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Preparation and pattern recognition of metallic Ni ultrafine powders by electroless plating

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Abstract

Using hydrazine hydrate as reductant, metallic Ni ultrafine powders were prepared from NiSO₄ aqueous solution by electroless plating method. The factors including concentration of NiSO₄, bathing temperature, ratio of hydrazine hydrate to NiSO₄, the pH of the solution, etc., on influence of the yield and average particle size of metallic Ni ultrafine powders were studied in detail. X-ray powders diffraction patterns show that the nickel powders are cubic crystallite. The average crystalline size of the ultrafine nickel powders is about 30 nm. The dielectric and magnetic loss of ultrafine Ni powders–paraffin wax composites were measured by the rectangle waveguide method in the range 8.2–12.4 GHz. The factors for Ni ultrafine powders are optimized by computer pattern recognition program based on principal component analysis, the optimum factors regions with higher yield of metallic Ni ultrafine powders are indicated by this way.

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Keywords: Metallic Ni; Ultrafine powders; Pattern recognition program; Principal component analysis; Electroless plating

1. Introduction

For its remarkable advantages, such as low cost, easy formation of a continuous and uniform coating on the surface of substrate with complex shape, electroless platings have found wide uses in many fields, nowadays, this method has also attracted a lot of interests in nanofabrications in optics and in the decoration on carbon nanotubes [1–4], SiC and other kinds of powders [5–8] and cenosphere particles [9–11].

Ultrafine Ni powders with uniform shape and high purity are increasingly required for specific uses in many technological areas, especially on the preparation of microwave absorbing materials, magnetic recording media, commercial batteries and the formation of catalysts [12,13]. Up to now, various methods have been reported to synthesize ultrafine powders of nickel, such as chemical reduction in solvents [14,15], microwavehydrothermal method [16], oil (w/o) microemulsion [17], precipitation in liquid polyol [18], sonochemical decomposition [19–21] and so on.

0925-8388/\$ - see front matter © 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2005.08.073 Patten recognition is one of important embranchments in artificial intelligence; it is a computational method mapping the patterns in multidimensional space to two-dimensional figures, along with some techniques for mapping the two-dimensional figures back to original multidimensional space. Now pattern recognition is of general interest for a multitude of purposes, from quality control, assurance problems, forensic investigations to gain the optimum process parameters for preparing composite.

This paper reports our results on preparation and microstructure of metallic Ni ultrafine powders by electroless plating method. The factors affecting the yield and average particle size of metallic Ni ultrafine powders are studied, the dielectric and magnetic loss of metallic Ni ultrafine powders are investigated. Pattern recognition analysis method based on principal component analysis (PCA) was introduced to analyze the experimental results, and to optimize the technological parameters for Ni powders preparation.

2. Experimental procedure

Solution of nickel ion was prepared by dissolving an analytical grade NiSO₄·6H₂O in distilled water. The pH values of the solutions were adjusted by sodium carbonate solution. Dodecylbenzenesulphonic sodium (DBS) was

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chosen as surfactant, sodium citrate (Na₃Cit) as complex agent and hydrazine hydrate as reducing agent. The mixture was heated to 40–90 °C. The metal powders was separated from the solution by filtration separation, and washed with distilled water followed by ethanol and acetone. The powders were finally dried in vacuum at 40 °C. Gray-black powders of nickel were obtained. Yield ratio was defined as the amount of obtained metal powders to the amount of Ni in starting material.

Differential thermal analysis (DTA) and thermogravimetric analysis (TG) of prepared Ni ultrafine powders were carried out on a NETZSCH STA-449C Thermal Analysis System with a rising temperature rate 10° C/min in flowing air. The sample weight was 30 mg. The sample pot was alumina with a depth of 5 mm and the reference material was alpha-alumina.

X-ray diffraction patterns were recorded from 15° to 90° (2 θ) with a step width of 0.02°, using a Philips X'Pert PRO diffractometer (using Cu K α radiation). The apparent crystallite size of the final powders was determined using the Scherrer formula (Eq. (1)):

$$\beta = \frac{k\lambda}{L\,\cos(\theta_0)}\tag{1}$$

where λ is the wavelength (=0.15406 nm), θ_0 the Bragg angle, β the additional broading (in radians), *k* the constant (=0.94) and *L* is the apparent crystallite size. The half-widths were obtained using the PHILIPS PROFILE FIT software.

Powders morphology was observed via scanning electron microscopy (SEM) (Model, JSM-5610LV, JEOL, Japan, 20 kV). The powders sample was ultrasoni-

cally dispersed into water, and the resultant suspension was spread on the surface of a silicon plate. All samples were coated with a thin layer of carbon for conductivity before observation.

