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Formation of Nickel Nanoparticles by Electroless Deposition Using NiO and Ni(OH)₂ Suspensions

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Nickel particles \sim 300 nm in diameter were fabricated by electroless deposition using hydrazine as a reducing agent in nickel hydroxide/ethylene glycol suspension at 353 K without any dispersing agent. The formation mechanism of nickel nanoparticles is discussed from the viewpoint of thermodynamics with in situ monitoring of nickel deposition and mixed potential. Specifically, in situ monitoring of mixed potential in combination with thermodynamic calculation is useful in discriminating whether or not nickel will be deposited in a reaction. The mixed potential drastically changed at the end point of the nickel deposition reaction, indicating that the cathodic reaction, which determined the mixed potential, switched from the nickel deposition reaction to hydrogen generation reaction.

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Ferromagnetic nanoparticles of iron, cobalt, and nickel have potential for applications in high-density magnetic recording, drug delivery, magnetic resonance imaging, biosensing, and catalysts. Many studies on the fabrication of nickel nanoparticles,¹⁻¹² nickel nanobelts,12 and nickel composite nanoparticles (Ni-Ag core-shell nanoparticles,¹⁴ Pt-Ru-Ni ternary nanoparticles¹⁵) have been conducted. Various methods have been reported to prepare nickel nano-particles (e.g., ballmilling, electroless deposition,¹⁻⁸ gas-phase reduction,⁹ spray pyrolysis,¹⁰ chemical vapor deposition,¹⁷ and laser-driven pyrolysis¹²). Electroless deposition is one of the most promising methods for preparing nickel nanoparticles and utilizes the oxidation-reduction reaction of nickel(II) species and reducing agents in liquid phase. For example, Chen et al. prepared nickel nanoparticles surface-capped with a self-assembled monolayer of dodecanethiol using hydrazine hydrate as a reducing agent. Couto et al. used sodium borohydride as the reducing agent and fabricated nickel nanoparticles.' Hou and Gao reported that monodispersed nickel nanoparticles \sim 3.7 nm diam were prepared by reduction of Ni(acethylacetone)₂ with sodium tetrahydridoborate in hexadecylamine.¹ Liu et al. controlled the rate of nickel deposition using sodium tartrate as a complexing agent, and formed nickel nanobelts by the reduction with sodium hypophosphite monohydrate.¹³ Wu and Chen formed nickel nanoparticles the reduction with sodium hypophosphite 9.2 nm diam from nickel chloride using hydrazine in ethylene glycol solution at 60°C and studied the effects of nickel chloride and hydrazine concentrations on particle size.² However, few discussions have been conducted from the viewpoint of thermodynamics, specifically electrochemistry.

We reported a formation process of copper nanoparticles by electroless deposition using hydrazine as a reducing agent in aqueous copper oxide suspension. We found that the driving force of copper deposition can be thermodynamically discussed with the oxidation-reduction potential of Cu^{2+}/Cu redox pair and mixed potential.¹⁶ The most critical point of this method is that a barely soluble source for metallic ions is used for the formation of metal nanoparticles. This maintains the activity of a metal aquo ion at an extremely low level and regulates the particle size. In the present work, we investigated the formation process of nickel nanoparticles by electroless deposition using hydrazine as a reducing agent and discussed the process thermodynamically.

Experimental

Reaction solutions were prepared using nickel oxide (NiO), nickel chloride hexahydrate (NiCl₂· $6H_2O$), sodium hydroxide (NaOH), and hydrazine monohydrate (N₂H₄·H₂O) (Nacalai Tesque, Inc.) as received. All chemicals were of reagent grade. Distilled water and ethylene glycol (Nacalai Tesque, Inc.) or their mixture were used as the solvent. Reaction was conducted in a Pyrex beaker 250 cm^3 in capacity. The solution was agitated at a rate of 500 rpm with a magnetic stirring unit.

