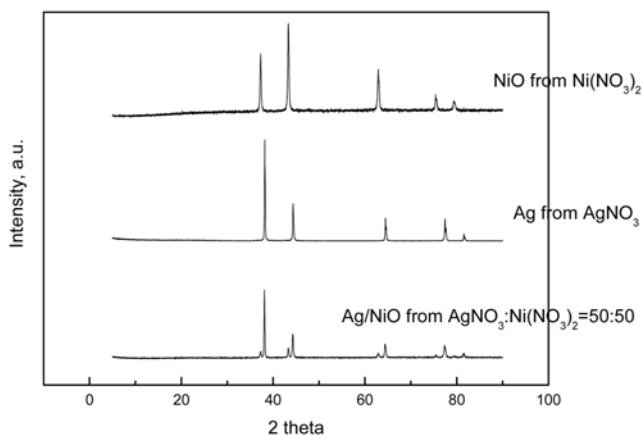
The apparatus for preparing the particles consisted of ultrasonic atomizer, hot wall tubular reactor heated by a single-zone heating furnace, filter and acid gas absorber, as described elsewhere [9]. Aqueous solution of AgNO<sub>3</sub> and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O maintained at 30 °C was ultrasonically atomized at a rate of 15 mL/h. The molar ratio of the two salts (reference ratio=50 : 50) was varied with the total concentration of the mixed salts kept at 0.5 M. The droplets were carried by either 100% N<sub>2</sub> or 10 vol% H<sub>2</sub>-90 vol% N<sub>2</sub> at 1 L/min (reference flow rate, corresponding to a residence time in the reactor of 25 s at 20 °C and 1 bar) to the electrically heated horizontal tubular reactor, 700 mm long with the diameter of 30 mm, maintained at 1,000 °C (reference temperature).

Process variables included the nature of carrier gas, furnace set temperature, residence time and initial molar ratio of the precursor salts in order to investigate their effects on metallization, size, morphology and crystallite growth of the particles. The particles exiting from the reactor were collected by a 0.5- $\mu$ m TEFLON fabric filter. The water and acid vapor formed from the reactor was finally absorbed in caustic solution before the waste gas was exhausted.

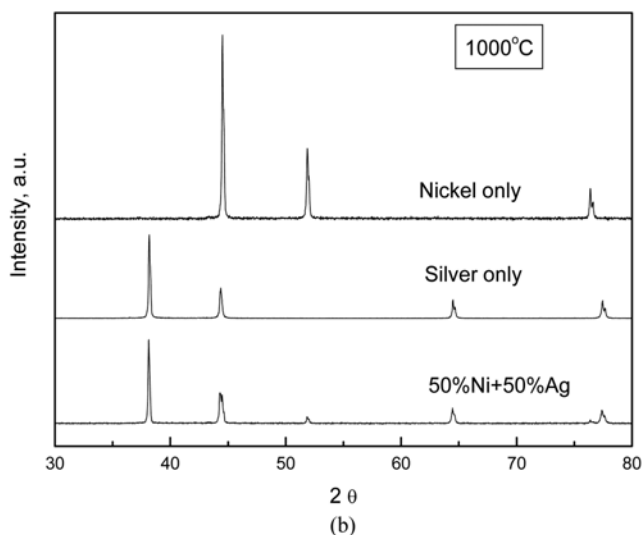
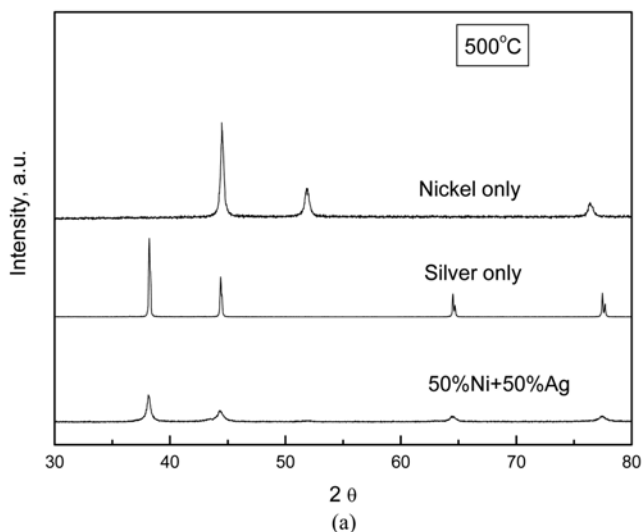
#### 1. Characterization of Particles

