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Preparation of basic nickel carbonate particles in solution system of Ni(Ⅱ)-NH_3-CO_3^{2-}-H_2O ①

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Abstract: Based on the principles of simultaneous equilibrium and mass balance, a series of thermodynamic equilibrium equations of Ni(Ⅱ)-NH_3-CO_3^{2-}-H_2O system at ambient temperature were deduced theoretically and the thermodynamic diagrams of lg[Ni]$_T$ versus pH at different solution compositions were drawn, which was quite effective to explain the formation mechanism of precipitation particles with different microscopic shapes. When pH of the solution is below 7.0, free nickel ions are dominant and when the precipitant is added, the fast coagulation will take place leading to the loose flocculation particles. While pH is above 7.0, because of the coordination of nickel ion with ammonia, the precipitation proceeds slowly accompanying with the release of Ni^{2+} from the multi-coordinated $Ni(NH_3)_n^{2+}$ ($n = 1, 2, \cdots, 6$), which easily leads to the formation of the dense spherical particles.

Key words: thermodynamic equilibrium; nickel ammonia complex; basic nickel carbonate; precipitation

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1 INTRODUCTION

Submicron metallic nickel and nickel oxide powders, as the very important functional materials, are in large demand, for multilayer ceramic capacitor and batteries as electrode materials[1-10]. In these applications, the characteristics, such as chemical composition, shape, mean particle size and size distribution, are most essential to influence the qualities of the final products. Therefore, it is very important to control the powder properties during the preparation process.

Precipitation followed by drying and calcination in the air or H_2 is the typical way to prepare the submicron metallic and oxide powders. Generally, the solution of ammonia carbonate is used as the precipitant in the practical plants because of its low cost and high purity. So it will be quite useful for the control of the precipitation process if the system of Ni(Ⅱ)-NH_3-CO_3^{2-}-H_2O is understood in detail. In the present paper, we did some study on this system from the point of view of the solution thermodynamics and then applied it to the preparation of fine basic nickel carbonate particles.

2 THERMODYNAMIC ANALYSIS OF Ni(Ⅱ)-NH_3-CO_3^{2-}-H_2O SYSTEM

In the system of Ni(Ⅱ)-NH_3-CO_3^{2-}-H_2O, the main chemical reactions involve the coordination of Ni^{2+} with ammonia, hydrolysis of Ni^{2+} in water, reaction of Ni^{2+} with CO_3^{2-}, and decomposition of weak acids and alkaline. The relevant reactions are listed in Table 1. Considering that for a certain precipitation process in the solution, the variables such as temperature, pressure are usually kept

Table 1 Equilibrium equations and constants of Ni(Ⅱ)-NH_3-CO_3^{2-}-H_2O system(T = 298 K)

No.	Equation	lg$K$(β)	Ref.
1	$Ni^{2+} + NH_3 = Ni(NH_3)^{2+}$	2.81	[11]
2	$Ni^{2+} + 2NH_3 = Ni(NH_3)_2^{2+}$	5.08	[11]
3	$Ni^{2+} + 3NH_3 = Ni(NH_3)_3^{2+}$	6.85	[11]
4	$Ni^{2+} + 4NH_3 = Ni(NH_3)_4^{2+}$	8.12	[11]
5	$Ni^{2+} + 5NH_3 = Ni(NH_3)_5^{2+}$	8.93	[11]
6	$Ni^{2+} + 6NH_3 = Ni(NH_3)_6^{2+}$	9.08	[11]
7	$Ni^{2+} + CO_3^{2-} = NiCO_3(s)$	8.18	[12]
8	$Ni^{2+} + 2OH^- = Ni(OH)_2(s)$	14.7	[12]
9	$Ni^{2+} + H_2O = NiOH^+ + H^+$	4.97	[12]
10	$Ni^{2+} + 2OH^- = Ni(OH)_2^0$	8.55	[12]
11	$Ni^{2+} + 3OH^- = Ni(OH)_3^-$	11.33	[12]
12	$H_2O = H^+ + OH^-$	-14	[12]
13	$HCO_3^- = H^+ + CO_3^{2-}$	-10.30	[12]
14	$H_2CO_3 = H^+ + HCO_3^-$	-6.35	[12]
15	$NH_3 + H^+ = NH_4^+$	9.27	[12]
16	$NH_3 + HCO_3^- = H_2NCOO^- + H_2O$	0.48	[13]

For the equations of No. 1 - 6, No. 9 - 11 equilibrium constant is β, and for the rest equations it is K

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constant, so in the present study the diagrams of lg $[Ni]_T$ versus pH at different solution compositions were drawn for further discussion.

