Preparation of mono-disperse Ni powders via the reduction of hydrazine complexes: The effect of source materials and impurities

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Abstract Mono-disperse and spherical Ni powders were prepared using a N_2H_4-based solution reduction route. The main focus was on manipulating the particle size by varying the source materials (Ni-chloride, Ni-sulfate and Ni-acetate) and impurity concentrations. The morphology and size of the Ni particle closely depended on the source materials. In addition, the particle size became significantly smaller with increasing Co concentration ranging from 0 to 350 ppm. The decrease in the Ni particle size was attributed to the promotion of nucleation by the rapid decomposition of the $CoCl_2-N_2H_4$ complex when adding a NaOH solution and the more active reduction of Co than that of Ni in the initial stages of the reaction.

Keywords Ni powder · Reduction in solution · Impurity · Mono-disperse powder · MLCC

1 Introduction

The Multilayer Ceramic Capacitors (MLCC) with Ni electrodes is one of the most widely used passive components for highly-integrated electronic and telecommunication devices [1]. The key concept is the large capacitance in a small volume, which is realized by the alternate stacking of $BaTiO_3$-based dielectrics and Ni-based electrode layers up to several hundred layers. Recently, the dielectric and electrode layers are being reduced to the sub-micron scale. Therefore, the facile synthesis of a well-defined Ni powder ranging in size from 100 to 300 nm and the manipulation of the particle size becomes increasingly important [2, 3].

The Ni powder for MLCC can be prepared via vapor phase methods [3], spray pyrolysis [4, 5], solution chemical routes such as the polyol process [6, 7], and reduction in an emulsion [8], aqueous [9–12] and non-aqueous solutions [13]. Among the various routes for Ni powder synthesis, the reduction in the solution is a cost-effective and promising approach for preparing crystalline and spherical Ni powders. The reduction of a complex between the Ni-salt and a reducing agent (N_2H_4) in the presence of OH^- ions is the typical reaction route. However, most studies focused on the change in the powder characteristics by varying the concentrations of the source material [11], hydrazine [8], and the surfactant [9]. During the reduction reaction, the type of source material, complex states and impurity concentrations can play important roles in the nucleation and growth of Ni particles. Therefore, in this study, Ni powder was prepared using a solution reduction method and varying the source materials ($NiCl_2$, $NiSO_4$, $Ni(CH_3COO)_2$) and the Co impurity concentrations. The main focus was placed upon the reproducible manipulation of the particle size and surface morphology.

2 Experimental procedure

The $NiCl_2 \cdot 6H_2O$ (Kisan Kanzoku Chemical Co., Ltd., Japan), $NiSO_4 \cdot 6H_2O$ (Aldrich Chemical Co., Ltd., USA), and $Ni(CH_3COO)_2 \cdot 2H_2O$ (97%, Shinyo Pure Chemical Co., Ltd, Japan), 80% $N_2H_4 \cdot H_2O$ (Extra pure, Dae Jung Chemical & Metal Co., Ltd., Korea), and 50% NaOH aqueous solution (Chemical Pure, Dae Jung Chemical & Metal Co., Ltd,

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Table 1 Experimental conditions used for preparing the Ni powders

Ni-source	Co-source	$[Ni^{2+}]$	$[Co^{2+}]_{imp.}$	$[Co^{2+}]_{added}$	$[Co^{2+}]_{total}$	Solvent
$NiCl_2 \cdot 6H_2O$	–	1.184 M	0 ppm	0 ppm	0 ppm	106.25 g H_2O
$NiSO_4 \cdot 6H_2O$	–	1.184 M	20 ppm	0 ppm	20 ppm	106.25 g H_2O
$Ni(CH_3COO)_2 \cdot 4H_2O$	–	1.184 M	3000 ppm	0 ppm	3000 ppm	106.25 g H_2O
$NiCl_2 \cdot 6H_2O$	$CoCl_2 \cdot 6H_2O$	1.184 M	0 ppm	200 ppm	200 ppm	106.25 g H_2O
$NiCl_2 \cdot 6H_2O$	$CoCl_2 \cdot 6H_2O$	1.184 M	0 ppm	350 ppm	350 ppm	106.25 g H_2O

Korea) were used as the source materials. The Co impurity concentrations in the Ni-chloride, Ni-sulfate, and Ni-acetate materials were quoted as 0 ppm, 20 ppm, and 3000 ppm, respectively.

