Preparation and Superior Absorbing of Electroless Deposited Ni-P-Fe₃O₄ Composite Powders

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Abstract. In this study, the Ni-P-Fe₃O₄ composite powders containing about 10% phosphorus were prepared by hydrothermal method. The phase, composition and morphology of the powders were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. The wave absorption properties of the Ni-P-Fe₃O₄ composite powders were estimated by vector network analyzer (VNA). The results showed that the saturation magnetization and resistivity of the as-obtained Ni-P-Fe₃O₄ composite powders were significantly reduced, however their dispersion as well as conductivity were improved. The electromagnetic wave absorbed by Ni-P-Fe₃O₄ composite powders was mainly attributed to the dielectric loss, and the absorption of electromagnetic wave in the low frequency can reach to 90% (the reflection loss is less than -10 dB).

Keywords: Electroless deposition, Ni-P-Fe₃O₄, composite powder, saturation magnetization, absorbing materials, microstructure.

1. Introduction
Electromagnetic wave pollution seriously damages the ecology and threatens human health. The application of absorbing materials is an effective method to solve electromagnetic pollution. Fe₃O₄ powder absorbent has the advantages of extensive raw materials, low cost, strong corrosion resistance, large absorption strength and non-toxic, but it is easy to aggregate, high density and poor characteristics at high temperature [1-3]. Composite absorbing materials can combine the advantages of each component to obtain the composite superposition effect of the electromagnetic properties of a single component.

Huang Y W et al. [4] obtained graphene/Fe₃O₄/Ni nanocomposites with good microwave absorption properties using RGO, FeCl₃·6H₂O and Ni as raw materials by one step hydrothermal method. The effective absorption bandwidth was about 3.60GHz and the maximum reflection loss was up to -16.38dB. Erqi Yang et al. [5] synthesized MoS₂-Fe₃O₄-C ternary nanocomposites by two-step synthesis. The minimum reflection loss (RL) value of MoS₂-Fe₃O₄-C nanocomposite is -53.03dB at 14.4GHz, but the matching thickness is relatively large. Li.x et al. [6] obtained Ni-B particles with shell-core structure by electroless plating with Fe₃O₄ particles catalyzed by Pd-Sn as the nucleus. It was found that Fe₃O₄ particles which coated with the Ni-B alloy film reduced metal deposition in the reaction solution, with stronger absorption capacity and wider electromagnetic wave absorption band, and the microwave absorption performance was better than that of pure Fe₃O₄ materials.

Electroless deposited Ni-P coatings are widely used in surface engineering and industry due to their
unique properties of wear resistance, high hardness and corrosion resistance. In electroless deposited Ni-P coatings, the change of phosphorus content affects the crystal structure and properties of the coating [7]. Li Y et al. [8] studied the structure and properties of electroless Ni-Fe$_3$O$_4$ composite on polyester fabric. The results show that NiFe$_3$O$_4$ composite coating has a subspherical structure of polyester fiber, and the composite coating belongs to amorphous phase. In addition, with the increase of coating weight, the saturation magnetization of Ni-Fe$_3$O$_4$ composite coating increased and the resistivity decreased. Li Z et al. [9] prepared nickel magnetite hollow spheres with a diameter of about 150nm by autocatalytic reduction. It was found that the dielectric constant decreased and the permeability increased with the increase of magnetite content. For the composite layer, the reflection loss is minimal at 10.8GHz and the matching thickness is 2.5 mm.

In this paper, sodium hypophosphite was used as reducing agent and sodium citrate as complexing agent to prepare high phosphorus Ni-P-Fe$_3$O$_4$ composite powder containing about 10% phosphorus.

2. Experiment

2.1. Materials
All chemical reagents used in this study were analytical pure and purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Nanometer iron tetroxide was purchased from McLean. The statistical results of particle size distribution of raw materials are shown in figure 1. According to the X-ray diffraction pattern, the average particle size of Fe$_3$O$_4$ powder was about 90nm, and the statistical results showed that the particle size of Fe$_3$O$_4$ powder met the normal distribution.