2.1 Analysis of equilibrium reactions and calculation of relevant variables

For the reaction of Ni^{2+} with CO_3^{2-}, it can be expressed as

$$Ni^{2+} + CO_3^{2-} = NiCO_3(s)$$

In this equation, the equilibrium constant is $K_{sp(NiCO_3(s))}$:

$$K_{sp(NiCO_3(s))} = [Ni^{2+}][CO_3^{2-}] \tag{1}$$

and CO_3^{2-} exists in the form of free CO_3^{2-}, HCO_3^-, H_2CO_3 and H_2NCOO^-, thus

$$[CO_3^{2-}]_T = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3] + [H_2NCOO^-] \tag{2}$$

$[CO_3^{2-}]_T$ is the total concentration of CO_3^{2-} in the solution.

Incorporating the constants of Equation 13 and 14 into Eqn. (2), then

$$[CO_3^{2-}] = [CO_3^{2-}]_T/(1 + 10^{10.30-pH} + 10^{16.65-pH}) \tag{3}$$

Combining Eqn. (3) with Eqn. (1), then

$$[Ni^{2+}] = K_{sp(NiCO_3(s))}/[CO_3^{2-}] = K_{sp}/\{[C]_T/(1 + 10^{10.30-pH} + 10^{16.65-pH})\} \tag{4}$$

For the hydrolysis of Ni^{2+},

$$Ni^{2+} + 2OH^- = Ni(OH)_2(s)$$

$$H_2O = H^+ + OH^-$$

$$K_w = [H^+][OH^-] = 10^{-14} \tag{5}$$

$$K_{sp(Ni(OH)_2(s))} = [Ni^{2+}][OH^-]^2 \tag{6}$$

Incorporating Eqn. (5) into Eqn. (6), then

$$[Ni^{2+}] = K_{sp(Ni(OH)_2(s))}/[OH^-]^2 = K_{sp(Ni(OH)_2(s))} \times 10^{28-2pH} \tag{7}$$

So the practical concentration of free Ni^{2+} in the solution $[Ni^{2+}]$ is deduced as follows:

$$[Ni^{2+}] = \min\{[Ni^{2+}] = K_{sp(NiCO_3(s))}/[CO_3^{2-}],\ K_{sp(Ni(OH)_2(s))} \times 10^{28-2pH}\} \tag{8}$$

Considering the coordination of Ni^{2+} with ammonia, that is:

$$Ni^{2+} + iNH_3 = Ni(NH_3)_i^{2+} \quad (i = 1, 2, \cdots, 6)$$

$$\beta_i = \frac{[Ni(NH_3)_i^{2+}]}{[Ni^{2+}][NH_3]^i} \tag{9}$$

For the coordination of Ni^{2+} with OH^-,

$$Ni^{2+} + jOH^- = Ni(OH)_j^{(2-j)} \quad (j = 1, 2, 3) \tag{10}$$

For the equilibrium reaction between NH_3 and NH_4^+,

$$NH_3 + H^+ = NH_4^+$$

$$K_1 = \frac{[NH_4^+]}{[NH_3][H^+]} \tag{11}$$

For the decomposition of carbonate acid,

$$H_2CO_3 = H^+ + HCO_3^-$$

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \tag{12}$$

For the decomposition of HCO_3^-,

$$HCO_3^- = H^+ + CO_3^{2-}$$

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \tag{13}$$

For the equilibrium reaction,

$$NH_3 + HCO_3^- = H_2NCOO^- + H_2O$$

$$K_2 = \frac{[H_2HCOO^-][H_2O]}{[NH_3][HCO_3^-]} \tag{14}$$

2.2 Mathematical model of lg$[Ni]_T$ versus pH

Based on the principles of simultaneous equilibrium and mass balance[14], the mathematic models of lg $[Ni]_T$ versus pH at different solution compositions were deduced. Making $[Ni]$, $[Ni]_T$, $[N]_T$ and $[C]_T$ stand for the concentration free of Ni^{2+}, the total concentration of various nickel species in solution, the concentration of ammonia, and the concentration of CO_3^{2-}.