A 1.184 M Ni-salt aqueous solution was prepared by dissolving 0.169 mol of the corresponding Ni-salt into distilled water and heating it in a water bath ($T = 50°C$). Subsequently, 70.43 g of 80% $N_2H_4 \cdot H_2O$ (1.014 mol of N_2H_4) was poured into solution with vigorous stirring, which increased the solution temperature up to ∼60°C as a result of the exothermic formation of a complex between the Ni-salt and N_2H_4. When the solution temperature reached 50°C, 71.93 g of a 50 wt% NaOH solution (1.014 mol of NaOH, the temperature of NaOH solution = 20°C) was quickly poured into the stock solution. After the complete reaction, the black Ni precipitate was attained and it was washed 6 times with distilled water and dried at room temperature for 16 h under constant ventilation. In order to investigate the effect of the Co impurity, corresponding amounts of $CoCl_2 \cdot 6H_2O$ were added to the $NiCl_2 \cdot 6H_2O$ aqueous solution prior to forming the complex. Table 1 shows the detailed experimental conditions.

3 Results and discussion

In the previous report, we prepared spherical Ni particles from $NiCl_2$ [14] source solution by the solution-reduction method using N_2H_4 and NaOH. Although the concentrations of source material and reaction conditions were slightly different, the evolution of phase during the reaction and reaction mechanism were similar to those of this study. Accordingly, in this contribution, the schematic diagram of reaction mechanism was given in Fig. 1 along with the X-ray diffraction (XRD) patterns of the typical reaction intermediates in $NiSO_4-N_2H_4$-NaOH system.

When the hydrazine solution was poured into the Ni-salt solution, a bright violet precipitate was formed. This was identified as the mixture of Ni-complexes ($[Ni(NH_3)_6]Cl_2$ and $[Ni(N_2H_4)_2]Cl_2$) for $NiCl_2$-N_2H_4 system ($[N_2H_4]/[NiCl_2] = 3.3$–12) [14] and as mostly $Ni[(N_2H_4)x]SO_4$ for $NiSO_4-N_2H_4$ system ($[N_2H_4]/[NiSO_4] = 5$) (Fig. 1(a)). The subsequent addition of a NaOH solution decomposed the Ni-complex and promoted the formation of a $Ni(OH)_2$ gel under highly basic condition, which was confirmed by the