![Figure 1. Statistical results of particle size distribution of raw materials.](image)

The composition of the plating bath was as follows: 40g/L NiSO$_4$·6H$_2$O, 50g/L NaH$_2$PO$_2$, 50g/L C$_6$H$_5$Na$_3$O$_7$·2H$_2$O, 20g/L H$_2$N$_2$O$_4$S, 20mL/L C$_3$H$_6$O$_3$, 5g/L Fe$_3$O$_4$, time for 30min.

2.2. Experimental Method
After acidifying Fe$_3$O$_4$ powder with 37% hydrochloric acid, the treated powder was sensitized and activated by successively prepared solutions of stannite chloride and palladium chloride, and then electroless deposition was carried out to produce Ni-P-Fe$_3$O$_4$ composite powder. Ammonia water is used to regulate pH during deposition.

2.3. Laboratory Equipment
The crystal structure was identified by using a Bruker D8 ADVANCE (Bruck, Germany) X-ray diffractometer (XRD), and the 2θ was measured in the range of 10°~80°. The sample components were identified using PHI-5000 Versaprobe X-ray photoelectron spectrometer (XPS). The
morphologies of the samples were observed using the Gemini SEM 500 Schottky field emission scanning electron microscope (Zeiss, Germany) and the JSM-7500F (electronic instruments, Japan) cold field emission scanning electron microscope (SEM). The transmission electron microscope (TEM) image of the sample was performed on JEOL-2010 transmission electron microscope with an acceleration voltage of 200 kV. The magnetic properties of the samples were measured using the integrated physical property measurement system (PPMS) of EC-II (9T) (Quantum Design, USA). The absorption performance of the sample was analyzed using the AV3692D vector network analyzer (VNA).

3. Results and Discussion

3.1. Effect of Temperature on Deposition Rate.

The temperature is one of important parameters for metal solution because of its remarkable effect on the diffusive rate, activation energy of ion. The relationship between temperature and deposition rate at pH=8 is presented in figure 2. Since the electroless plating reaction is endothermic, temperature is one of the important factors affecting the deposition rate. It can be seen from figure 2 that, with the increasing of temperature, the deposition rate increased greatly.

It is because the deposition process is an endothermic reaction, when the temperature is low, the activity of nickel ions is poor, the reducing ability of reducing agent is weak, the reaction rate is slow. In addition, the increase of bath temperature increases the ion diffusion rate in the bath and the increase of reactivity will also increase the reaction rate. However, the high deposition temperature will cause the rapid evaporation and self-decomposition of the bath, and the reaction environment will fluctuate greatly, so the deposition rate will decrease. Therefore, the experimental temperature of the bath should be controlled at 70-80℃.

X-ray diffraction (XRD) pattern is used to confirm the phase and structure of the prepared samples. Figure 3 shows the XRD patterns of the samples. As can be seen that, when the reaction temperature is 60℃ and 90℃, the sample has a strong diffraction peak of Fe₃O₄. The low reaction rate lead to the Ni content in the sample is less than 5%, so that the weak diffraction peak signal. With the increase of the deposition rate, the Ni content in the samples increased. The samples with reaction temperatures of 70℃ and 80℃ show a diffuse peak near 45°, indicating that the Ni-P alloy coating was amorphous.

Figure 2. Relationship of temperature and deposition rate.
Figure 3. X-ray diffraction patterns of composite powders at different temperatures.

