Preparation of Dispersed Nickel Oxalate Dihydrate by Aqueous Solution Process and its Thermal Decomposition

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Abstract

Synthesis of a nickel oxalate dihydrate (NiC₂O₄·2H₂O) powder was developed using a nickel hydroxide (Ni(OH)₂) slurry. The nickel oxalate dihydrate was then decomposed thermally to produce a nickel powder with morphologically controlled particles and uniform dispersion. The particle morphology and aggregation characteristics of the nickel oxalate dihydrate were first investigated as a function of pH, temperature and ripening time. A nickel oxalate dihydrate powder containing rectangular parallelepiped shape ($0.5 \times 0.8 \mu m^2$) particles free of aggregation was obtained from a reaction mixture at pH 6.0 and 333 K. At 293 K, the size of the nickel oxalate dihydrate particles became smaller, but the powder did not show any aggregation. Finally, a nickel metal powder was produced from the thermal decomposition of the nickel oxalate dihydrate powder prepared at pH 6.0 and 333 K. Heating at 683 K in a helium atmosphere yielded a nickel powder with rectangular parallelepiped shape ($0.3 \times 0.6 \mu m^2$) particles.

Keywords: nickel powder; nickel oxalate; morphology-control; rectangular parallelepiped; thermal decomposition

1. INTRODUCTION

Noble-metal nanoparticles, such as gold and silver, have been studied extensively in recent years primarily because of their unique magnetic, mechanical, optical, and physical properties are different from those of the bulk materials [1]. Less-noble metal nanoparticles such as nickel powder are already used for battery and fuel cell electrodes, catalysts, conductive pastes and internal electrodes of multi-layer ceramic capacitors (MLCC), because nickel metal is inexpensive compared with noble metals. The application and the performance of metallic powders depend largely on the particle size and morphology. In addition, size and morphology are mostly determined during the preparation process. Several processes for preparing nickel powder have been reported, such as the carbonyl method, hydrometallurgical (chemical reduction) method, and the atomization method [2]. Currently, INCO Ltd. produces commercial high-purity nickel powders by a carbonyl method that relies on the thermal decomposition of nickel tetracarbonyl (Ni(CO)₄) [3]. This process can produce nickel particles with various morphologies, described as spiky, filamentous, spherical, chain-like, and fibrous. The dimensions of thus obtained nickel powder are approximately in the micrometer range. In contrast, with the hydrometallurgical method, in which nickel ion is directly reduced to metallic nickel by a chemical agent,

the particles can be reduced to nanosize by varying the experimental parameters, such as temperature, pH, solvent, and reductant [4-9]. However, particle aggregation in an aqueous solution presents a serious problem. Therefore, it is necessary to add a surfactant or to prepare metallic nickel particles in non-aqueous media in order to inhibit aggregation. In addition, the nickel particles produced by the hydrometallurgical method are almost spherical in shape.

A process was developed for preparing needle-shaped nickel powders that involved preparation of a nickel precursor containing oxalate and ammonia, followed by thermal decomposition of the precursor [10]. Although it was possible to control the morphology and the size of the nickel precursors by varying ammonia concentration, temperature, pH and ripening time, there was a tendency for aggregation [11].

In this paper, we have investigated the reaction conditions for source materials, temperature, and ripening time for the preparation of non-aggregated precursors in aqueous solution without ammonia.

2. EXPERIMENTAL

Reagent grade nickel chloride hexahydrate (NiC₂O₄·6H₂O), sodium oxalate (Na₂C₂O₄), sodium hydroxide (NaOH), and oxalic acid dihydrate (H₂C₂O₄·2H₂O) were purchased from Nacalai Tesque,



Fig. 1 Preparation procedure of NiC₂O₄·2H₂O

Japan, and used as received. Each reagent was dissolved in distilled water and diluted to a certain concentration.

A flow chart for the preparation and precipitation of NiC₂O₄·2H₂O particles is shown in Fig. 1. A 30 ml solution of 1 M NaOH was added to a reactor containing 100 ml of 0.2 M NiCl₂·6H₂O solution. The solution was agitated at 293 or 333 K to precipitate Ni(OH)₂ (Step 1). A 20 ml solution of 0.25 M Na₂C₂O₄ was added to the reactor containing Ni(OH)₂ slurry (Step 2). Without interval, a solution of 0.2 M H₂C₂O₄·2H₂O was added at a rate of 0.1 mL/s until reaching at pH 6.0, in order to transform the precipitate from nickel hydroxide to nickel oxalate (Step 3). A pump equipped with a pH probe and controller (EH/W, Iwaki, Japan) was used for Step 3. The solution was then agitated continuously for 1 hour at pH 6.0 for ripening. The precursors obtained after ripening were separated by filtration, then rinsed with distilled water, and dried for 24 hours at room temperature.