Fig. 1 Schematic diagram of the reaction procedure and (a), (b), (c), (d) X-ray diffraction patterns of reaction intermediates for $NiSO_4-N_2H_4-NaOH$ system. ($[N_2H_4]/[NiSO_4] = 5$)
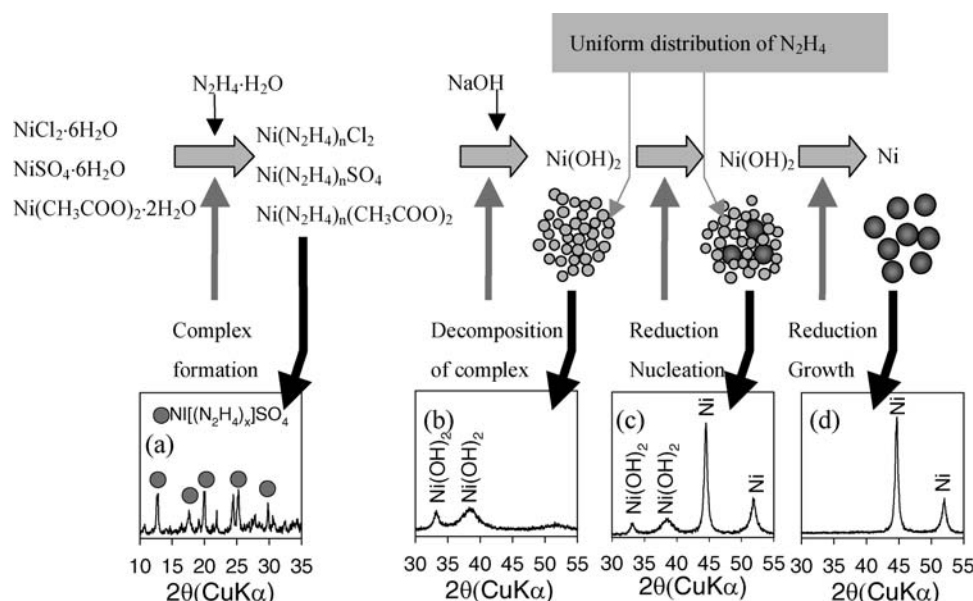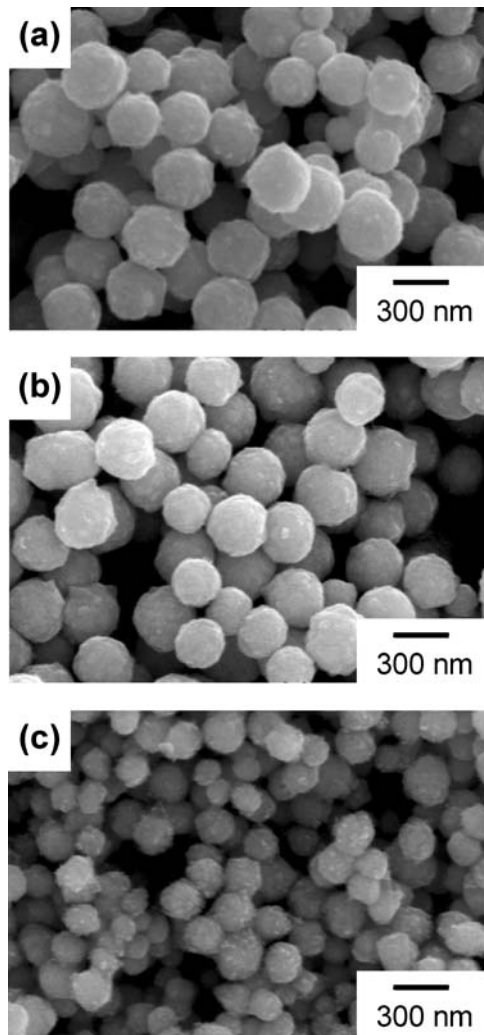
Fig. 2 SEM images of the Ni powders prepared from (a) NiCl$_2$·6H$_2$O, (b) NiSO$_4$·6H$_2$O, and (c) Ni(CH$_3$COO)$_2$·2H$_2$O

respectively. In comparison, the Ni-acetate-derived powder showed a relatively rough surface and was 195.2 ± 45.3 nm in size. The variation in the particle size and morphology can be explained partly by the differences in the acidity of the solution and the chemistry of the Ni-salt-complex. In addition, it should be noted the Co concentration in the Ni-acetate (3000 ppm) was significantly higher than in Ni-chloride and Ni-sulfate.