SEM micrographs of the composite powders at different temperatures are shown in figure 4. The microstructures present that the sample size reaches its maximum at 80°C with the temperature increased. When the reaction temperature is 60°C, polyhedral Fe₃O₄ particles exist widely in the composite powder, and only a few spherical shapes began to appear. When the temperature of the reaction is 70°C, complete spherical particles appear in the samples, the particle size is about 100nm, but there are still obvious polyhedral Fe₃O₄ particles. When the reaction temperature is 80°C, the samples are all spherical particles, and the average particle size increases to 300nm, and the crystal nucleus is formed again on the surface of the sphere. However, when the temperature of the reaction system increases to 90°C, the samples are dominated by polyhedral Fe₃O₄ particles, with almost no spherical particles. It can be seen that this reaction has the highest crystallization rate near 80°C, which is consistent with both figure 2 and figure 3.

Figure 4. (a) - (d) composite powder scanning electron micrograph with reaction temperature of 60°C-90°C.

3.2. Effect of pH on Deposition Rate

Figure 5 shows the relationship between pH value and deposition rate at a temperature of 80°C. It can be seen from figure 4 that the deposition rate increases with the increase of pH value when pH≤8. In this experiment, the electroless plating process was adopted. Sodium hypophosphite was used as reducing agent to provide electrons in alkaline environment, while nickel ion received electrons and
was reduced to nickel atom. The newly generated nickel atoms were adsorbed and deposited on the surface of nanometer Fe₃O₄. Through heterogeneous nucleation, they gradually grew up to form metallic nickel layer, and finally obtained nanometer Ni-coated Fe₃O₄ composite powder. The Redox reaction process is as follows:

Anodic reaction: \[ \text{H}_2\text{PO}_2^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{PO}_3^- + 2\text{H}^+ + 2\text{e}^- \] (1)

Oxidant reaction: \[ \text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni} \] (2)

\[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \] (3)

\[ \text{H}_2\text{PO}_2^- + 2\text{H}^+ + \text{e}^- \rightarrow \text{P} + 2\text{H}_2\text{O} \] (4)

Overall reaction: \[ \text{Ni}^{2+} + \text{H}_2\text{PO}_2^- + \text{H}_2\text{O} \rightarrow \text{HPO}_3^- + \text{Ni} + 3\text{H}^+ \] (5)

It can be seen that the accumulation of H⁺ in the solution during the reaction is not conducive to the further reaction. Under alkaline condition, the presence of a large amount of OH⁻ neutralizes the H⁺ generated during the reaction and promotes the reaction to continue. When the pH value of the solution increased to 10, the deposition rate decreased significantly and almost stopped. It is because nickel ions tend to produce a large amount of Ni(OH)₂ precipitation at high concentration of OH⁻, resulting in a sharp decline in the concentration of nickel ions in the bath, resulting in a rapid decrease in the reaction speed.

Figure 5.

Figure 6 shows the X-ray diffraction pattern (XRD) of the samples. It can be seen from figure 6 (a) that, the sample has a strong diffraction peak of Fe₃O₄. However, with the increase of the deposition rate, the samples with the solution pH value of 7-9 showed obvious diffuse peaks near 45°, indicating that the Ni-P alloy coating is amorphous.
Figure 6. X-ray diffraction patterns of samples at different pH values.

Figure 7 (a) - (d) scanning electron micrograph of composite powder at pH 7-10.

Figure 7 shows SEM images of composite powders at different pH value. As can be seen from figure 7, with the increase of temperature, the sample size reaches its maximum at pH was 9. When the pH value was 7, the samples showed spherical shape with a particle size of about 100nm. When the pH value of the reaction system was 8, the samples showed complete spherical particles with the particle size of about 300nm. When the pH value 9, the spherical particles further increase, the average particle size is about 300nm, and the crystal nucleus is formed on the surface of the sphere, and the coating further grows. When the pH value was 10, the samples were mainly polyhedral Fe$_3$O$_4$, with almost no spherical particles. It can be seen that the maximum crystallinity of the reaction rate is best when the pH value is between 8 and 9, which is consistent with figure 4 and figure 5.