Total concentration of the coordination compounds of Ni^{2+} with ammonia is

$$[NiNH_3]_T = \sum_{i=1}^{6}[Ni(NH_3)_i^{2+}]$$

Total concentration of the coordination compounds of Ni^{2+} with OH^- is:

$$[NiOH]_T = \sum_{j=1}^{3}[Ni(OH)_j^{(2-j)}]$$

So the total concentration of Ni^{2+} in the solution is

$$\begin{aligned}[Ni]_T &= [Ni] + [NiNH_3]_T + [NiOH]_T \\ &= [Ni] + [Ni][NH_3]\sum_{i=1}^{6}\beta_i[Ni(NH_3)_i]^{i+1} + [Ni][OH]\sum_{j=1}^{3}\beta'_j[NiOH]^{j-1} \\ &= [Ni](1 + 10^{2.81}[NH_3] + 10^{5.08}[NH_3]^2 + 10^{6.85}[NH_3]^3 + 10^{8.12}[NH_3]^4 + 10^{8.93}[NH_3]^5 + 10^{9.08}[NH_3]^6 + 10^{pH-9.03} + 10^{2pH-19.45} + 10^{3pH-30.67})\end{aligned} \tag{15}$$

And the total concentration of ammonia in the solution is

$$\begin{aligned}[NH_3]_T &= [NH_3] + [NH_4^+] + [H_2NCOO^-] + \sum^{i}\beta_i[NH_3]^i \\ &= [NH_3]\ (1 + 10^{9.27-pH} + 10^{10.78-pH}[CO_3^{2-}] + 10^{2.81}[Ni] + 2\times10^{5.08}[Ni][NH_3] + 3\times10^{6.85}[Ni][NH_3]^2 + 4\times10^{8.12}[Ni][NH_3]^3 + 5\times10^{8.93}[Ni][NH_3]^4 + 6\times10^{9.08}[Ni][NH_3]^5)\end{aligned} \tag{16}$$

For a given value of [C]$_T$ and [N]$_T$, at a certain pH, [CO_3^{2-}] can be calculated from Eqn. (3), and from Eqns. (4) − (8), [Ni] can be deduced. Incorporating the above obtained values into the Eqn. (16), [NH_3] can be determined by Newton iteration[15], and then from Eqn. (15), a series of quantitative values of lg[Ni]$_T$ versus pH can be calculated and thereby the thermodynamic diagrams can be drawn.

2.3 lg[Ni]$_T$ − pH curves

A series of curves of lg[Ni]$_T$ versus pH at different solution compositions were drawn and shown in Figs. 1 − 6. From the figures, the main results were generalized as follows.

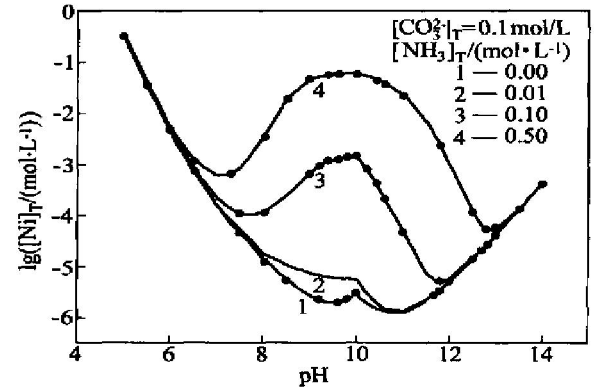

Fig. 1 lg[Ni]$_T$ − pH curves for Ni(II)-NH_3-CO_3^{2-}-H_2O system at low total concentration of ammonia (T = 298 K)