The precursors were examined by differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) in a helium atmosphere at a heating rate of 20 K/min, using a thermal decomposition gas chromatograph mass spectrometer (TG-DTA/GCMS; TG8120/GCMS-QP5050A, Rigaku/Shimadzu Co., Japan). The precursors and thermally decomposed products were characterized using a scanning electron microscope (SEM; S-800, Hitachi Co., Japan), and an X-ray diffractometer (XRD; XRD-6000, Shimadzu Co., Japan) with Cu-Kα radiation.

3. RESULTS AND DISCUSSION

Almost all 20 mmol of Ni^{2+} ions reacted with 30 mmol of hydroxide ions in Step 1, and 5 mmol of oxalate ions in step 2, according to reactions (1) and (2) given below, respectively. The solubility products, K_{sp} , for both reactions are small enough to produce precipitates [12, 13].

$$Ni^{2+} + 2OH^{-} = Ni(OH)_{2}$$
 (1)
 $K_{sn}(1) = 1.0 \times 10^{-16} (mol/L)^{3}$

$$Ni^{2+} + C_2O_4^{2-} + 2H_2O = NiC_2O_4 \cdot 2H_2O$$
(2)



Fig. 2 (a) XRD pattern of the precipitates obtained from the mixed solution of 1 M NaOH solution and 0.2 M NiCl₂·6H₂O solution at 333 K. (b) XRD pattern of precipitates obtained immediately after 0.25 M Na₂C₂O₄ was added in Ni(OH)₂ slurry.



Fig. 3 (a) SEM micrograph of the precipitates obtained from the mixed solution of 1 M NaOH solution and 0.2 M NiCl₂·6H₂O solution at 333 K. (b) SEM micrograph of precipitates obtained immediately after 0.25 M Na₂C₂O₄ was added in Ni(OH)₂ slurry.



Fig. 4 XRD patterns of the precipitates obtained (a) 20 min, (b) 40 min and (c) 70 min from the start of Step 3.

 $K_{sp}(2) = 7.8 \times 10^{-10} (mol/L)^2$

Figure 2 shows the XRD patterns for the precipitates formed in Steps 1 and 2 at 333 K. Nickel hydroxide was detected in both steps. Although the formation of nickel oxalate crystal seeds were predicted in Step 2, nickel oxalate was not clearly found in the XRD pattern.



Fig. 5 SEM micrographs of the precipitates obtained (a) 20 min, (b) 40 min and (c) 70 min from the start of Step 3.

Therefore, $NiC_2O_4 \cdot 2H_2O$ was hardly formed in Step 2. The SEM micrograph of the $Ni(OH)_2$ particles is shown in Fig. 3. They were irregular in shape and size.

The pH changed from 7.4 in Step 1 to 8.3 in Step 2. This suggests that the following reaction also took place slightly in addition to eq. (2).

$$Ni(OH)_2 + C_2O_4^2 + 2H_2O = NiC_2O_4 \cdot 2H_2O + 2OH^-$$
 (3)

In Step 3, pH was decreased until pH 6.0 by dropping of 0.2 M H₂C₂O₄·2H₂O solution. It took 70 minutes and required 74 ml of 0.2 M H₂C₂O₄·2H₂O. Initially, the pH behavior showed a gradual decrease within the first 10 min, and then remained constant at pH 7 until 40 min, followed by a secondary decrease to pH 6.0. Figures 4 and 5 show the XRD patterns and SEM micrographs for the precipitates obtained at 20, 40 and 70 min, respectively. The diffraction patterns were in agreement with that for α -NiC₂O₄·2H₂O. The morphology of the particles changed to rectangular parallelepiped with dimensions of ca. $0.4 \times 0.8 \ \mu m$ from an irregular size and shape. Irregular particles were still observed in precipitates at 20 min. The irregular particles observed in the region of rectangular parallelepiped particles is probably Ni(OH)2. However, this was not detected in the XRD patterns. As can be seen in Fig. 5(b)(c), the irregular particles eventually disappeared after 40 min, corresponding to the secondary decrease of pH 7 to pH 6.0. Thus, the following transformation reaction from $Ni(OH)_2$ to NiC_2O_4 · $2H_2O$ might take place in the plateau region at pH 7, between 10 and 40 min.

$$Ni(OH)_2 + H_2C_2O_4 = NiC_2O_4 \cdot 2H_2O$$
 (4)

 $NiC_2O_4.2H_2O$ was formed by reaction between Ni^{2+} , dissociated from $Ni(OH)_2$, and $C_2O_4^{-2-}$ added in Step 3. In this process, $NiC_2O_4.2H_2O$ particles did not aggregate with each other (Fig. 5).