Preparation of reaction suspension .-- Nickel oxide colloidal suspension and nickel chloride solution were prepared by dispersing 0.060 mol of nickel oxide and dissolving 0.060 mol of nickel chloride hexahydrate in 60.0 cm³ of distilled water or ethylene glycol using ultrasound. Nickel oxide consists of particles $\sim 1 \ \mu m$ diam, and nickel chloride hexahydrate consists of particles of $>10 \ \mu m$ diam. The initial pH of the solution was adjusted to 12.0 at 298 K by 10.0 mol dm⁻³ sodium hydroxide aqueous solution with a pH meter (Horiba D-21). Nickel chloride dissolved in the solution is almost all hydrolyzed to nickel hydroxide. The temperature of the solution was kept at reaction temperature in a water bath with nitrogen gas bubbling (50 cm³ min⁻¹), which was started 30 min before the reaction and lasted throughout the reaction to eliminate the effect of dissolved oxygen. Next, 1.00 mol dm⁻³ hydrazine aqueous or ethylene glycol solution of 60.0 cm³ was kept at reaction temperature with nitrogen gas bubbling $(50 \text{ cm}^3 \text{ min}^{-1})$ for 30 min. The initial pH of the hydrazine solution was adjusted to 12.0 by 10.0 mol dm⁻³ sodium hydroxide aqueous solution at 298 K before increasing the temperature. The hydrazine solution was then added to the nickel oxide or nickel hydroxide suspension as a reducing agent to deposit nickel particles. The total amount of the reaction suspension was 120.0 cm³, and thus, the reaction suspension was 0.50 mol dm^{-3} hydrazine solution with dispersed 0.50 mol dm⁻³ nickel oxide or nickel hydroxide. It should be noted that the reaction suspension includes some amount of water introduced from sodium hydroxide aqueous solution added for pH adjustment and the hydrate starting materials, such as nickel chloride hexahydrate and hydrazine monohydrate, even if ethylene glycol is used as the solvent.

Observation and analysis.— The precipitates obtained were analyzed by X-ray diffraction [(XRD), MAC Science M03XHF22], using a molybdenum X-ray tube. The morphology of the precipitates was observed by a field-emission scanning electron microscope [(SEM), JEOL JSM-6500F]. The rate of nickel deposition was estimated in situ by electrochemical quartz crystal microbalance (QCM) using round 9 MHz AT-cut quartz crystal substrates (QCM substrates), on both sides of which Au layers with a 5.0 mm diam were sputtered with an underlying Ti buffer layer. The Au-plated QCM substrate was fixed inside a dipping-type Teflon holder (Seiko EG&G QCA917-21) with a circular window so that one surface of the substrate was exposed to deposition solutions through the window while the other surface was isolated from the solutions; the

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Figure 1. (Color online) XRD patterns of precipitates obtained at (a) 298 and (b) 353 K in aqueous nickel oxide suspension by 0-2 h reaction.

electrochemically active area of the QCM substrate on one side was thus 0.196 cm². The holder with an oscillating circuit was connected to a frequency counter (Seiko EG&G QCA917) with a coaxial cable. Immersion potential of the QCM substrate was concomitantly measured during several experimental runs, and it was assumed that the immersion potential measured was almost the same as mixed potential in reaction suspension in this reaction system. A Ag/AgCl electrode (Horiba 2565A-10T) was used as a reference electrode. Internal liquid of the reference electrode was separated into two rooms by porous ceramics. The internal room involving a Ag/AgCl electrode was always filled with 3.33 mol dm⁻³ KCl aqueous solution saturated with AgCl. In the measurement of mixed potential in ethylene glycol solution, the external room neighboring the reaction suspension was filled with the 1:1 mixture (weight ratio) of ethylene glycol and 3.33 mol dm⁻³ KCl aqueous solution to minimize the effect of liquid junction potential difference caused by the difference of transference numbers of cationic species and anionic species. The external room was filled with 3.33 mol dm⁻³ KCl aqueous solution in the case of the measurement in aqueous solution. The three kinds of internal liquids (i.e., 3.33 mol dm⁻³ KCl aqueous solution, 3.33 mol dm⁻³ KCl aqueous solution saturated with AgCl, and 1:1 mixture of ethylene glycol and 3.33 mol dm⁻³ KCl aqueous solution) were replaced in each experimental run. In this work, discussion proceeds on the basis that the effect of the liquid junction potential difference is small enough to be ignored.