The dielectric and magnetic loss of prepared Ni ultrafine powders was measured in 8.2–12.4 GHz by the waveguide method described by Zhao et al. [22]. The Ni ultrafine powders were randomly dispersed in paraffin wax with weight fraction 50%, then die-pressed to form rectangle samples with $3.0 \text{ mm} \times 10.16 \text{ mm} \times 22.86 \text{ mm}$, then the samples were set in a brass holder with inner size $3.0 \text{ mm} \times 10.16 \text{ mm} \times 22.86 \text{ mm}$ which fills the rectangular waveguide. After calibration with an intermediate of a short circuit and blank holder, reflection and transmission coefficients were obtained with the help of an automated measuring system (Agilent E8326B network analyzer). Both dielectric loss and magnetic loss were calculated. The intrinsic ultrafine Ni powders properties were isolated using the Lichtenecker effective medium expressions.

3. Preparation of Ni ultrafine powders by electroless plating

Table 1 shows the preparation conditions, yield ratio and crystalline size of ultrafine Ni powders by electroless plating. From the results, it can be seen:

Table 1

Technological parameters and experiment result of ultrafine Ni powders by electroless plat	ing
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Code	Plating co	onditions		Ni powders yield (%)	Crystalline size (nm)			
	$T(^{\circ}C)$	pH	Ni (mol/l)	NN (molar ratio)	SN (molar ratio)	t (min)		
1#	40	9.6	0.2	2:1	0	90	0	_
2#	50	9.6	0.2	2:1	0	90	0	_
3#	60	9.6	0.2	2:1	0	90	43	16
4#	70	9.6	0.2	2:1	0	90	68	18
5#	80	9.6	0.2	2:1	0	90	72	17
6#	90	9.6	0.2	2:1	0	90	93	20
7#	90	7.6	0.2	2:1	0	90	58	19
8#	90	8.5	0.2	2:1	0	90	60	20
9#	90	9.0	0.2	2:1	0	90	90	19
10#	90	10.8	0.2	2:1	0	90	74	27
11#	90	12	0.2	2:1	0	90	0	-
12#	90	9.6	0.2	0.5:1	0	90	0	_
13#	90	9.6	0.2	1:1	0	90	0	_
14#	90	9.6	0.2	1.5:1	0	90	0	-
15#	90	9.6	0.2	2.5:1	0	90	92	17
16#	90	9.6	0.2	3:1	0	90	90	16
17#	90	9.6	0.2	3.5:1	0	90	82	16
18#	90	9.6	0.05	2:1	0	90	0	-
19#	90	9.6	0.1	2:1	0	90	0	-
20#	90	9.6	0.15	2:1	0	90	93	15
21#	90	9.6	0.25	2:1	0	90	95	16
22#	90	9.6	0.25	2:1	1:4	90	92	13
23#	90	9.6	0.25	2:1	1:2	90	84	16
24#	90	9.6	0.25	2:1	1:1	90	55	23
25#	90	9.6	0.25	2:1	3:2	90	31	26
26#	90	9.6	0.25	2:1	2:1	90	0	_
27#	90	9.6	0.25	2:1	1:4	20	44	12
28#	90	9.6	0.25	2:1	1:4	40	67	14
29#	90	9.6	0.25	2:1	1:4	60	72	13
30#	90	9.6	0.25	2:1	1:4	80	90	13
31#	90	9.6	0.25	2:1	1:4	100	93	14
32#	90	9.6	0.25	2:1	1:4	120	95	16
33#	90	9.6	0.25	2:1	1:4	140	94	15
34#	90	9.6	0.25	2:1	1:4	160	95	16
35#	90	9.6	0.25	2:1	1:4	180	96	15

T: bathing temperature; Ni: [Ni²⁺]; NN: [N₂H₄·H₂O]/[Ni²⁺]; SN: [Na₃Cit]/[Ni²⁺]; t: time.



Fig. 1. XRD results of Ni ultrafine powders synthesized at different pH by electroless plating.