Figure 8 is the EDS spectrum of the Ni-P-Fe$_3$O$_4$ composite powders. Figure 8 (a) reviews the elementary composition changes at different pH value. After that, the P element contents are shown in figure 8 (b). When the reaction system pH value settled at 7, 8 and 9, sample phosphorus contents were 9.7%, 9.1%, 10.8%, which belong to high phosphorus plating [10]. At pH 10, the reaction almost stopped. At that time, there was no Ni or P in the sample. The Ni and P contents increase with the increasing pH value from 7 to 9. After that the contents decrease to 0% at pH 10. As it can be seen from figure 7 (d), when the pH value of the reaction system was 10, the sample morphology has rarely changed. Based on figure 2 (b), it can be concluded that the reaction process is extremely slow under such conditions.
Figure 8. EDS results of composite powders at different pH values (a) and contents of P elements (b).

XPS not only quantify the composition of elements, but also reveal their chemical states. The XPS spectra of the Ni-P-Fe₃O₄ composite powders could provide further information about the structure and chemical state of Ni-P-Fe₃O₄ composite powders as shown in figure 9.

Figure 9. (a) XPS characterization results of composite powders. (b) High resolution XPS of Ni2p and corresponding fitting results. (c) High resolution XPS of Fe2p and corresponding fitting results.

Figure 9 (a) shows a typical XPS wide scan spectrum, indicating that all the standard photoelectron lines of elemental Ni, Fe, O and C are present: Ni 2p, Fe 3p, Fe 2p, P 2p, O 1s, and C 1s. As can be seen from figure 9 (a), the five peaks of 282.38eV-290.63 eV, 392.58eV-405.08eV, 524.58ev-537.08eV, 849.48eV-889.98eV and 927.58ev-967.48 eV are marked as P2p, C1s, O1s, Fe2p and Ni2p,
respectively. Since there is no C element in the sample, the C1s peak is only used for charge correction and is not analyzed. As shown in the figure 9 (b), the sample Ni2p spectrum showed three peaks in the Ni2p3/2 region at ~852.7 eV, ~855.3 eV, and ~861.0 eV, and three peaks in the Ni2p1/2 region at ~869.9 eV, ~872.7 eV, and ~879.8 eV, respectively. According to the literature [11-17], the two peaks with the highest intensity at ~852.7 eV and ~869.9 eV are the peaks in the zero-valence state Ni, indicating that the samples are mainly Ni in the metallic state. The peaks at ~ 855.3 eV and ~ 873.5 eV belong to the peak of oxidized Ni, which may be caused by the adsorption of oxygen in the air by a small amount of exposed Ni surface. The other two peaks at ~ 861.0 eV and ~ 879.8 eV are satellite peaks. In figure 9 (c), ~ 129.6 eV and ~ 133.1 eV correspond to reduced P (P-) and oxidized P (P5+), respectively [18], indicating the presence of Ni-P alloy compounds in the samples.

The hysteresis loops of raw materials and composite powders at room temperature (300K) are shown in figure 10. The results show that the magnetization of the raw material and composite powder increases with the increase of magnetic field. When the magnetic field intensity reaches ±10kOe, the material reaches saturation magnetization and exhibits obvious ferromagnetism. However, under the effect of external magnetic field, the composite powder quickly reaches the saturation magnetization, and the saturation magnetization decreases greatly compared with the raw material, showing the paramagnetic characteristic curve, and the coercivity at room temperature can be almost ignored.