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 the particles was observed with X-ray diffractometer (XRD, Scintag-SDS 2000) and the transmission electron microscope. Bulk chemical composition was measured with the XRD and energy dispersive spectroscopy (EDS, Model: Voyager, Noran). Intraparticle distribution of the elements was obtained with energy dispersive spectroscopy (EDS, Oxford) attached to TEM (JEM-

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**Fig. 1.** XRD patterns of particles from nickel, silver and 50 : 50 silver/nickel composite particles prepared at different furnace temperatures under  $N_2$  environment. Total salts: 0.5 M; Residence time: 25.4 s; Temperature: 1,000 °C.



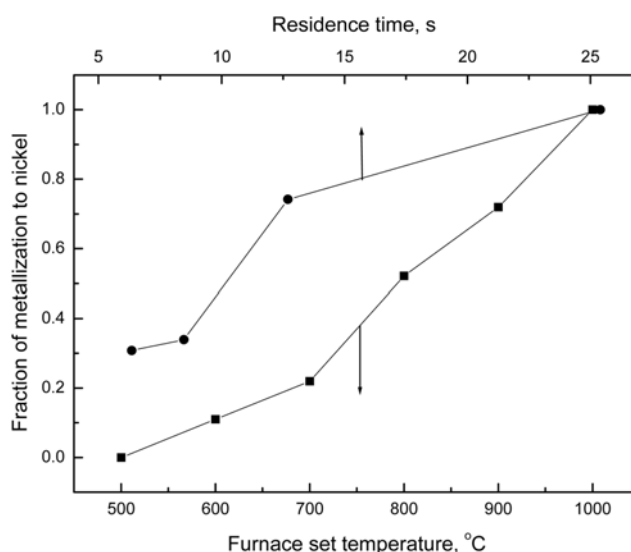
**Fig. 2.** Comparison of particles prepared from nickel nitrate, silver nitrate and 50-50 mixed nitrate at (a) 500 °C and (b) 1,000 °C. Otherwise under reference conditions.

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## RESULTS AND DISCUSSION

### 1. Conversion to Metals

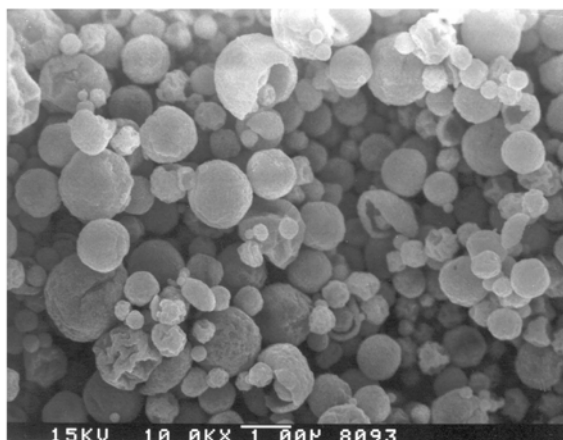
The particles prepared from the mixed salt will be abbreviated as “SN” while those from pure silver and nickel nitrate as “S” and “N,” respectively. Fig. 1 shows the XRD patterns of N, S and SN particles prepared by using pure  $N_2$  gas at a furnace set temperature of 1,000 °C otherwise under reference condition. The S particles obtained were completely reduced to phase-pure silver, while the N particles were identified as nickel oxide with no trace of metallic nickel. The SN particles were found to be a composite of metallic silver and nickel oxide. Therefore, in succeeding experiments for the N and SN particles pure nitrogen was replaced by 10 vol%  $H_2$ -90 vol%  $N_2$  in order to get metallic nickel. Fig. 2 shows comparison of the XRD patterns of the N, S and SN particles prepared at 500 °C and 1,000 °C, respectively. The XRD patterns of the composite SN particles shown in the Fig. 2 indicate that all the peaks belonged to silver, nickel oxide or nickel without any other additional peaks representing an alloy between them. At 500 °C the N and S particles were completely reduced to phase-pure nickel and silver, respectively. However, at the same temperature the XRD pattern of the SN particles had metallic silver peaks but none of metallic nickel. Instead, there appeared nickel oxide whose primary and secondary peaks were, though, obscured to broaden (110) and (211) peaks of silver, respectively, due to the closeness of the corresponding peaks. However, the increase in the temperature to 1,000 °C could completely convert the mixed salt all to metallic nickel as well as silver. Based on EDS results of the particles, the fractional conversions to metallic nickel were calculated and shown in Fig. 3 for the composite SN particles prepared at different furnace set temperatures. It is confirmed that the conversion increased slowly up to 700 °C and then rapidly approached 100% at 1,000 °C. Fig. 3 also shows