Results

Electroless deposition using nickel oxide suspension.— Figure 1 shows XRD patterns of precipitates obtained by the reaction for 2 h at 298 and 353 K in aqueous nickel oxide suspension of pH 12.0. The peaks derived from nickel metal are not observed, and only peaks of nickel oxide exist, suggesting that the nickel oxide starting material was not reduced to metallic nickel under these conditions. The SEM images of these precipitates shown in Fig. 2 indicate that nickel oxide is not dissolved at all because the particles are as large as the starting nickel oxide particles, $\sim 1 \mu m$ diam.

Using ethylene glycol as a solvent, electroless deposition was conducted under the same conditions as aqueous suspension. Figure 3 shows XRD patterns of precipitates obtained at 353 and 373 K. Nickel oxide peaks only are observed except in the XRD pattern



Figure 2. SEM images of precipitates obtained at (a) 298 and (b) 353 K in aqueous nickel oxide suspension by 2 h reaction.



Figure 3. (Color online) XRD patterns of precipitates obtained at (a) 353 and (b) 373 K in nickel oxide/ethylene glycol suspension by 0–2 h reaction.

corresponding to the precipitates obtained by the reaction at 373 K for 2 h. Figure 4 shows SEM images of the precipitates obtained in nickel oxide/ethylene glycol suspension by the reaction for 2 h. These precipitates consist of particles $\sim 1 \mu$ m diam and are almost the same as the starting nickel oxide particles. Black precipitates were included in the precipitates obtained by the reaction at 373 K for 2 h. Figure 5 shows an SEM image and an XRD pattern of the black precipitates separated by a magnet. Both nickel and nickel oxide peaks are observed in the XRD pattern of the black precipitates. Therefore, the agglomerated spinous particles of $\sim 1 \mu$ m diam, seen in Fig. 5a, consist of nickel and nickel oxide.

Electroless deposition using nickel hydroxide suspension.—Figure 6 shows XRD patterns of precipitates obtained by 2 h reaction at 353 K in aqueous nickel hydroxide and nickel hydroxide/ethylene glycol suspensions of pH 12.0. In both cases, the nickel chloride starting material dissolved in the solutions was hydrolyzed to nickel hydroxide before the reaction. Nickel peaks are observed in XRD patterns of the precipitates obtained by the reaction for >1 h using aqueous nickel hydroxide suspension. In contrast, strong nickel peaks are observed in XRD patterns of the precipitates of the precipitates obtained by the reaction for since by the reaction for more than 30 min using nickel hydroxide/ethylene glycol suspension. Thus, the reduction speed of nickel(II) species is higher in nickel hydroxide/ethylene glycol suspension than that in aqueous nickel hydroxide suspension. The color of the ethylene glycol suspension suddenly changed from green to intense black at the



Figure 4. SEM images of precipitates obtained at (a) 353 and (b) 373 K in nickel oxide/ethylene glycol suspension by 2 h reaction.



Figure 5. (Color online) (a) SEM image and (b) corresponding XRD pattern of black precipitates obtained at 373 K in nickel oxide/ethylene glycol suspension by 2 h reaction.



Figure 6. (Color online) XRD patterns of precipitates obtained at 353 K in (a) aqueous nickel hydroxide suspension and (b) nickel hydroxide/ethylene glycol suspension by 0-2 h reaction.

reaction time of ~13 min. In contrast, the color of the aqueous suspension gradually changed from green to greenish black in the 2 h reaction. This indicates that the reduction reaction did not entirely finish in the aqueous suspension within 2 h, but finished in the ethylene glycol suspension. Figure 7 shows SEM images of the precipitates obtained in the aqueous nickel hydroxide suspension and the nickel hydroxide/ethylene glycol suspension in the 2 h reaction. Particles ~500 nm diam were obtained from the aqueous suspension, and particles of ~300 nm diam were obtained from the ethylene glycol suspension. These particles are nickel metal, but the surface of the particles may be nickel hydroxide, because tiny and broad peaks of nickel hydroxide are also seen in the corresponding XRD patterns shown in Fig. 6.