(1) pH 9–10 is suitable for the preparation of pure ultrafine powders. No gray-black powders can be produced if the pH < 7.6. Also, the obtained gray-black powders will be mixtures of nickel and nickel hydroxide if the pH > 12. This is clearly illustrated in Fig. 1 showing the XRD patterns of specimen prepared at pH 7.6–12. In this work, hydrazine hydrate and Na₂CO₃–NaHCO₃ were chosen as reductant and buffer agent, respectively. The following chemical reactions may be occur [10]:

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

$$Ni^{2+} + CO_3^{2-} = NiCO_3 \downarrow$$
(3)

$$2Ni^{2+} + N_2H_4 + 4OH^- = 2Ni \downarrow + N_2 \uparrow + 4H_2O$$
 (4)

$$2Ni(OH)_2 + N_2H_4 = 2Ni \downarrow + N_2 \uparrow + 4H_2O$$
(5)

$$2NiCO_3 + N_2H_4 + 2CO_3^{2-} = 2Ni \downarrow + N_2 \uparrow + 4HCO_3^{-}$$
(6)

It is obvious that reactions (4)–(6) cannot occurred smoothly if pH value is lower than 7.6. However, if pH value is high (pH > 12), a lot of Ni(OH)₂ was obtained by reaction (2). This may be the reason why the reducing process is pH dependent.

- (2) The yield ratio of ultrafine Ni powders increases with the bathing temperature increasing, 90 °C is suitable for the preparation of pure ultrafine powders. Ultrafine Ni powders cannot be manufactured if temperature is lower than 50 °C. XRD patterns of specimens prepared at 50–90 °C (Fig. 2) showed the only crystalline phase is metallic nickel when the bathing temperature is over 70 °C and no crystalline phase can be obtained when the bathing temperature is 50 °C.
- (3) When the values of molar ratio of $[N_2H_4 \cdot H_2O]/[Ni^{2+}]$ is less than 1.5, the yield ratio of ultrafine Ni powders is about zero. XRD patterns of specimens prepared with different molar ratio of $[N_2H_4 \cdot H_2O]/[Ni^{2+}]$ (Fig. 3) showed the only metallic nickel crystalline phase is formed when the value of $[N_2H_4 \cdot H_2O]/[Ni^{2+}]$ is over 2.0; however, Ni(OH)₂ will be the main crystalline phase when $[N_2H_4 \cdot H_2O]/[Ni^{2+}] \le 1.0$.
- (4) The yield ratio of ultrafine Ni powders increases with the concentration of [Ni²⁺] increasing, the experiment results



Fig. 2. XRD results of Ni ultrafine powders synthesized at different temperatures by electroless plating.



Fig. 3. XRD results of Ni ultrafine powders synthesized with different molar ratios of $[N_2H_4\cdot H_2O]/[Ni^{2+}]$ by electroless plating.

show that $[Ni^{2+}] = 0.20 \text{ M}$ is suitable for the preparation of pure ultrafine powders. No ultrafine Ni powders are synthesized if the concentration of $[Ni^{2+}]$ is lower than 0.15 M. Fig. 4 shows the effect of concentration of $[Ni^{2+}]$ on the XRD results of Ni powders, which indicates that the only crystalline phase is Ni(OH)₂ when the concentration of $[Ni^{2+}]$ is 0.05 M.

(5) The yield ratio of Ni ultrafine powders increase with bathing time increasing at first, and show only appreciably change when bathing time is over 90 min, which



Fig. 4. XRD results of Ni ultrafine powders synthesized with different concentrations of $[Ni^{2+}]$ by electroless plating.



Fig. 5. XRD results of Ni ultrafine powders synthesized with different molar ratios of $[Ni^{2+}]/[Na_3Cit]$ by electroless plating.

indicates that 90 min is enough for Ni formation by electroless plating method. In this work, sodium citrate is added to prevent bath decomposition during plating, the yield ratio of ultrafine Ni powders is sodium citrate content dependent, which decrease with the molar ratio of $[Na_3Cit]/[Ni^{2+}]$ increasing. Pure ultrafine Ni powders cannot be prepared if $[Na_3Cit]/[Ni^{2+}]$ is higher than 1.0; however, Ni₂(CO₃)(OH)₂ will be formed as the main crystalline phase when the value of $[Na_3Cit]/[Ni^{2+}]$ is 2.0. The XRD results of ultrafine Ni powders prepared with different molar ratio of $[Na_3Cit]/[Ni^{2+}]$ are shown in Fig. 5.

(6) The crystalline size of ultrafine Ni powders is about 10–30 nm as determined by the XRD line-broadening technique. The bathing temperature (*T*), the concentration of NiSO₄ ([Ni²⁺]), the ratio of the contention of N₂H₄·H₂O to

the contention of NiSO₄ ($[N_2H_4 \cdot H_2O]/[Ni^{2+}]$), pH of the solution, plating time (*t*) and the ratio of the contention of sodium citric to the contention of NiSO₄ ($[Na_3Cit]/[Ni^{2+}]$) show little influence on the crystalline size of prepared Ni powders.