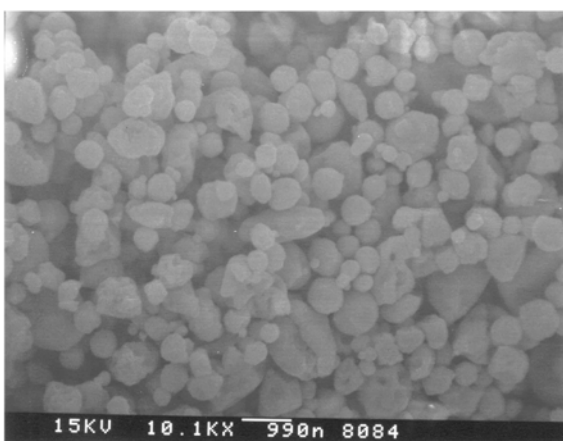
**Fig. 3.** Fraction of metallization to nickel with respect to furnace set temperature and residence time for 50-50 silver-nickel composite particles prepared otherwise under reference conditions.

the effect of residence time on the fractional conversion for the SN particles. It gradually increased from 30% at the residence time of 6.25 s to 100% at 25.4 s. However, in the case of N and S particles the conversion remained 100% for such range of the residence time [8,9]. For the SN particles the reduction to nickel was retarded by

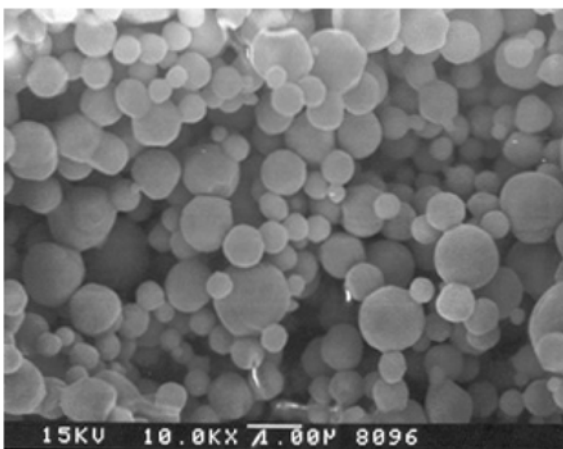
the existence of silver. It was proposed that silver ions with lower ionization tendency, meaning more reducible, reduced preferentially, leaving the particle environment in a kind of oxidative state, which delayed the reduction of the less reducible nickel ions. In order to reduce the latter in the SN particles, it is necessary to in-



(a)