Discussion

The overall nickel deposition reactions in this system can be expressed as follows:

Nickel oxide

$$NiO + \frac{1}{2}N_2H_4 \rightarrow Ni + \frac{1}{2}N_2 + H_2O$$
 [1]

$$NiO + 2N_2H_4 \rightarrow Ni + N_2 + 2NH_3 + H_2O$$
 [2]

Nickel hydroxide

$$Ni(OH)_2 + \frac{1}{2}N_2H_4 \rightarrow Ni + \frac{1}{2}N_2 + 2H_2O$$
 [3]

$$Ni(OH)_2 + 2N_2H_4 \rightarrow Ni + N_2 + 2NH_3 + 2H_2O$$
 [4]

In this section, these overall reactions are separated to partial reactions, and the mechanism of nickel deposition reaction is thermodynamically discussed in detail. All the data considered and used for thermodynamic calculation are listed in Table I.

Nickel oxide and nickel hydroxide are barely soluble to aqueous solution and ethylene glycol. The activity of Ni^{2+} aquo ions dissolved in aqueous nickel oxide or nickel hydroxide suspension under an equilibrium state at 298 K can be expressed as a function of pH by thermodynamic calculation using the standard chemical potential of each chemical, ¹⁷

Table I. List of standard chemical potentials and stability constants at 298 K considered and used for thermodynamic calculation.

Chemical species	Standard chemical potential (kJ mol ⁻¹)	Ref.
H ₂ O	-237.3	17
OH⁻	-157.4	17
Ni ²⁺	-48.26	17
NiO	-216.4	17
Ni(OH) ₂	-453.3	17
$Ni(OH)_2(aq)$	-406.0	20
NH ₃	-26.6	17
N ₂	0.0	17
N_2H_4	127.9	17
Nickel(II) complex	Stability constants	
formation reactions	log K	Ref.
$Ni^{2+} + N_2H_4 = [Ni(N_2H_4)]^{2+}$	2.81	18
$Ni^{2+} + 2N_2H_4 = [Ni(N_2H_4)_2]^{2+}$	5.08	18
$Ni^{2+} + 3N_2H_4 = [Ni(N_2H_4)_3]^{2+}$	6.85	18
$Ni^{2+} + 4N_2H_4 = [Ni(N_2H_4)_4]^{2+}$	9.20	18
$Ni^{2+} + 5N_2H_4 = [Ni(N_2H_4)_5]^{2+}$	10.75	18
$Ni^{2+} + 6N_2H_4 = [Ni(N_2H_4)_6]^{2+}$	11.99	18

Nickel oxide

$$\ln(a_{\rm Ni^{2+}}) = 27.9 - 4.605 \rm{pH}$$
[5]

Nickel hydroxide

$$\ln(a_{Ni^{2+}}) = 28.1 - 4.605 \text{pH}$$
 [6]

where $a_{Ni^{2+}}$ is the activity of Ni²⁺ aquo ions and the following equilibrium reactions are considered, respectively:

Nickel oxide

$$NiO + H_2O = Ni^{2+} + 2OH^{-}$$
 [7]

Nickel hydroxide

$$Ni(OH)_2 = Ni^{2+} + 2OH^{-}$$
 [8]

Equations 5 and 6 are derived by considering that both the changes in Gibbs free energy of Reactions 7 and 8 equal zero in an equilibrium state. For example, Eq. 5 can be obtained by considering the following equation and substituting ΔG by 0

(a) Aqueous suspension

(b) Ethylene glycol suspension



Figure 7. SEM images of precipitates obtained at 353 K in (a) aqueous nickel hydroxide suspension and (b) nickel hydroxide/ethylene glycol suspension by 2 h reaction. D586

$$\Delta G = \Delta G^{0} + RT \ln \left(\frac{a_{\text{Ni}^{2+}} \cdot a_{\text{OH}^{-}}^{2}}{a_{\text{NiO}} \cdot a_{\text{H}_{2}\text{O}}} \right)$$