Fig. 6 shows particle morphology of the ultrafine Ni powders prepared by electroless plating. It revealed that these Ni particles possessed global structures with diameters of about $0.5-1.5 \mu m$. As those particles overlap, it is not possible to observe one of them individually. EDS result confirmed those particles are pure Ni powders further more, the observed carbon elements can be attributed to the coated carbon layer for conductivity before SEM observation, the observed silicon elements can be ascribed to the silicon plate for bearing prepared Ni powders.

In order to understand the stability of the prepared Ni powders in air which were also characterized by using thermogravimetry (TG–DTA). As shown in Fig. 7, the pure nickel powders began to be oxidized around 400 °C, the final weight gain is about 20% that are a little different with the theoretical weight gain (27.3%) for perfect conversion of pure Ni to NiO. This datum indicates that the particles consist of pure nickel, and the oxidation process from Ni to NiO is not complete yet at about 1000 °C.

Fig. 8 shows the frequency dependence of dielectric loss and magnetic loss in the range 8.2–12.4 GHz for ultrafine Ni powders. The dielectric loss is observed to be small with values less than 0.2 at nearly all frequencies. The magnetic loss with values about 2 in the lower frequency region below 9 GHz, decrease appreciably with increasing frequency. It shows that prepared Ni ultrafine powder may be a suitable candidate material for microwave absorbing.



(a)

Ni powders ×5000



(b) Ni powders ×10000



Fig. 6. SEM photograph and EDS result of Ni ultrafine powders by electroless plating.



Fig. 7. Differential thermal analysis and thermogravimetric of Ni ultrafine powders prepared by electroless plating.

4. Principal component analysis and inverse projection results of Ni ultrafine powders

The theory of principal component analysis is well documented in textbooks concerning multivariate data analysis [23–25]. Therefore, this concept will not be introduced further more in this section.

As a complicated process, many factors influence on the preparation of metallic Ni ultrafine powders by electroless plating, such as the bathing temperature, the concentration of NiSO₄ and reduction agent, pH of the solution, bathing time, the content of surfactant, etc. Cross-test can only get very limited optimum parameters of Ni ultrafine powders preparation because it is impossible to take so many factors and levels into account. In fact, the optimum parameters to prepare Ni ultrafine powders are not just one, some new ones will get when certain factors are changed. In this case, computer pattern recognition will be a very effective way to optimize experimental results, differentiate those parameters with optimum yield ratio from those with inferior ones. In the present work, pattern recognition based on principal component analysis was used to optimize the parameters.

The yield ratio of Ni ultrafine powders is used as criterion targets. The samples are defined as 'optimum points' when the yield ratio is higher than 90%, and 'inferior points' when Ni ultrafine powders is less than 90%. The bathing temperature (*T*), the concentration of NiSO₄ ([Ni²⁺]), the molar ratio of N₂H₄·H₂O to



Fig. 9. Classification of Ni content by pattern recognition.

NiSO₄ ($[N_2H_4 \cdot H_2O]/[Ni^{2+}]$), pH of the solution, plating time (*t*) and the molar ratio sodium citric to NiSO₄ ($[Na_3Cit]/[Ni^{2+}]$) are chosen as six characteristic parameters. The experimental results of 35 samples shown in Table 1 are composed into the original data set ((35 × 6)-dimensional matrix). A target optimum region with better differentiation ability is obtained by principal analysis method, and the project diagram of samples on classifying plane is shown in Fig. 9.

The down-triangle marks in Fig. 9 denote the 'optimum points' (the yield ratio higher than 90%), the cross marks present the 'inferior points' (the yield ratio lesser than 90%). As can be seen from Fig. 9, 'optimum' region (area A) and 'inferior'

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Code	X	Y	Code	X	Y	Code	X	Y
1#	0.21	-0.17	18#	0.11	-0.41	6#	0.02	-0.25
2#	0.18	-0.19	19#	0.08	-0.35	15#	-0.02	-0.27
3#	0.14	-0.21	23#	0.02	0.03	20#	0.05	-0.30
4#	0.10	-0.22	24#	0.05	0.25	21#	-0.007	-0.20
5#	0.06	-0.24	25#	0.07	0.48	22#	0.005	-0.08
7#	-0.12	-0.22	26#	0.09	0.71	31#	0.001	-0.09
8#	-0.05	-0.24	27#	0.04	-0.02	32#	-0.007	-0.12
10#	0.11	-0.27	28#	0.03	-0.04	33#	-0.02	-0.14
11#	0.20	-0.29	29#	0.02	-0.06	34#	-0.03	-0.16
12#	0.15	-0.19	9#	0	0	35#	-0.03	-0.18
13#	0.10	-0.21	16#	0	0			
14#	0.06	-0.23	30#	0	0			
17#	-0.09	-0.31						



Table 2

Fig. 8. Frequency dependence of $\varepsilon''/\varepsilon'$ and μ''/μ' of ultrafine Ni powders by electroless plating.

