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Preparation of Ni/C core-shell composite powders by electroless plating method

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Abstract: Ni/C core-shell composite powders were prepared by electroless nickel-plating. The effects of concentration of $NiSO_4$, bathing temperature, ratio of hydrazine hydrate to $NiSO_4$, pH of the solution, amounts of complexing reagent and surfactant, bath load of activated carbon and reaction time, and so on, on the preparation of Ni/C core-shell composite powders were studied. The results show that the principal factors for Ni/C composite powders preparation are bathing temperature, ratio of hydrazine hydrate to $NiSO_4$ and pH of the solution. The optimum conditions are plating at 90 ℃ with pH10.7 and molar ratio of $N_2H_4\cdot H_2O$ to Ni^{2+} of 3.0. The plated nickel powders are observed to be sphere-like in morphology with size about 100 nm. The maximum dielectric loss of Ni/C core-shell composite powders is about 0.35, and its magnetic loss was low with value about 0 in 2−16 GHz.

Key words: Ni/C; core-shell powders; electroless plating; preparation

1 Introduction

Electroless plating has found wide uses in many fields for its remarkable advantages, such as low cost, easy formation of a uniform and continuous coating over all surfaces of any profiles of metallic or electrically non-conductive materials[1]. Recently, Electroless plating has also attracted a lot of interests in preparation of low dimensional nanostructure material. Some results have been reported to deposit metals or metals compounds on the surface of carbon nanotubes, SiC nano or micro particles, and Al_2O_3 powders, etc[2−7].

Ultrafine Ni and carbon powders are all potential candidates for preparing microwave-absorbing materials for its magnetic and dielectric loss, respectively. Ni/C composite powders constructed with core of carbon and coating shell of nano Ni may be an excellent microwave absorbing materials for its possession of dielectric loss and magnetic loss simultaneous. The preparation and microstructure of metallic Ni/C core-shell composite powders by electroless plating method were studied in this work, and the dielectric and magnetic loss of Ni/C core-shell composite powders in 2−16 GHz were also investigated.

2 Experimental

The starting activated carbon powders used in this work were prepared by the decomposition of sucrose. The average size of those activated carbon powders is about 10 μm. First, activated carbon powders were immersed in acetone and then in HF(aq) with ultrasonic vibration for 15 min. After that the cleaned activated carbon powders were sensitized in a stannous chloride ($SnCl_2\cdot H_2O$) and hydrochloric acid (HCl) solution for 1 h and then activated in palladium chloride ($PdCl_2$) and hydrochloric acid for further 1 h. Solution of nickel ion was prepared by dissolving an analytical grade $NiSO_4\cdot 6H_2O$ in distilled water. Cetyltrimethyl ammonium bromide (CTMAB) was chosen as surfactant, sodium citrate (Na_3(Cit)) as complex reagent, and hydrazine hydrate as reducing reagent. The mixture powders were separated from the solution by filtration separation, and washed with distilled water followed by ethanol and acetone. The powders were finally dried at 60 ℃ for 12 h.

X-ray diffraction patterns were recorded using a Philips X'Pert PRO diffractometer. The apparent crystallite size of the plated nickel was determined using the Scherrer's formula. Powders morphology was

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observed via scanning electron microscopy (SEM) (Model, JSM-5610LV, JEOL, JAPAN, 20 kV) and field emission scanning electron microscopy (FESEM) (Model, JSM-6700F, JEOL, JAPAN, 15 kV). The samples were coated with a thin layer of platinum for conductivity before SEM and FESEM observation. The zeta potential of activated carbon and Ni/C core-shell composite powders in suspension was measured by Malvern Instruments′ Zetasizer systems (Model, Malvern Zetasize 3000HSA). A network analyzer (Agilent PNAL N5230A Network Analyzers) was employed to determine the values of ε'(real part of permittivity), ε''(imaginary part of permittivity), μ'(real part of permeability) and μ''(imaginary part of permeability) in the frequency range of 2−16 GHz by using a reflection/transmission technique.

3 Results and discussion

3.1 Preparation of Ni/C core-shell composite powders

Fig.1 shows the relative sedimentation volume of activated carbon with different amounts of CTMAB added. It indicates that using CTMAB as surfactant can increase the hydrophilic property of the activated carbon powders. The relative sedimentation volume of activated carbon was nearly 100% with 1% CTMAB (relative to activated carbon mass) added at pH10, which shows that 1% CTMAB addition and pH10 of the bathing solution may be suitable for preparing a well coated Ni/C core-shell composite powders by electroless plating.