= $(\mu_{\text{Ni}^{2+}}^{0} + 2\mu_{\text{OH}^{-}}^{0} - \mu_{\text{NiO}}^{0} - \mu_{\text{H}_{2}\text{O}}^{0})$
+ $RT \ln \left(\frac{a_{\text{Ni}^{2+}} \cdot a_{\text{OH}^{-}}^{2}}{a_{\text{NiO}} \cdot a_{\text{H}_{2}\text{O}}} \right)$ [9]

where ΔG is the change in Gibbs free energy of the reaction, *R* is the gas constant (8.314 J mol⁻¹ K⁻¹), *T* is temperature (298 K), μ^0 is the standard chemical potential of a chemical written in subscript, and *a* is the activity of a chemical written in subscript. The activities of H₂O and NiO are 1 in this case.

The activity of Ni²⁺ aquo ions drastically decreases with the increase in pH, and $a_{Ni^{2+}}$ is determined to be 1.3×10^{-12} at pH 12 by Eq. 5. The direction of reaction can be predicted using thermodynamic calculation in comparison to mixed potential measured in this system. Nickel can be deposited when the mixed potential is below the oxidation-reduction potential of Ni²⁺/Ni redox pair, i.e., $E_{\text{Ni}^{2+}/\text{Ni}} = -0.60 \text{ V}$ vs standard hydrogen electrode (SHE) at pH 12. Actually, the reaction of nickel deposition is far more complicated, but it should be noted that the oxidation-reduction potentials of any Ni(II)/Ni redox pairs are the same, -0.60 V in the presence of abundant nickel oxide or nickel hydroxide in equilibrium. For example, it is known that Ni2+ ions form complexes with hydrazine and ammonia.18 Because ammonia generated by Reactions 2 and 4 readily volatilizes at high reaction temperatures over 353 K, the ammonium complexes can be ignored and only the complexes with hydrazine are considered. The activity of one of the most predominant nickel(II) species. $[Ni(N_2H_4)_6]^{2+}$, is calculated to be 0.023 using the data in Table I. The oxidation-reduction potential of $[Ni(N_2H_4)_6]^{2+}/Ni$ redox pair is also -0.60 V at $a_{[Ni(N_2H_4)_6]^{2+}} = 0.023$. In addition, more precise nickel(II) species and revised Pourbaix diagram¹⁹ (potential-pH diagram) are reported by Beverskog and Puigdomenech,²⁰ and they mentioned an un-charged aqueous nickel(II) complex, Ni(OH)₂(aq). The oxidationreduction potential of Ni(OH)2(aq)/Ni is also calculated to be -0.60 V. Thus, an expression, Ni(II)/Ni redox pair is used here for simplicity, where Ni(II) or nickel(II) includes all the divalent nickel species present in the reaction system.

In general, the oxidation-reduction potentials of Ni²⁺/Ni redox pair and $[Ni(N_2H_4)_6]^{2+}/Ni$ redox pair are different because $[Ni(N_2H_4)_6]^{2+}$ is much more stable than Ni²⁺ aquo ion. For example, $E_{Ni^{2+}/Ni}$ is -0.25 V and $E_{[Ni(N_2H_4)_6]^{2+}}$ is -0.60 V when the activities of Ni²⁺, $[Ni(N_2H_4)_6]^{2+}$, and N₂H₄ are all one in aqueous solution at 298 K. In the system of the present work, however, the activities of Ni²⁺ and $[Ni(N_2H_4)_6]^{2+}$ are different. The activities of Ni(II) ionic species are determined by the presence of enough amount of Ni(II) ionic source (i.e., nickel oxide or nickel hydroxide), and all the Ni(II) species such as Ni²⁺, $[Ni(N_2H_4)_6]^{2+}$, and nickel oxide or hydroxide are in equilibrium. The activity of stable $[Ni(N_2H_4)_6]^{2+}$ is much larger than that of unstable Ni²⁺ aquo ion in equilibrium, and this compensates the potential difference caused by the difference in the stability of ionic species.