Table 3 Inversed parameters and experimental results of ultrafine Ni powders synthesis

Sample no.	Coordinate		Test para	meters of	Experiment results				
	X	Y	$\overline{T(^{\circ}C)}$	pН	Ni (mol/l)	NN (molar ratio)	SN (molar ratio)	t (min)	Relative content of Ni (%)
Point 1	0.06	-0.36	90	10	0.18	3.0	0.1	73	>90
Point 2	0.03	0.53	55	7.8	0.34	1.13	1.9	50	<90
Point 3	-0.1	0.51	65	8.3	0.098	5.87	2.0	35	
Point 4	-0.04	0.4	45	8.0	0.06	5.84	1.8	55	
Point 5	-0.07	0.35	50	6.8	0.10	4.37	1.4.	40	
Point 6	-0.02	0.13	55	7.0	0.01	4.51	1.2	35	
Point 7	-0.06	0.33	55	7.0	0.15	3.71	1.2	35	

T: temperature; Ni: [Ni²⁺]; NN: [N₂H₄·H₂O]/[Ni²⁺]; SN: [Na₃Cit]/[Ni²⁺]; *t*: time.

region (area B) were obviously separated, and absolutely all the 'optimum points' located in target optimum region (in the quadrangle, area A), the correctness prediction rate was 100%. The values of projection coordinates (*X*, *Y*) corresponding to each sample point are also shown in Table 2, the relationship between the values of projection coordinates (*X*, *Y*) and temperature (*T*), the concentration of NiSO₄ ([Ni²⁺]), the molar ratio of N₂H₄·H₂O to NiSO₄ ([N₂H₄·H₂O]/[Ni²⁺]), pH of the solution, bathing time (*t*) and the molar ratio of sodium citric to NiSO₄ ([Na₃Cit]/[Ni²⁺]) is as following:

$$X = -0.0039T + 0.0725 \text{pH} - 0.609 \text{[Ni]}$$

- 0.0811([N₂H₄ · H₂O]/[Ni²⁺])
+ 0.528([Na₃Cit]/[Ni²⁺]) - 0.0004t (7)

$$Y = -0.0015T - 0.0153 \text{pH} + 1.0167 \text{[Ni]}$$

- 0.0403([N₂H₄ · H₂O]/[Ni²⁺])
+ 0.4558([Na₃Cit]/[Ni²⁺]) - 0.001t (8)

As to any giving parameters to prepare Ni ultrafine powders, the expected yield ratio can be predicted by pattern recognition analysis. In addition, the proper parameter can also be determined by an inverse projection. In order to verify the correctness of the pattern recognition program, 1 point in 'optimum' region and 6 points in 'inferior' region are chosen, respectively, and also defined as 'inverse points'. The corresponding technological parameters of those 'inverse points' can be calculated by inverse projection. The experimental results based on these technological parameters show that this pattern recognition program is reliable. The corresponding technological parameters and experimental results are shown in Table 3.

5. Conclusions

Ultrafine Ni powders were formed by electroless plating process using hydrazine hydrate, NiSO₄, etc., as studying materials. The principal factors influencing ultrafine Ni powder synthesis are—(1) pH of bathing solution: pH 9–10 is recommended; (2) bathing temperature: 90 °C is effective for ultrafine Ni powders synthesis; (3) molar ratio of $[N_2H_4 \cdot H_2O]/[Ni^{2+}]$: the suitable molar ratio of $[N_2H_4 \cdot H_2O]/[Ni^{2+}]$ is 2.0; (4) the concentration of

 $[Ni^{2+}]$: $[Ni^{2+}] = 0.20 \text{ M}$ is recommended. The Ni powders prepared by electroless plating are ultrafine grained, mostly with sizes of approximately 1.0 μ m.

The dielectric loss of prepared Ni ultrafine powders is small with values less than 0.2 in 8.2–12.4 GHz. The magnetic loss of synthesized Ni powders with values about 2 in the frequency region below 9 GHz, decrease appreciably with increasing frequency. Pattern recognition based on principal component analysis is used to optimize the parameters and to predict the expected values. This method gave 100% reliable recognition.

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