The background impurity concentration of the chemicals fluctuates according to the production batches. Furthermore, well-defined Ni powder for MLCC applications needs to be prepared reproducibly from economic source materials. Therefore, if the Co impurity concentration in a source material was a critical factor in determining the particle size, its effect should be known and controlled. Therefore, Co concentration was varied from 0–350 ppm in a Ni-chloride system. (Table 1) Then results are shown in Fig. 3.The average particle sizes of the Ni powder prepared from the solutions containing 200 and 350 ppm of Co were 279.6 ± 65.9 nm
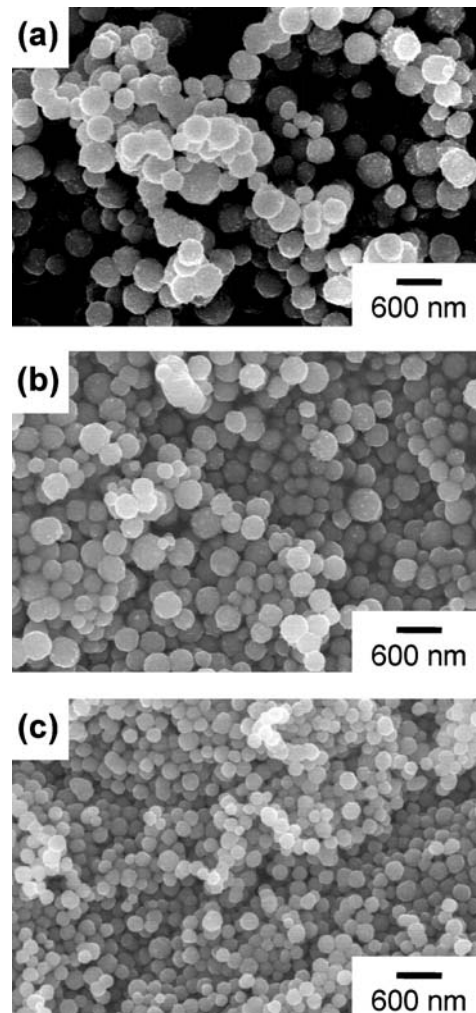

Fig. 3 SEM images of the Ni powders prepared from NiCl$_2$·6H$_2$O with varying Co concentrations: (a) 0 ppm, (b) 200 ppm, and (c) 350 ppm

phase identification of the reaction intermediates (Fig. 1(b)). Subsequently, the Ni^{2+} ion was dissolved from the Ni(OH)$_2$ gel and reduced to mono-disperse and spherical Ni particles by a reaction with the N$_2$H$_4$ produced by the decomposition of the Ni-salt-N$_2$H$_4$ complex and OH$^-$ ions provided by the NaOH (Fig. 1(c) and (d)). The formation of Ni(OH)$_2$ by the addition of NaOH and its subsequent reduction into Ni was also found in NiCl$_2$−N$_2$H$_4$−NaOH system [14].

Figure 2 shows the morphology of the Ni particles prepared from Ni-chloride, Ni-sulfate, and Ni-acetate. All the particles showed mono-disperse characteristics, which indicate that the reduction in solution using a Ni-salt, hydrazine and NaOH is a promising route for preparing a well-defined Ni powder. The difference can be found in the particle size and surface morphology. The powders prepared from Ni-chloride and Ni-sulfate showed the clean surface morphology and were 336.6 ± 91.0 nm and 437.0 ± 68.8 nm in size,

and 175.8 ± 32.4 nm (Fig. 3(b) and (c)), respectively, which was significantly smaller than that prepared from the Co-free solution. (336.6 ± 91.0 nm) (Fig. 3(a)). This suggests that the Co concentration is an important parameter in the preparation of a Ni powder.

