PREPARATION OF ULTRAFINE NICKEL POWDER①

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ABSTRACT   A novel technology for preparing ultrafine nickel powder has been studied. Ultrafine Ni powder of average 0.058 μm in size was precipitated through chemical reduction by hydrazine hydrate from aqueous mixture containing nickel sulphate, ammonium tartrate and sodium hydroxide in the presence of an agitator. The purity of Ni powder reached 99.5%. Furthermore, the primary factors affecting the particle size of Ni powder were investigated.

Key words   ultrafine nickel powder   nickel sulphate   hydrazine

1   INTRODUCTION

Nickel powders have important industrial applications. They are commonly used in alkaline batteries, as catalysts and pigments in anti-corrosion paints. In addition, they have found recently several other applications which depend on their magnetic properties[1]. There are many methods of preparing Ni powder commercially, e.g., laser evaporation[2], atomization[3], electrodeposition[4], hydrogen reduction[5], carbonyl process[6] and so on; different method is adopted according to different performance requirement.

At present, it is urgent that novel functional material needs ultrafine Ni powder. Therefore, the present study was carried out in attempt to prepare ultrafine Ni powder directly by chemical reduction precipitation under milder conditions and simple equipment.

2   PRINCIPLE ANALYSIS

The method that Ni powder is prepared by chemical reduction precipitation is mainly based on E-pH diagram of Ni-H_2O system, as seen in Fig. 1.

From Fig. 1, at 25 ℃, the reduction potential of Ni^{2+}/Ni is $-0.221V$; when pH value is equal to 4.2, Ni powder can be reduced by H_2. But under normal pressure, the reaction is difficult to be carried out, because of kinetic factors during gas-liquid reaction. And the solid reducing agent with more negative potential is easy to pollute Ni powder. So, strong basic hydrazine hydrate was elected as reducing agent. The pH is about 6.2 when $Ni(OH)_2$ forms, and the higher the temperature, the lower the pH forming $Ni(OH)_2$ precipitation. Thus, a complexing agent must be added in the solution in order to depress precipitation of $Ni(OH)_2$ and decrease growth rate of Ni particle. Based on complexing

Fig. 1 E-pH diagram of Ni-H_2O system
(solid line: 25 ℃; dashed line: 100 ℃)

coefficiency of some complexing agents and the experimental results, ammonium tartrate is regarded as a more proper complexing agent.

3 EXPERIMENTAL METHOD

3. 1 *Raw Material*

Nickel sulphate, ammonium tartrate, sodium hydroxide and hydrazine were chemically pure. TN was used as dispersing agent.

3. 2 *Experimental*

In a container with $NiSO_4$, ammonium tartrate was added as complexing agent, several drops of TN as dispersing agent and NaOH was used to adjust pH value. At 80 ℃, hydrazine was added into the solution slowly and the mixture was stirred for some time. After the reaction finished, the products were filtered, dried and sieved. Finally, average particle size and purity of Ni powder were analyzed.

4 RESULTS AND DISCUSSION

4. 1 *Single Factor Experiment*

The factors affecting particle size of Ni powder were investigated, such as total concentration of Ni^{2+}, concentration of NaOH, concentration of hydrazine (volume ratio) and temperature, etc. The experimental results are shown in Figs. 2~ 5, respectively.

Figs. 2~ 5 show that the average particle size of Ni powder ($\bar{d}$) increases with [Ni^{2+}] and [$N_2H_4 \cdot H_2O$], and finer Ni powder can be obtained when increasing [NaOH]. The effect of temperature on the size of Ni powder is less, but the elevating temperature is favorable to accelerate the reaction.

4. 2 *Orthogonal Experiment*

On the basis of the single experimental results, the three factors-three levels orthogonal experimental method (L_9 (3^4)) was adopted. Primary factors affecting the reduction were investigated, e. g. [Ni^{2+}], [NaOH] and [$N_2H_4 \cdot H_2O$]. The experimental conditions and results are listed in Table 1.

Table 1 shows that when the reaction conditions are controlled properly, [Ni^{2+}] is 29. 35 g/ L, [$N_2H_4 \cdot H_2O$] is 1: 1, [NaOH] is 60 g/ L, and ultrafine Ni powder with an average particle size of 0. 058 μm can be prepared.