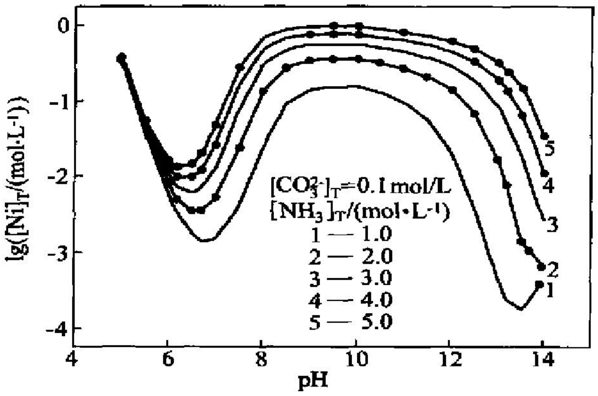

Fig. 2 lg[Ni]$_T$ − pH curves for Ni(II)-NH_3-CO_3^{2-}-H_2O system at high total concentration of ammonia (T = 298 K)

1) Figs. 1 and 2 show the lg[Ni]$_T$ − pH curves for Ni(II)-NH_3-CO_3^{2-}-H_2O system (T = 298 K) at different [NH_3]$_T$. Because the shapes of the curves for the low or high concentration of total ammonia are some different, the two groups of curves were drawn in the separated figures. From these two figures, it is easy to find that the curves are made up of two parabolas, that is, the total concentration of nickel ion in the solution goes down with pH to a minimum point, and then goes up to a maximum point, then down and up once again.

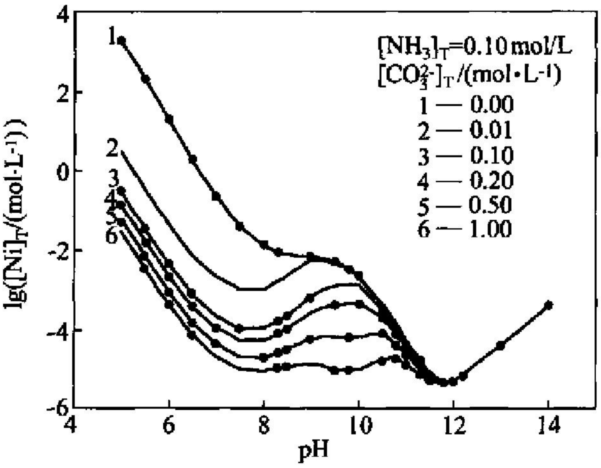

Fig. 3 lg[Ni]$_T$ − pH curves for Ni(II)-NH_3-CO_3^{2-}-H_2O system at different [CO_3^{2-}]$_T$ with [NH_3]$_T$ = 0.10 mol/L (T = 298 K)

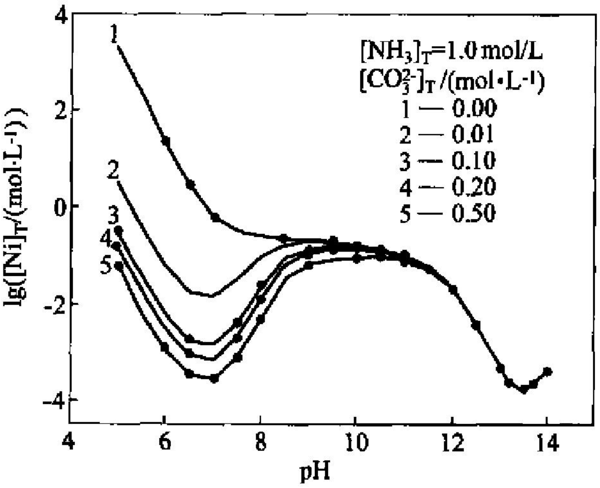

Fig. 4 lg[Ni]$_T$ − pH curves for Ni(II)-NH_3-CO_3^{2-}-H_2O system at different [CO_3^{2-}]$_T$ with [NH_3]$_T$ = 1.0 mol/L (T = 298 K)