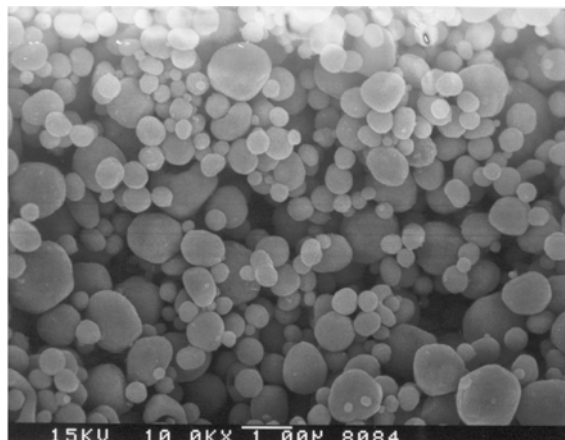


(b)

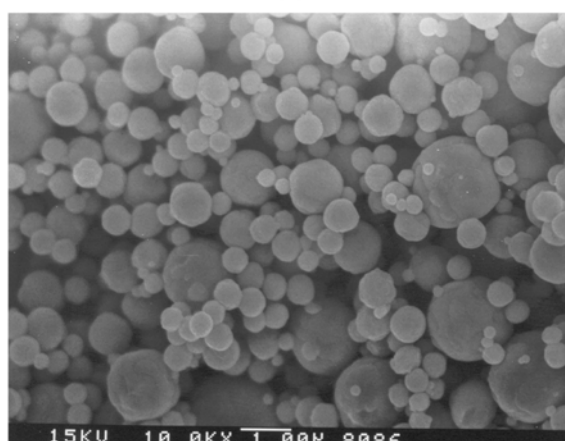


(c)

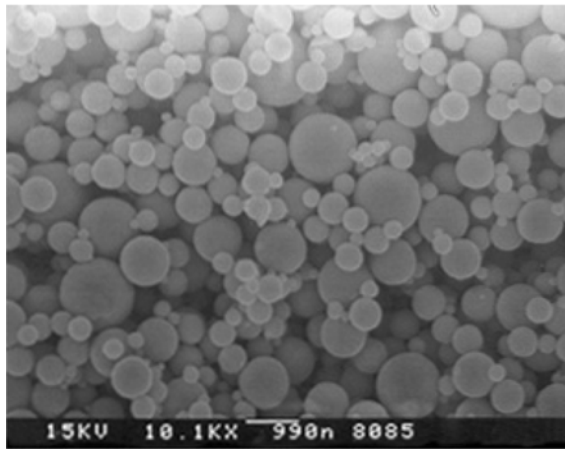
Fig. 4. SEM micrographs of particles prepared from (a) nickel nitrate, (b) 50-50 mixed nitrate and (c) silver nitrate at 500 °C, otherwise under reference conditions.



(a)



(b)



(c)

Fig. 5. SEM micrographs of particles prepared from (a) nickel nitrate, (b) 50-50 mixed nitrate and (c) silver nitrate at 1,000 °C, otherwise under reference conditions.

crease either the furnace set temperature or residence time. The minimum temperature required for complete reduction to nickel increased from 410 °C for the N particles [9] to about 1000 °C for the SN particles.

## 2. Morphology of the Particles

Fig. 4 shows SEM micrographs of the N, S and SN particles prepared at 500 °C, otherwise under the reference condition. The N particles, already identified as metallic nickel as described before, were far from spherical with rough surface (SEM image in Fig. 4(a)), due to the on-going sintering of the nickel crystallites (TEM image in Fig. 4(a)) just converted from nanosized oxide crystallites which had been hardly sinterable [4,10]. The S particles, which were found phase-pure silver, were spherical with smooth surfaces as shown in Fig. 4(c), due to its high sintering nature [11]. On the other hand, the SN particles looked apparently in-between (Fig. 4(b)). As a matter of fact, inside each SN particle, nickel existed as hardly sinterable nickel oxide nanocrystallites, between which the interstices were filled by highly sinterable silver constituent during the formation of each SN particle, which was verified by the elemental mapping with TEM observation [8]. At 1,000 °C, as shown in Fig. 5, the SN particles (Fig. 5(b)) approached to the same degree of sphericity as the S particles (Fig. 5(c)). As the temperature increased, the reduction to nickel proceeded and the subsequent sintering among the nickel crystallites began. Due to the low miscibility between silver and nickel [1,6,7], the increase in the preparation temperature enhanced the intraparticle sintering of nickel crystallites to bring about segregation of each metallic element. From EDS attached to TEM in the previous study [8], it was found that silver, the more mobile phase, move out to the shell of the particles while the less mobile nickel gathered in their core. Thus the same sphericity as the S particles was achieved in the SN particles by the surface silver.