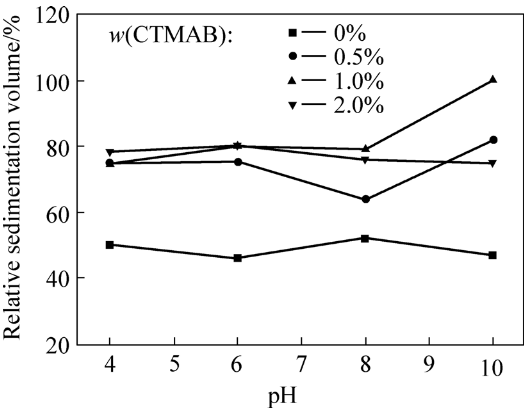

Fig.1 Sedimentation volumes of activated carbon and Ni/C composite powders by electroless plating

The sedimentation results of raw activated carbon and Ni/C core-shell composite powders in water show that most of the raw activated carbon floating above water indicates that it is still hydrophobic. Almost all the nickel coated activated carbon powders sinking in water shows that the composite powders are hydrophilic. Since the nickel coated activated carbon composite powders were washed orderly with distilled water, ethanol and acetone in a careful way, it could be concluded that the transformation from the hydrophobic to hydrophilic of the prepared composite powders was not due to the presence of the CTMAB, it should be resulted from a new coating formed in the electroless plating.

By changes in zeta potential of the raw activated carbon and the Ni/C core-shell composite powders shown in Fig.2, it can be concluded that the surface properties of those two kind of powders are absolute different from each other. This also demonstrates that a new surface is coated on raw activated carbon particles.

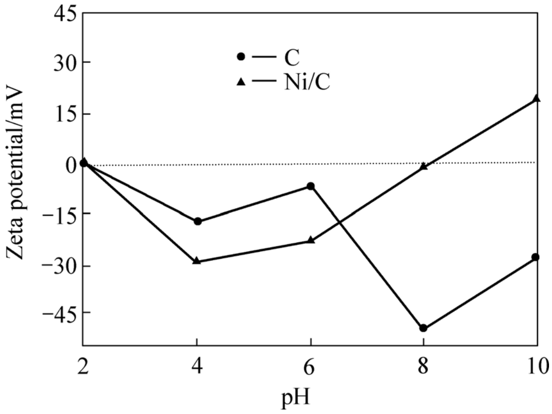

Fig.2 Plot of zeta potential vs pH for activated carbon and Ni/C composite powders

The preparation results show that:

1) pH 9.6−11.8 is suitable for preparation of Ni coated activated carbon composite powders, the obtained gray-black powders will be nickel hydrogencarbonate at pH 8.5. This is clearly illustrated in Fig.3, showing the XRD patterns of specimen prepared at pH 8.5−11.8.

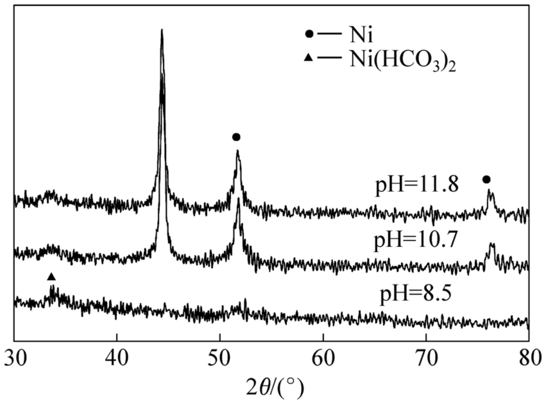

Fig.3 XRD patterns of Ni/C composite powders synthesized at different pH by electroless plating

2) The yield ratio of coated Ni on the activated carbon increases with the bathing temperature increasing, 80−90 ℃ is suitable for preparation of the composite powders. Pure Ni coating cannot be manufactured if the temperature is lower than 70 ℃ (Fig.4). The XRD

patterns of specimens prepared with different molar ratios of $N_2H_4{\cdot}H_2O$ to Ni^{2+} ($n(N_2H_4{\cdot}H_2O)/n(Ni^{2+})$) show that pure Ni coating is prepared when $n(N_2H_4{\cdot}H_2O)/n(Ni^{2+})$ is over 2.0, and $Ni(OH)_2$ (Fig.5) will be formed in coating when $n(N_2H_4{\cdot}H_2O)/n(Ni^{2+})$ is less than 1.0. The concentration of Ni^{2+} shows little effect on the coating phase, pure Ni coating is formed in the range of Ni^{2+} concentration from 0.25 to 0.35 mol/L.