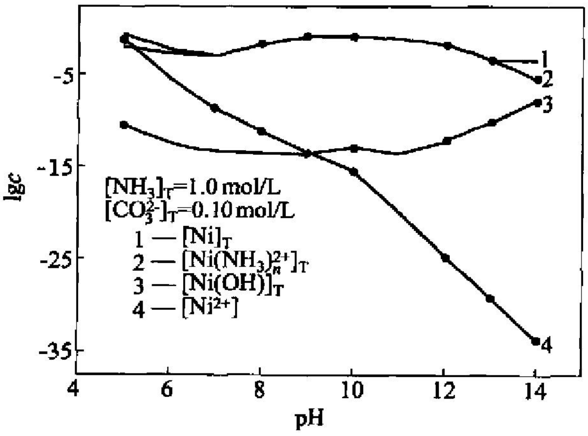

Fig. 5 lg$c$ − pH curves for each nickel species in Ni(II)-NH_3-CO_3^{2-}-H_2O system (T = 298 K)

2) When [C]$_T$ = 0.1 mol/L and [N]$_T$ = 1.0 mol/L, the obtained curve of lg[Ni]$_T$ − pH shown in Fig. 2 is taken for example for further discussion.

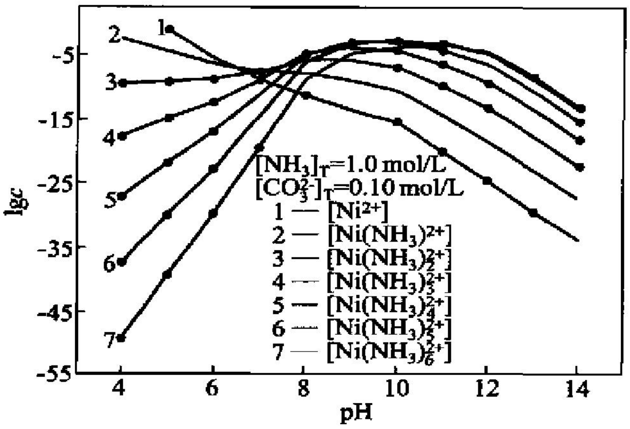

Fig. 6 lg$c$ —pH curves for each nickel ammonia species in Ni(Ⅱ)-NH_3-CO_3^{2-}-H_2O system(T = 298 K)

When pH < 7.0, $[NH_3]$ is low and nickel species exist in the form of free Ni^{2+} dominantly, so with increase of pH, free Ni^{2+} decreases as the precipitation occurs, which leads to the decrease of total concentration of nickel ion in the solution. When 7.0 < pH < 10.0, more free ammonia exists in the solution, and more nickel ammonia compounds are formed, so the total concentration of Ni^{2+} goes up with pH increasing. When 10.0 < pH < 13.5, for the strong destruction ability of alkaline, with pH going up, the nickel ammonia compounds would decompose gradually to precipitate in the form of $Ni(OH)_2$ and basic nickel carbonate, leading to decrease of the total concentration of nickel ion in the solution. When pH > 13.5, the coordination of OH^- with Ni^{2+} is strengthened, so some precipitated solid will redissolve, which increases the concentration of total nickel ion in the solution.

3) Figs. 1 and 2 also show that with increase of total concentration of ammonia in the solution, the pH range for the stable nickel species in the solution becomes broader. It implies that if by decreasing pH or heating the solution, the nickel ammonia compounds would decompose gradually to release the nickel ion, which can be used to control the precipitation process.

4) Figs. 3 and 4 show the lg$[Ni]_T$ —pH curves for Ni(Ⅱ)-NH_3-CO_3^{2-}-H_2O system(T = 298 K) at different $[CO_3^{2-}]$ and $[NH_3]_T$. Two figures show that when total concentration of CO_3^{2-} increases, more nickel ions precipitate as the solid particles and $[Ni]_T$ in the solution will not increase until it reaches at the high pH range at least 12. In Fig. 4, at pH = 7.0, the curve of lg$[Ni]_T$ —pH reaches a minimum value, which means the precipitation near this pH is anticipated for the production. So if increasing pH of the solution toward 7.0 by feeding the alkaline reagent, the precipitation process by this way is named direct precipitation; while decreasing pH of the solution toward 7.0 from the higher pH by feeding the acid reagent or by heating the solution to deconstruct of the nickel ammonia compounds, this way is named coordinated precipitation process. For the easier controllability for the latter precipitation process, it is often used to prepare some fine powders with excellent properties.