CoNi alloys can be prepared conveniently via the polyol process [7] due to the similar standard reduction potentials of Co^{2+} and Ni^{2+} ions [15]. Moreover, it was reported that Co can be also prepared via the formation of a Co-salt-N_2H_4 complex and its subsequent reduction to Co [16]. Accordingly, the evolution of the Co component during the reaction can be regarded as being similar to that of the Ni component. The above shows that Ni particles can become smaller if the reduction of Co^{2+} ions occurs before that of Ni^{2+} and promotes nucleation. The reduction reaction into Ni contains the following three serial reactions: (1) the decomposition of the Ni-hydrazine complex and the formation of $Ni(OH)_2$ (2) the dissolution of Ni^{2+} ion from $Ni(OH)_2$, and (3) its subsequent recrystallization into Ni by a reduction reaction. Therefore, in order to understand the effect of Co impurity on the Ni particle size, the decomposition of a Co-hydrazine complex, the dissolution of Co^{2+} ions from $Co(OH)_2$ and its reduction into Co should be compared with those of the Ni-based reactions.

XRD identified the $NiCl_2$–N_2H_4 complex to be a mixture of $Ni(N_2H_4)_2Cl_2$ and $Ni(NH_3)_6Cl_2$ [14]. When a 50% NaOH solution was added, the solution color changed from a short to long wave length (from pale violet via blue to green), which indicates a decrease in the concentration of NH_3 or N_2H_4 radicals in the Ni-complex [4]. This suggests that the supply of OH^- promotes the decomposition of a Ni-complex. In order to compare the binding energy of the complex, a $NiCl_2$–N_2H_4 complex and $CoCl_2$–N_2H_4 complex were prepared at $[NiCl_2] = [N_2H_4] = 1$ M and $[CoCl_2] = [N_2H_4] = 1$ M, respectively, and their thermal decomposition behaviors were investigated using DTA(Differential Thermal Analysis) and TGA(Thermo Gravimetric Analysis) (Fig. 4).The $CoCl_2$–N_2H_4 complex showed the two distinct exothermic peaks at ~200 and 250°C and weight loss was complete at ~500°C while the $NiCl_2$–N_2H_4 complex showed an exothermic peak at ~300°C and weight loss was complete at ~650°C. These shows that the decomposition of $CoCl_2$–N_2H_4 is easier that that of the $NiCl_2$–N_2H_4 complex.

The pH of the solution increased abruptly from 9.7 to 13.4 when NaOH solution was added, which let to $Co(OH)_2$ and $Ni(OH)_2$ precipitation. Considering the easier decomposition of the $CoCl_2$–N_2H_4 complex, the formation of $Co(OH)_2$ prior to that of $Ni(OH)_2$ can be deduced. The uniform distribution of the reducing agent (the N_2H_4 radical) can be established by the decomposition of the Ni- and Co-complex, and the Ni^{2+} and Co^{2+} ions dissolved from the $Ni(OH)_2$ and $Co(OH)_2$ precipitates will be reduced by the following
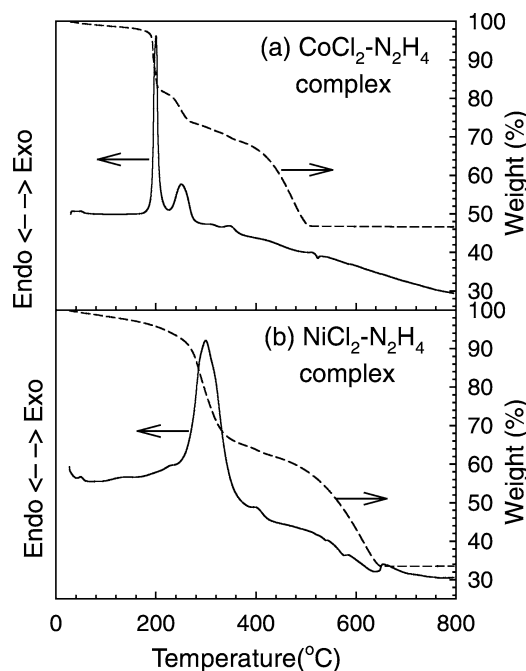