In ethylene glycol with some water, the oxidation-reduction potential may be different from that in water; thus, the value in water is used as a reference also in the discussion on ethylene glycol reaction system.

Figure 8 shows mixed potentials measured during the reaction in aqueous and ethylene glycol suspensions. The mixed potential measured in aqueous suspension at 298 K is always above $E_{\text{Ni}(\text{II})/\text{Ni}}$, and that at 353 K is almost always above $E_{\text{Ni}(\text{II})/\text{Ni}}$ during the reaction. Therefore, it is impossible to deposit nickel no matter how much time is spent using aqueous suspension. In contrast, the mixed potential measured in ethylene glycol suspension at 353 K is below $E_{\text{Ni}(\text{II})/\text{Ni}}$ except for the first 8 min, and it is thermodynamically pos-



Figure 8. (Color online) Changes in mixed potential measured during the reaction in aqueous nickel oxide suspension at (a) 298, (b) 353 K, and (c) in nickel oxide/ethylene glycol suspension at 353 K.

sible to deposit nickel if the oxidation-reduction potential, $E_{\rm Ni(II)/Ni}$, in ethylene glycol is the same or similar as that in water. However, nickel was not obtained as shown in Fig. 3a. This can be a kinetic problem, and nickel can be obtained by increasing the reaction rate. One easy way to increase the reaction rate is to increase the temperature. In fact, a part of the nickel oxide was successfully reduced to nickel metal particles by the 2 h reaction at 373 K as shown in Fig. 5.

Another way to increase the reaction rate is to increase the area where the reaction proceeds. For example, it can be effective to decrease the size of reactant in order to increase the interface between the reactant and the solvent. Using nickel chloride as a starting material, Ni²⁺ ions dissolved in the solutions are almost all hydrolyzed to deposit minute nickel hydroxide particles by the addition of sodium hydroxide aqueous solution. Minute nickel hydroxide particles deposited have a cross-bridged structure by weak hydrogen bonding and form a network between themselves and the solvent. As shown in Fig. 6, nickel was successfully obtained from this minute nickel hydroxide as the reactant. Figure 9 shows the time transient in mixed potential measured during the reaction at 353 K using aqueous nickel hydroxide suspension and nickel hydroxide/ ethylene glycol suspension. In ethylene glycol suspension, the mixed potential is below -0.8 V vs SHE for the first 12 min and jumps up to approximately -0.5 V at 13 min. In contrast, the mixed potential is always around -0.8 V during the reaction in aqueous solvent. Nickel can be deposited at -0.8 V, and it is impossible to deposit nickel at -0.5 V thermodynamically when $E_{\text{Ni(II)/Ni}}$ is about -0.6 V. Figure 10 shows XRD patterns of precipitates obtained before (at 8 min) and after (at 18 min) the point at which the mixed



Figure 9. (Color online) Changes in mixed potential measured during the reaction in (a) nickel hydroxide/ethylene glycol suspension and (b) aqueous nickel hydroxide suspension at 353 K.



Figure 10. (Color online) XRD patterns of precipitates obtained by the reaction for (i) 8 and (ii) 18 min in nickel hydroxide/ethylene glycol suspension at 353 K.

potential suddenly increased, i.e., 13 min. Before this point, the peaks of nickel are not observed, but strong peaks of nickel are observed after the point.

This change of the mixed potential can be explained by taking into account that mixed potential is defined as a potential where the total current of anodic reactions counterbalances the total current of cathodic reactions. In this system, anodic reactions are mainly the oxidation reactions of hydrazine as follows

$$N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e$$
 [10]

$$N_2H_4 + OH^- \rightarrow \frac{1}{2}N_2 + NH_3 + H_2O + e$$
 [11]

The oxidation-reduction potentials of N_2/N_2H_4 and N_2 -NH₃/N₂H₄ redox pairs in aqueous solution at 298 K can be calculated as a function of pH using the standard chemical potential of each chemical¹⁷

$$E_{\rm N_2/N_2H_4}$$
 (/V vs SHE) = - 0.327 - 0.0591pH [12]

$$E_{\text{Na-NH}_2/\text{Na}_4}$$
 (/V vs SHE) = - 1.584 - 0.0591pH [13]