The average particle size of the reaction products has direct relation to the reaction rate. The faster the reaction is, the more Ni crystal nuclei forms, the finer the Ni particle size is. So the average effect of each factor and each level on

Fig. 2 Effect of [Ni^{2+}] on the particle size of Ni powder
(θ = 80 ℃, t = 1 h, [NaOH] = 20 g/ L; volume ratio of $N_2H_4 \cdot H_2O$= 1: 2, 360 r/ min)

Fig. 3 Effect of [NaOH] on the particle size of Ni powder
([Ni^{2+}] = 58. 70 g/ L, volume ratio of $N_2H_4 \cdot H_2O$= 1: 2, [NaOH] = 40 g/ L, t = 1 h, θ = 80 ℃, 360 r/ min)

Table 1　The experimental conditions and results

Sample No.	$[Ni^{2+}]/g \cdot L^{-1}$ (factor A)	$[N_2H_4 \cdot H_2O]$ (volume ratio) (factor B)	$[NaOH]/g \cdot L^{-1}$ (factor C)	Average diameter/μm	Reducing efficiency/%
1	29. 35	1: 3	20	1. 23	99. 98
2	29. 35	1: 2	40	1. 28	99. 97
3	29. 35	1: 1	60	0. 058	99. 99
4	58. 70	1: 3	40	0. 53	99. 96
5	58. 70	1: 2	60	0. 38	99. 98
6	58. 70	1: 1	20	1. 47	99. 99
7	88. 05	1: 3	60	1. 32	99. 97
8	88. 05	1: 2	20	2. 04	99. 96
9	88. 05	1: 1	40	1. 88	99. 95

Note: $\theta = 80$ ℃; $t = 1$ h; 360 r/ min.

Fig. 4　Effect of $[N_2H_4 \cdot H_2O]$ (volume ratio) on the particle size of Ni powder

($[Ni^{2+}] = 58. 70$ g/ L, $[NaOH] = 60$ g/ L, $\theta = 80$ ℃, $t = 1$ h, 360 r/ min)

the reduction was investigated according to the average particle size of Ni powder(Table 2).

It can be drawn from the above analyses that average particle size of Ni powder is affected first by the concentration of $[NaOH]$; second by $[Ni^{2+}]$; and then by $[N_2H_4 \cdot H_2O]$.

4. 3　Chemical Component of Ni Powder

Ni powder was analyzed, the results are listed in Table 3.

From Table 3, it can be seen that the purity of Ni powder is larger than that of industrial products.

Fig. 5　Effect of temperature on the particle size of Ni powder

($[Ni^{2+}] = 58. 70$ g/ L, volume ratio of $N_2H_4 \cdot H_2O = 1: 2$, $[NaOH] = 40$ g/ L, $t = 1$ h, 360 r/ min)

Table 2　The average effect of each factor and each level on the reduction

		Factor A	Factor B	Factor C
Average effect	$\Sigma 1/ 3$	0. 86	1. 03	1. 58
of each factor	$\Sigma 2/ 3$	0. 79	1. 23	1. 23
and each level	$\Sigma 3/ 3$	1. 74	1. 14	0. 59
Maximum difference between levels		0. 95	0. 20	0. 99
Influence order		$C > A > B$		

Table 3　Chemical component of Ni powder(%)

Ni, ≮	Impurity elements, ≯				
	Co	Zn	Al	Si	
99. 5	0. 3	0. 069	0. 021	0. 0068	
	Fe	Pb	Sb	Bi	Cd
	0. 041	0. 00063	0. 001	0. 0001	0. 0003
	Mn	Mg	As	Sn	Cu
	0. 0064	0. 004	0. 011	0. 0005	0. 0079

5　CONCLUSIONS

(1) With ammonium tartrate being complexing agent and NaOH adjusting pH value, the $NiSO_4$-bearing solution was reduced by hydrazine directly. Under the conditions of 29. 35 g/ L[Ni^{2+}], 1: 1 [$N_2H_4 \cdot H_2O$], 60 g/ L[NaOH] and stirring at 80 ℃ for 1 h, ultrafine Ni powder with an average particle size of 0. 058 μm and purity larger than 99. 5% was obtained.

(2) Orthogonal experimental results showed that the particle size of Ni powder was affected first by [NaOH], second by [Ni^{2+}], and then by [$N_2H_4 \cdot H_2O$].

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(6) Under the optimum technical conditions, the highest current efficiency may reach 98%, which is 13% ~ 15% higher than those reported both at home and abroad[1– 4] . The current efficiency decreases with the extension of electrolysis time and the increase of calcium content in lead; after 6 h electrolysis, this current efficiency reaches 82% .

(7) The present electrolysis technique with co-deposition of Ca^{2+} and Na^+ at the liquid lead cathode was first put forward.

(8) A Pb-Ca-Na ternary master alloy at a lower electrolysis temperature was successfully produced, thus providing a new material which was superior in quality to Pb-Ca alloy for manufacture of grid applied alloy used in the maintenance-free lead acid batteries.

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