Figure 11 is the relative complex dielectric constant (εr=ε′-jε″), complex permeability (μr=μ′-jμ″) and loss tangent (tanδμ and tanδε) curve of the sample (content of 70%). The real part (ε′ and μ′) of the complex permittivity and complex permeability shows the ability to absorb electromagnetic waves, while the imaginary part (ε″ and μ″) of the complex permittivity and complex permeability shows the ability to attenuate electromagnetic waves [19]. Figure 11 (a) and 7 (b) are the variation curves of the real and imaginary parts of the sample relative to the complex dielectric constant in the frequency range of 2.0~18.0 GHz. Both the real and imaginary permittivity of the composite powder samples were significantly increased. It can be seen from figure 11 (a) that the real part of the relatively complex dielectric constant of the composite powder drops sharply at 5GHz, which weakens the absorbing effect, so the absorbing ability of the composite powder is poor in the high frequency region. It can be seen from figure 11 (b) that the resistivity of the composite powder decreases significantly, and relaxation peaks occur at 5GHz and 15GHz. Under electromagnetic wave excitation, the interface relaxation is caused by charge redistribution between Fe3O4 and Ni-P cladding. The coating of Ni-P effectively reduces the agglomeration of particles and improves the dispersion of particles. The space charge polarization of nanoparticles also leads to relaxation and improves the dielectric properties of composite powders.

Figure 11 (c) and (d) are the real part (μ′) and imaginary part (μ″) of the complex magnetic
permeability of the raw material and composite powder in the frequency range of 2.0~18.0 GHz. There was no significant difference between before and after coating in the $\mu'$ and $\mu''$. Since the imaginary part of the permeability is physically meaningless, electromagnetic waves radiated from the composite may cause negative values [20-21]. As shown in figure 11 (e), the tangent value of the composite powder increases sharply at the high frequency, indicating that the frequency band is mainly controlled by dielectric loss. The tangent value of the material is always small, indicating that the dielectric loss of the material to electromagnetic waves is small. The tangent fraction of the composite powder is less than that of the raw material, indicating that the magnetic particles have a lower load density and lower magnetic loss. The tangent value drops to zero at high frequencies, which means that the magnetic loss doesn't work.

Figure 11. Real part (a) and imaginary part (b) of the relative complex dielectric constant of raw materials and composite powders, real part (c) and imaginary part (d) of the relative complex permeability, tangent of dielectric loss Angle (e) and tangent of magnetic loss Angle (f).

The absorption properties of raw materials and composite powders are shown in figure 12. It can be seen that when the sample thickness is less than 1mm, there is little difference in the absorption properties of samples before and after coating. As the thickness increases, the matching frequency of the composite powder's absorbing wave moves rapidly to the low frequency region. When the thickness is between 1.5-5mm, the intensity of the reflection loss peak does not change much, approaching -10db. It can be seen from figure 10 that the low hysteresis loss of the composite powder greatly affects its absorption performance in the high frequency region. The better dielectric property is beneficial to improve the absorption performance of the sample in the low frequency region. From
the above results, we can know that the absorption of composite powders in low frequency electromagnetic wave is a combination of dielectric loss and magnetic loss, while only dielectric loss plays a role in the high frequency band.

![Figure 12](image-url) Reflection loss of raw material (a) and composite powder (b).

4. Conclusion
Ni-P-Fe₃O₄ composite powder was prepared by electroless plating with sodium hypophosphite as reducing agent. The results showed that the reaction deposition rate first increased and then decreased with the increase of reaction temperature, reaching the maximum between 75°C and 80°C. When the reaction pH value was between 7 and 10, the deposition rate first increased and then decreased as the pH value increased, approaching the maximum value at pH=8. Therefore, the optimized reaction temperature is 80°C and the pH value is 8-9. Under the reaction conditions, the coating was amorphous Ni-P alloy. After the reaction for 30min, the composite Ni-P-Fe₃O₄ powder with an average particle size of 300nm and a microscopic morphology of sphericity could be obtained. Compared with Fe₃O₄ powders, the magnetic properties of the composite powders obtained by this method are weakened and the electrical conductivity is improved. Ni-P-Fe₃O₄ composite powder mainly absorbs electromagnetic wave through dielectric loss. In the range of 2GHz-4GHz and by adjusting thickness, the absorption of electromagnetic wave can reach 90% (the reflection loss is less than -10db), and has a good absorption effect on electromagnetic wave in the low frequency region.

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