## 3. Crystallization of the Particles

Fig. 2(a) shows that at 500 °C the height of the primary peak (110) of silver was noticeably reduced by forming SN particles, compared to that for the S particles. For the SN particles, as shown in

the previous paper [8], with the increase in the temperature both silver and nickel peaks gradually grew and sharpened while nickel oxide peaks faded out. It was 1,000 °C until the peaks of the silver recovered those of the S particles, as shown in Fig. 2(b). However, all the nickel peaks for the SN particles prepared at 1,000 °C were still considerably small compared to the corresponding peaks for the N particles. In order to explain this, the crystallite size of the metals were calculated from the half width of the peaks according to Scherrer equation and shown in Fig. 6. The crystallite size of silver in the composite particles monotonically increases from 25 nm to 50 nm with the furnace set temperature, while the size of the crystallites in the S particles was almost saturated around 50 nm. This means that inside the SN particles the silver, even though easily formed by reduction at as low as 500 °C, still had a long way to go for growing of its crystallites, which was achieved by further increasing the furnace set temperature and/or residence time in the reactor. On the other hand, it was 500 °C that for the S particles, reduction, sintering and crystallization were all completed [8]. Fig. 6 indicates that the crystallite size of silver increased rapidly at 700 °C where the conversion to nickel was accelerated, as shown in Fig. 4. At low preparation temperature metallic silver so reduced filled the interstices of nickel oxide crystallites and was thus prevented from further growing and crystallization. However, the increase in the temperature promoted the metallization and sintering of nickel as well as the mobility of silver to segregate the two components into core-shell structure. Crystallite size of nickel vs. furnace set temperature was plotted for the N and SN particles, respectively, as shown in Fig. 7. As the temperature increased from 700 °C to 1,000 °C, the nickel crystallite size in the SN particles, which had been retarded in reduction, was always smaller than that in the N particles. It is concluded that the inclusion of nickel retarded the crystallization of silver as well as the reduction and crystallization of nickel, due to their insolubility between the two metals in the composite particles.

## 4. Effect of Incompatibility of the Metals on Particle Growth

Fig. 8 shows the variation of the number average diameter of the

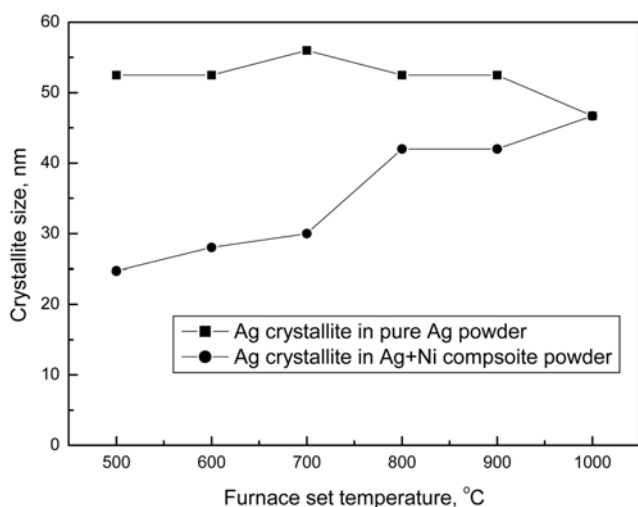


Fig. 6. Variation in silver crystallite size with respect to furnace set temperatures for pure silver particles and silver-nickel composite particles, prepared otherwise under reference conditions.