5) Figs. 5 and 6 show the lg$c$ —pH curves for each nickel species and nickel ammonia species respectively in Ni(Ⅱ)-NH_3-CO_3^{2-}-H_2O system(T = 298 K) with $[C]_T$ = 0.1 mol/L and $[N]_T$ = 1.0 mol/L. Fig. 5 shows that when pH < 5.4, the free Ni^{2+} is the dominant species in the solution, while pH > 5.4, nickel ammonia compounds are the main existing form of nickel species. Fig. 6 shows further that when pH < 7.0, $[Ni(NH_3)_n^{2+}]$(n = 1) dominates, and when 7.0 < pH < 10.0, $[Ni(NH_3)_n^{2+}]$(n = 2－6) is the main nickel species.

3 EXPERIMENTAL

In this study, several groups of experiments were conducted to compare the two precipitation processes, i. e., direct and coordination precipitation, whose definition has been mentioned above.

$NiCl_2$, $Ni(NO_3)_2$, $(NH_4)_2CO_3$, $NH_3 \cdot H_2O$, NaOH and other chemical reagents used were analytically pure, and all the solutions were prepared using distilled water and filtered to remove the insoluble impurity before experiments.

Direct precipitation: 50 mL 0.8 mol/L $NiCl_2$ solution was adjusted to make its initial pH equal to 4.5, and then 50 mL 1.0 mol/L $(NH_4)_2CO_3$ solution was fed into it rapidly. Then the suspension was filtered, washed and dried at 50 ℃ for 5 h.

Coordination precipitation: 50 mL 1.0 mol/L nickel ammonia solution prepared by mixing $NiCl_2$ and $NH_3 \cdot H_2O$ solutions was mixed with 50 mL 1.2 mol/L Na_2CO_3 solution, with its initial pH being adjusted to 8.8, and then the obtained solution was heated to its boiling point. The suspension was filtered, washed and dried at 50 ℃ for 5 h.

The solid powders were inspected by scanning electron microscopy (SEM) (JEOL － 5600LV, Japan). The composition and structure were evaluated by X-ray diffraction(3014Z, Japan), and thermogravimetric analysis(TGA) by Dupout-9900 instruments(air, 100 mL/min, 10 ℃/min).

4 RESULTS AND DISCUSSION

Fig. 7 shows that the powder prepared by direct precipitation is loose in bulk , and when