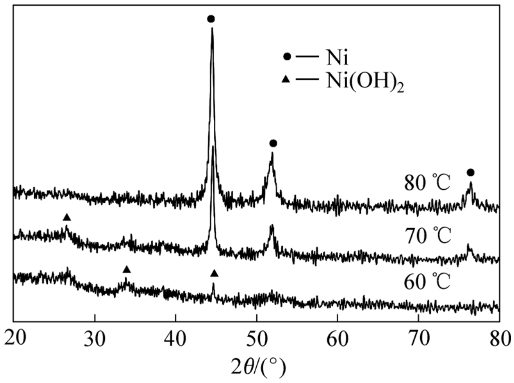

Fig.4 XRD patterns of Ni/C composite powders synthesized at different temperatures by electroless plating

3) In this study, sodium citrate is added to prevent bath solution decomposition during plating. Pure Ni coating cannot be prepared if $n(Na_3Cit)/n(Ni^{2+})$ is higher than 1.0, and $Ni_2(CO_3)(OH)_2$ will be formed as the main crystalline phase in the coating. The activated carbon loading and bathing time shows little influence on the preparation of coated nickel on the activated carbon, pure nickel coating can be formed either in the loading range from 5 to 40 g/L or in the bathing time range from 20 to 120 min.

4) The crystalline size of coated Ni on the surface of carbon is about 10−30 nm as determined by the XRD line-broadening technique. The bathing temperature, the concentration of $NiSO_4$, the ratio of the contention of $N_2H_4{\cdot}H_2O$ to the contention of $NiSO_4$, pH of the solution, plating time and the ratio of the contention of sodium citric to the contention of $NiSO_4$ show little influence on the crystalline size of coated Ni.

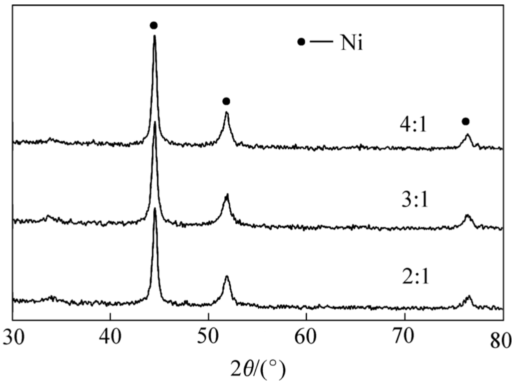

Fig.5 XRD patterns of Ni/C composite powders synthesized with different molar ratios of $N_2H_4{\cdot}H_2O$ to Ni^{2+} by electroless plating

3.2 SEM characteriation of Ni/C core-shell composite powders

Fig.6(a) shows the morphology of Ni coated activated carbon composite powders by electroless plating, the average particle size is about 10 μm, which is similar to that of the raw activated carbon powders (Fig.6(b)).

Comparing Fig.6(a) with the morphology of starting activated carbon, it is shown that the surface of coated