3.1 Effect of Ripening and Temperature

After Step 3, the solution containing NiC₂O₄·2H₂O particles was agitated continuously to ripen under a constant pH of 6.0. Figure 6(a) and (b) show the SEM micrographs of the precipitates after ripening for 1 and 4 hours, respectively. The size and shape of the precipitates after ripening for 4 hours were almost the same as those before ripening (Fig. 5(c)). It is important to ripen under continuous agitation, in order to form a needle-like precursor in the presence of ammonia, as previously reported [10]. In this process, however, it is thought that the particles did not undergo any further transformation during continuous agitation, after pH 6.0 was reached. It

was found that the reaction between Ni^{2+} ions and $C_2O_4^{2-}$ ions was completed within 40 min, before the second pH decrease. Therefore, ripening is not necessary to obtain rectangular $NiC_2O_4 \cdot 2H_2O$ precursors.

The effect of temperature on the morphology of the precipitate is shown in Fig. 7. The NiC₂O₄·2H₂O particles prepared at 293 K were smaller than those at 333 K. The particles were cubic shaped and ca. 0.4 μ m in size. In addition, aggregation did not take place among nickel oxalate dihydrate particles at 293 and 333 K. As reported in a previous paper [10, 11], well-dispersed nickel oxalate particles were not obtained from the direct mixture process of the solution with 0.2 M NiCl₂ and 1.2 M NH₃ at pH 6, and the solution with 0.2 M Na₂C₂O₄ at pH 6. It is thought that aggregation was prevented by the use of Ni(OH)₂ as a mediator.

3.2 Characterization of precursor and Thermal decomposition

Figure 8 shows TG-DTA curves for the NiC₂O₄·2H₂O precursor prepared at 333 K and ripened for 1 hour. In the DTA curve, large endothermic peaks appeared at approximately 500 and 650 K. In the TG curve, a two step mass loss took place concomitantly with respective endothermic peaks, and eventually the mass loss was completed at 670 K. A peak of m/z = 18 derived from H₂O, and that of m/z = 44 derived from CO₂, were



Fig. 6 SEM micrographs of the precipitates after ripening for (a) 1 h and (b) 4 h at 333 K.



Fig. 7 SEM micrograph of the precipitates prepared by continuing agitation for 1 hour at 293 K.



Fig. 8 TG-DTA curves of NiC_2O_4 , $2H_2O$ prepared at 333 K by continuing agitation for 1 hour.

detected near 500 and 650 K, respectively by GCMS (m and z are the mass and charge number, respectively). It is possible to conclude that the following dehydration reaction takes place at ca. 450 K.

$$NiC_2O_4 \cdot 2H_2O = NiC_2O_4 + 2H_2O$$
 (5)

In addition, the following decomposition of $\rm NiC_2O_4$ occurs at ca. 620 K.

$$NiC_2O_4 = Ni + 2CO_2 \tag{6}$$

The thermally decomposed products were examined using NiC₂O₄·2H₂O particles heated to 683 K in a helium atmosphere with a heating rate of 20 K/min, and then cooled. The results of XRD and SEM observations are shown in Fig. 9 and Fig. 10, respectively. The diffraction peaks are mainly attributed to Ni. Other small peaks are NiO, which seems to form on the Ni surface during the handling operation after thermal decomposition. The metal particles maintain a rectangular parallelepiped shape that is 0.3 × 0.6 μ m on average, which is little smaller than precursor.

From these results, it was found that rectangular parallelepiped shape Ni particles were successfully obtained from rectangular parallelepiped NiC_2O_4 ·2H₂O precursors prepared from a Ni(OH)₂ source.

4. Conclusions

A non-aggregated NiC₂O₄·2H₂O precursor was obtained from Ni(OH)₂ precipitates and H₂C₂O₄·2H₂O solution by controlling the pH of the solution. Rectangular parallelepiped precursors with dimensions of ca. 0.4×0.8 µm were transformed from irregular Ni(OH)₂ particles with a decrease in the pH over a period of approximately 40 minutes. The precursors were well-dispersed, indicating that the selection of a suitable source material is important to prevent aggregation. A metallic nickel powder was obtained by heating to 683 K, and the particle size was slightly smaller than the rectangular parallelepiped precursor particle size.

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Fig. 10 SEM micrograph of the precipitates after heat treatment of NiC₂O₄·2H₂O at 683 K.

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