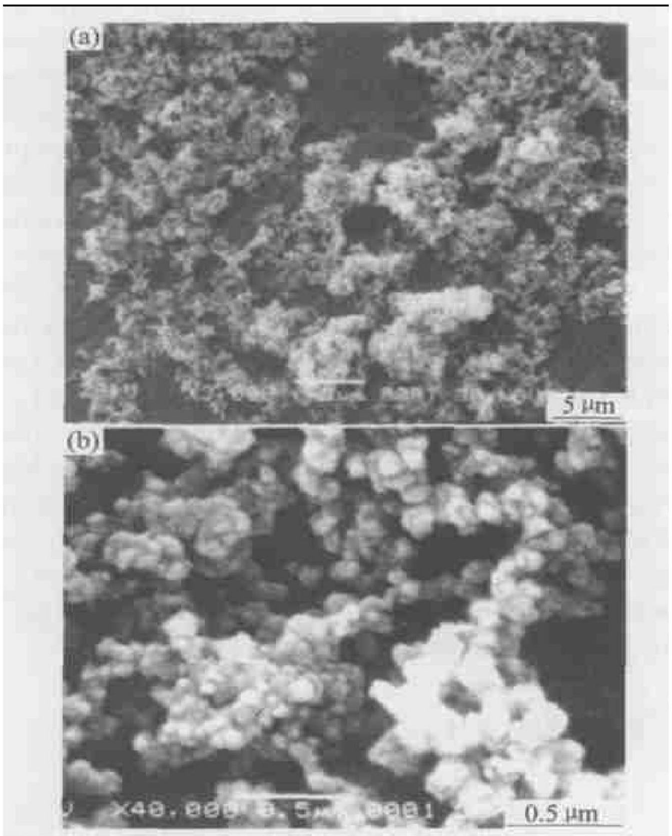

Fig. 7 SEM images of powders prepared by direct precipitation

inspected in high-resolution SEM, the powder actually consists of a number of nanosized particles which aggregate into larger ones. While for the powder prepared by coordination precipitation it is dense particles as shown in Fig. 8, which has quite different morphology from that of the direct precipitation. In order to know more details about these two powders, X-ray diffraction, thermal and chemical analyses were conducted on the samples.

Figs. 9(a) and (b) show the X-ray diffraction patterns for the powders prepared by direct and coordination precipitation processes, respectively. It shows that the crystal particles prepared by coordination precipitation grows better than that from the direct one because the diffraction peaks of the former sample are much more sharper.

Figs. 10(a) and (b) show the TGA curves of the two kinds of powders. Considering that in the preparation, these powders were washed and dried, so the impurities such as ammonia, anions and cations have almost been removed, and the mass loss below 100 ℃ could be ascribed to mass loss of the adsorption water. By measuring and calculating, the mass loss from the temperature range of 100－500 ℃ were 26.0% and 30.3% respectively for two powders, which are quite consistent with the mass loss for $NiCO_3\cdot 2Ni(OH)_2$ (26.3%) and $NiCO_3\cdot Ni(OH)_2$ (29.3%) decomposing into NiO at the same pyrolysis temperature range respectively. So the corresponding chemical composition of the powders obtained by direct and coordination precipitation can be confirmed as $NiCO_3\cdot 2Ni(OH)_2$ and $NiCO_3\cdot Ni(OH)_2$ respectively.