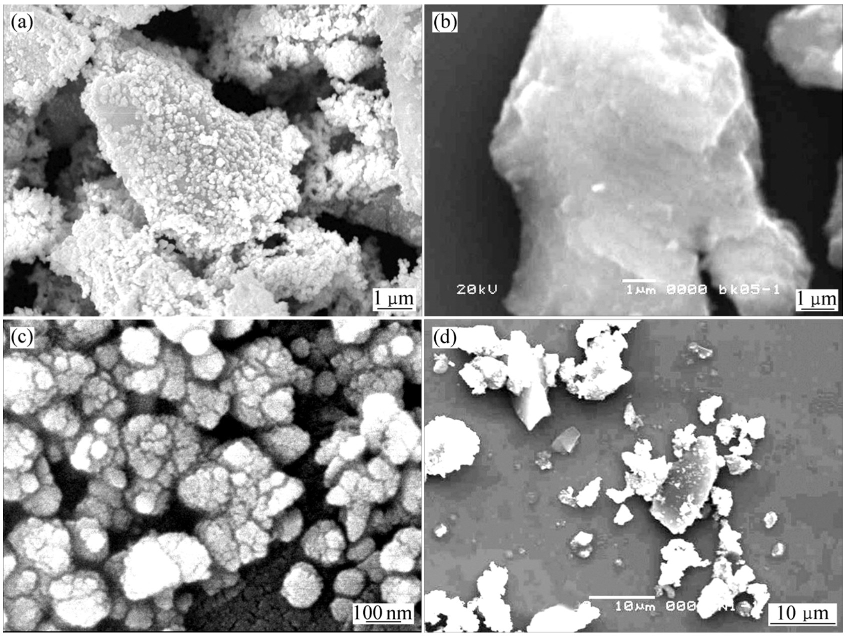

Fig.6 SEM images of Ni/C composite powders and Ni ultrafine powders by electroless plating: (a) Ni/C core-shell powder (SEM); (b) Starting carbon powder (FESEM); (c) Ni/C core-shell powder (FESEM); (d) Ni/C core-shell powder (SEM)

composite powders is uneven and covered with a layer of small particles with size about 100 nm (Fig.6(c)), however, the surface of activated carbon is very smooth. Table 1 lists the EDS results of nickel coated activated carbon particles in Fig.6(d), it can be seen that the elements Ni, C, Si and O are all found, the observed silicon element can be ascribed to the silicon plate to bear composite powders, the oxygen element may be due to part oxidation of coated nickel during drying stage. Based on the result, we can assure that the prepared composite powders are Ni/C core-shell composite powders, which is constructed with the core of activated carbon and the coating shell of nano-sized Ni particles.

Table 1 EDS results of Ni/C composite powders in Fig.6(d) (mass fracton, %)

Spectrum	C	O	Si	Ni
1	43.21	9.58	26.48	19.63
2	29.15	10.81	13.21	46.83
3	9.22	2.16	41.66	46.86
4	56.24	12.99	23.09	6.69
5	33.56	15.05	39.28	12.10
6	24.66	8.49	40.64	26.21

3.3 Microwave properties of Ni/C core-shell composite powders

Fig.7 shows the frequency dependence of the dielectric and magnetic loss of Ni/C core-shell composite powders in 2−16 GHz. It indicates that a dielectric loss peaks is observed, whose corresponding frequency is about 12 GHz. The maximum dielectric loss is about 0.35. The magnetic loss is low in all measuring frequencies with value about 0, it may be due to the presence of oxygen in the coated nickel.

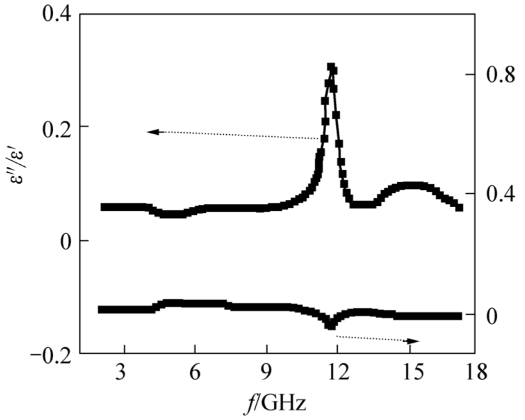

Fig.7 Frequency dependence of ε″/ε′ and μ″/μ′ of Ni-C powders-wax composites by electroless plating

4 Conclusions

1) Ni/C core-shell composite powders are prepared by electroless plating process using hydrazine hydrate, $NiSO_4$, activated carbon, etc, as starting materials.

2) The principal factors influencing Ni/C composite powders synthesis are as follows: pH of bathing solution of 9.6−10.6, bathing temperature of 80−90 ℃, the molar ratio of $N_2H_4{\cdot}H_2O$ to Ni^{2+} of 3.0 and the Ni^{2+} concentration of 0.20−0.25 mol/L.

3) The average particle size of the obtained Ni/SiC composite powders is 10 μm in diameter, the crystalline size of coated nickel is about 30 nm. For the prepared Ni/C core-shell composite powders, the maximum dielectric loss is about 0.35, the magnetic loss of is small with values about 0.

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