Fig. 4 DTA and TG analyses of (a) $CoCl_2$–N_2H_4 complex and (b) $NiCl_2$–N_2H_4 complex. The complexes for analysis were prepared by the gradual addition of an 80% N_2H_4 solution to the 1 M $CoCl_2 \cdot 6H_2O$ or 1 M $NiCl_2 \cdot 6H_2O$ aqueous solution. Complex precipitate was washed for 4 times using distilled water and then dried at room temperature for 16 h under constant ventilation

dissolution-recrystallization reactions.

$$2Ni^{2+} + N_2H_4 + 4OH^- \rightarrow 2Ni + N_2 + 4H_2O \qquad (1)$$

$$2Co^{2+} + N_2H_4 + 4OH^- \rightarrow 2Co + N_2 + 4H_2O \qquad (2)$$
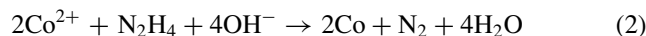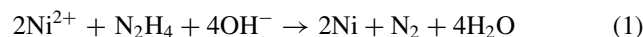
When $[N_2H_4]$ and $[OH^-]$ are fixed, the Co^{2+} impurity changes the Ni particle size when reduction (2) occurs actively before the reaction (1). Besides the decomposition kinetics of the Ni- and Co-complexes, two important parameters that determine the reduction reactions (1) and (2) are the solubility of the reducing ions and the activation energies of the reduction reactions.

The addition of easily-reducible impurities such as Ag- and Pd-salts to a Ni^{2+}-containing starting solution decreases the Ni particle size in the solution reduction [9, 13] and polyol process [7]. Considering the large differences in the standard reduction potential ($E°(Pd^{2+}/Pd) = 0.83$ V, $E°(Ag^{2+}/Ag) = 0.80$ V, $E°(Ni^{2+}/Ni) = -0.23$ V) [15], the decrease in particle size can be attributed to the promotion of the heterogeneous nucleation of Ni on the seeds of Pd or Ag. The standard reduction potential of Co^{2+} ($E°(Co^{2+}/Co) = -0.28$ V) is slightly lower than that of Ni^{2+} ($E°(Ni^{2+}/Ni) = -0.23$ V). In the sole viewpoint of the reduction potential, reduction to Ni is slightly easier than the reduction to Co. Accordingly, the promotion of heterogeneous nucleation by the large difference

in reduction potential can be excluded. Finally, the dissolution of Co^{2+} from $Co(OH)_2$ and Ni^{2+} from $Ni(OH)_2$ should be taken into account for reactions (1) and (2). The solubility product of $Co(OH)_2$ and $Ni(OH)_2$ at 25°C are 1.1×10^{-15} and 5.5×10^{-16}, respectively [17]. Considering the pH of the solution (pH— 13.4, $[OH^-] = 10^{-0.6}$), the $[Co^{2+}]$ and $[Ni^{2+}]$ in the $Co(OH)_2$ and $Ni(OH)_2$ precipitates can be calculated as 1.74×10^{-14} and 8.72×10^{-15}, respectively. If the activation energy for reduction is disregarded, the higher solubility of Co^{2+} ions can result in a higher rate of Co reduction than Ni reduction. From the above discussion, the decrease in the Ni particle size can be explained by the fact that Co plays the role of a nucleating agent due to the faster decomposition of the $CoCl_2-N_2H_4$ complex and the resulting higher concentration of Co^{2+} ions at the initial stage of the dissolution-recrystallization reaction.

4 Conclusion

Mono-disperse Ni powders were prepared from Ni-chloride, Ni-sulfate, and Ni-acetate source solutions via a solution-reduction route using N_2H_4 and NaOH. The particle size and morphology depended closely on the source materials. When Ni-chloride was used as the source materials, the average particle size of the Ni powder decreased with increasing Co impurity concentrations from 0 to 350 ppm. The results were attributed to the promotion of nucleation by the rapid decomposition of the $CoCl_2-N_2H_4$ complex and the earlier reduction of Co^{2+} than that of Ni^{2+} in the initial stage of the dissolution-recrystallization reaction.

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