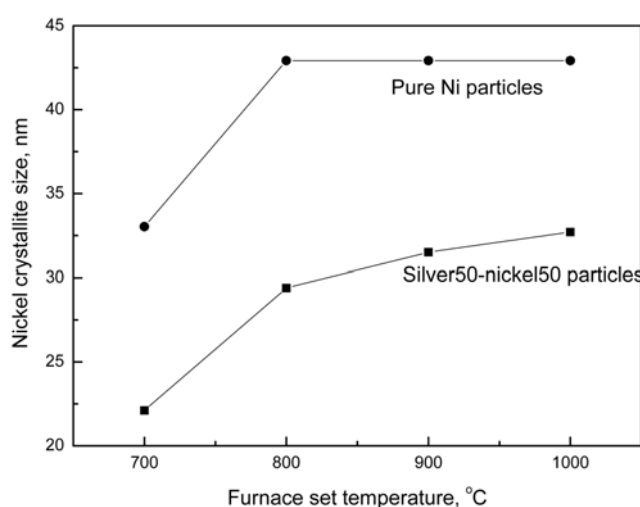
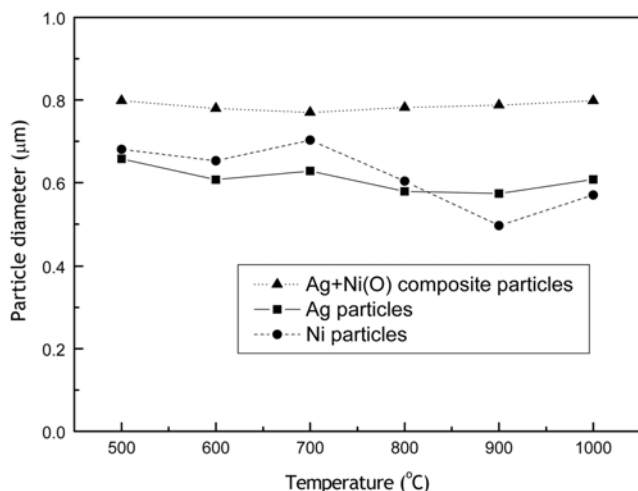


Fig. 7. Variation in nickel crystallite size with respect to furnace set temperatures for pure nickel particles and silver-nickel composite particles, prepared otherwise under reference conditions.



**Fig. 8.** Variation in number mean diameters of pure silver and nickel particles, and silver-nickel composite particles with respect to furnace set temperature, prepared otherwise under reference conditions.

N, S and SN particles with respect to the furnace set temperature. The sizes of the N and S particles decreased from 650 nm to 590 nm and from 680 nm to 550 nm, respectively, with the temperature due to the densification caused by intraparticle sintering. Despite low sinterability of nickel, the effect of the densification was more pronounced for the N particles whose intraparticle sintering was actively in progress at the temperatures in such range shown [9]. On the other hand, for the SN particles the size was always higher than either N or S particles, varying only between 790 nm and 800 nm with respect to the temperature, showing a minimum at 700 °C: The size increase for the SN particles probably resulted from lower density of nickel oxide than nickel and insufficient sintering of silver below 700 °C, and the incompatibility between silver and nickel above 700 °C. While the crystallite size decreased with the temperature as nickel oxide converted to nickel and crystallization of silver proceeded, it increased as active metallization began, as described before, due to looser atomic arrangement at the interface of the two phases.

## CONCLUSIONS

Composite particles were prepared by spray pyrolysis of aque-

ous solution of  $\text{AgNO}_3$  and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with 10 vol%  $\text{H}_2\text{-N}_2$  and compared the phase-pure silver and nickel particles from the corresponding salts with nitrogen and 10 vol%  $\text{H}_2\text{-N}_2$ , respectively. The two metallic constituents did not form an alloy at such relatively mild condition made in the spray pyrolysis. The reduction to nickel and thus subsequent crystallization were all delayed probably due to the existence of the more reducible silver. Even though the reduction to silver took place at low temperature, the subsequent sintering and crystallization of the silver were delayed by the dispersed nickel oxide crystallites, which were least sinterable. Due to the retardation of nickel reduction and silver sintering, and incompatibility of nickel and silver, the composite particles were always larger than phase-pure metallic particles.

## ACKNOWLEDGMENTS

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