At pH 12, E_{N_2/N_2H_4} and $E_{N_2-NH_3/N_2H_4}$ are -1.04 and -2.29 V, respectively. Meanwhile, cathodic reactions can be mainly the reaction of nickel deposition and hydrogen generation reaction as follows

$$Ni(II) + 2e \rightarrow Ni$$
 [14]

$$2\mathrm{H}_{2}\mathrm{O} + 2\mathrm{e} \rightarrow \mathrm{H}_{2} + 2\mathrm{OH}^{-}$$
 [15]

As illustrated in Fig. 11, the reaction of nickel deposition is prefer-



Figure 11. (Color online) Schematic diagram of mixed potential measured in this system.



Figure 12. Mass change of QCM substrate during the reaction in (a) nickel hydroxide/ethylene glycol suspension and (b) aqueous nickel hydroxide suspension at 353 K.

ential to the hydrogen generation reaction in the early stage of the reaction; thus, the mixed potential is defined by the oxidation reactions of hydrazine and the reaction of nickel deposition. After most of the nickel(II) species have been consumed, the hydrogen generation reaction becomes mainly a cathodic reaction and the mixed potential is defined by the oxidation reactions of hydrazine and the hydrogen generation reaction. In our preliminary experiment, nickel hydroxide was not completely reduced to nickel by the reaction in ethylene glycol solvent at 353 K when 1 mol dm⁻³ sodium hydroxide aqueous solution was used to adjust pH instead of 10 mol dm⁻² sodium hydroxide aqueous solution. Figure 12 shows the mass change of QCM substrate during the reaction in aqueous nickel hydroxide suspension and nickel hydroxide/ethylene glycol suspension at 353 K. Although the mass simply increases in both cases, the increase in mass stops after 13 min using the nickel hydroxide/ ethylene glycol suspension. The increase in mass is due to nickel deposition, and this also confirms that the main cathodic reaction was switched from the nickel deposition reaction to the hydrogen generation reaction at 13 min in ethylene glycol suspension although the main cathodic reaction was still the reaction of nickel deposition in aqueous suspension.

It is highly possible that the difference in the mixed potentials, as seen in Fig. 8 and 9, is also attributed to the difference in the balance of each partial reaction (e.g., nickel deposition reaction, hydrogen generation reaction, and the oxidation reaction of hydrazine). When the balance is changed by the kind of nickel precursor, mixed potential can vary even if the precursor has almost the same chemical potential and there is little difference in Gibbs free energy change of the total reaction. Considering the present system, the standard chemical potentials of nickel oxide and nickel hydroxide are almost the same, but the reaction path and activation energy of nickel deposition might be different. This difference can change the balance of the cathodic partial currents of nickel deposition and that of hydrogen generation in the total cathodic current, resulting in the difference in mixed potential. It is interesting that mixed potential is determined kinetically although the value of mixed potential itself can be treated as a thermodynamic parameter. Thermodynamic consideration performed in this work can also be applied to other reaction systems to predict whether or not metal nanoparticles will be deposited by electroless deposition.

Conclusion

We have investigated the electrochemical formation process of nickel nanoparticles by electroless deposition in aqueous and ethylene glycol suspensions. Through the present work, we have obtained the following results.

Nickel particles approximately 300 nm diam were obtained by the reaction using hydrazine as a reducing agent in nickel hydroxide/ ethylene glycol suspension at 353 K without any dispersing agent. The reaction rate using nickel hydroxide was much faster than that using nickel oxide as a starting material. In situ monitoring of mixed potential in combination with thermodynamic calculation revealed the reaction possibility. Mixed potential drastically increased approximately from -0.8 to -0.5 V vs SHE on reaching the end point of the nickel deposition reaction using nickel hydroxide/ethylene glycol suspension at 353 K because the cathodic reaction that determined the mixed potential switched from the nickel deposition reaction to the hydrogen generation reaction. Thus, real-time monitoring of mixed potential can be used to find the end point of the reaction. Mass change measurement on QCM substrate during the reaction also supported this result.

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