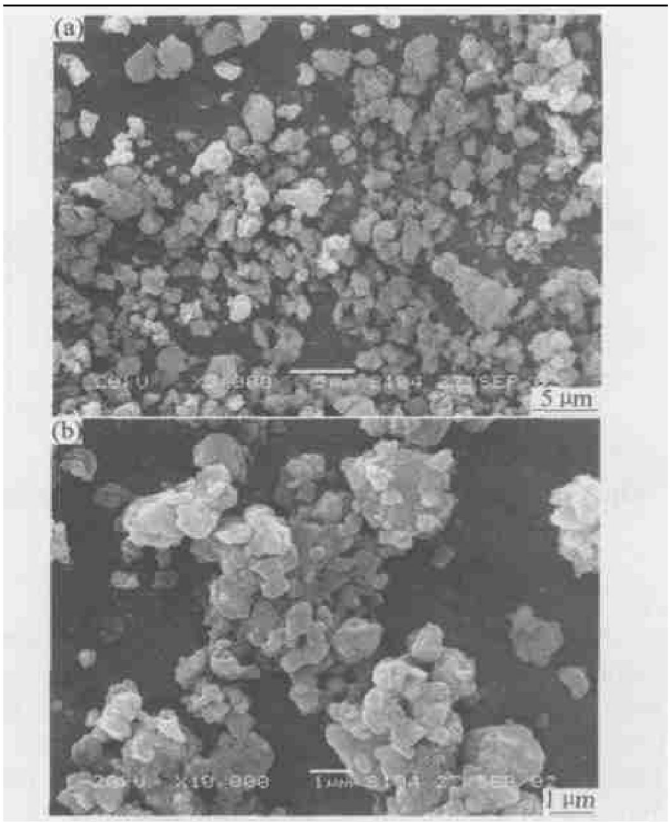

Fig. 8 SEM images of powders prepared by coordination precipitation

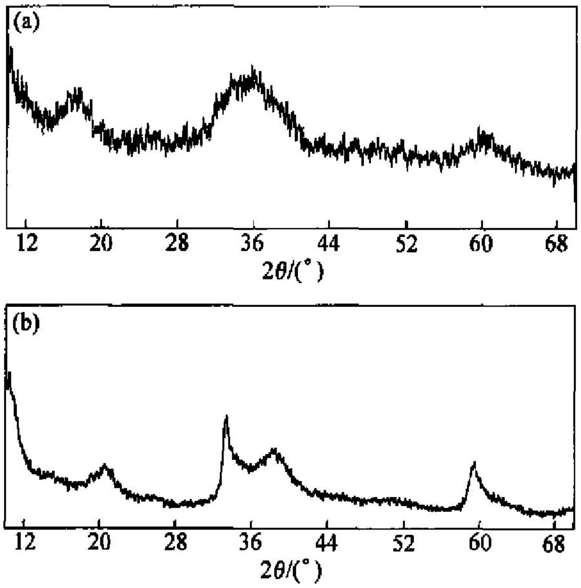

Fig. 9 X-ray diffraction patterns for solid powders prepared by direct precipitation(a) and coordination precipitation(b)

Obviously, the different precipitation processes lead to the differences in morphology, structure and chemical composition. In direct precipitation, initial pH of the solution was below 7.0, and according to the thermodynamic equilibrium analyses for $Ni(II)-NH_3-CO_3^{2-}-H_2O$ system, it is easy to know that nickel species exist dominantly in the form of nickel ions

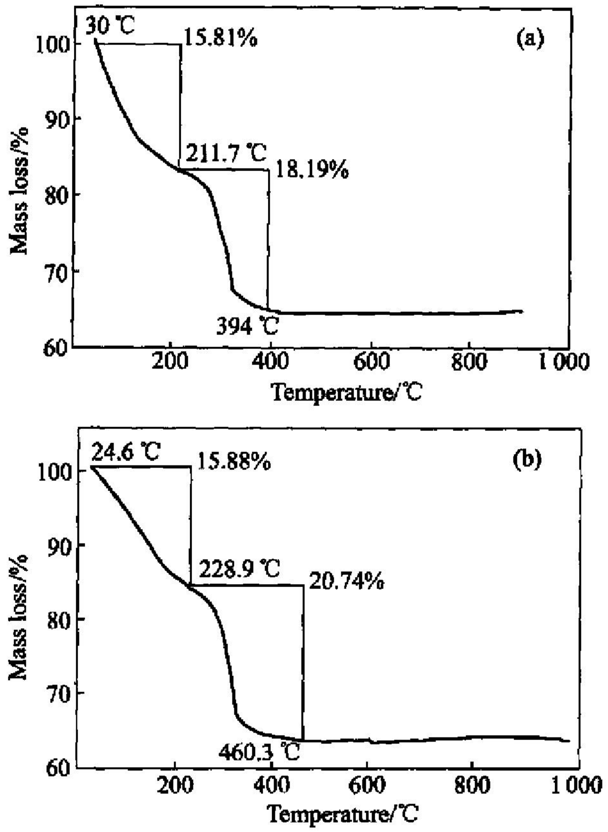

Fig. 10 TGA curves for solid powders prepared by direct precipitation(a) and coordination precipitation(b)

in the solution. When the precipitant of $(NH_4)_2CO_3$ was fed in, pH of the solution increases leading to the burst nucleation, and a large number of nuclei collide each other at random. Fast coagulation is the dominant growth pattern under this condition, and thereby loose flocculation powder is produced. So the prepared powder is often amorphous.

Thermodynamic equilibrium analyses for Ni(Ⅱ)-NH_3-CO_3^{2-}-H_2O system shows that while pH is above 7.0, because of the coordination of nickel ion with ammonia, nickel ammonia compounds are the dominant nickel species in the solution. When heating the mixed solution, ammonia can volatilize from the solution and so Ni^{2+} releases from the multi-coordinated $Ni(NH_3)_n^{2+}$ ($n = 1, 2, \cdots, 6$), which makes the mixed solution turn to unstable state gradually. Thus the concentration of Ni^{2+} increases with the heating time prolonging, and reaches at the supersaturation point, so nucleation occurs. Under this condition, these nuclei can grow by diffusion of solutes, which easily leads to the formation of the dense spherical particles with better crystalline structure.

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