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Preparation and characterization of magnetic hollow glass microspheres by electroless plating

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ABSTRACT

Magnetic hollow glass microspheres (HGM) were prepared by electroless plating technique. Morphology, composition, structure, infrared radiation and magnetic property of hollow glass microspheres before and after plating were characterized by SEM, EDS, XPS, XRD, IR and VSM, respectively. The results showed that Ni-P plating, composed of particles of 1~2 μm diameters, was uniformly coated on surfaces of HGM. Because of the existence of Ni-P plating, peak intensity of the plated HGM in IR and XRD were lower than those before. Since the plated HGM own anti-infrared radiation and magnetic property, they are useful in some special areas.

KEYWORDS

Hollow glass microsphere;
Electroless plating;
Magnetic;
Preparation;
Characterization.

INTRODUCTION

Hollow glass microsphere (HGM) is a kind of material with many advantages, such as low density, huge surface area, excellent thermal resistance, high wearing resistance and fine fluidity, so it has been widely used in plastic, rubber, paint and coating systems[1-4]. If the HGMs are coated with a layer of magnetic metal or alloy, they will combine the properties of both the two components, and allow them to be used in wider areas, such as immunoassay, catalyst, magnetorheological fluids, electromagnetic shielding and microwave absorbing materials[5-7]. Many methods have been applied to deposit a layer of magnetic metal or alloy on the surface of HGMs, such as physical vapor deposition (PVD), chemical vapor deposition (CVD), vacuum deposition, magnetron sputtering and electroless plating[8-12]. Due to spheric shape and low density of HGMs, it is very difficult to deposit a continuous and uniform coating on the surface of HGMs.

Electroless plating owns many advantages, such as low cost, easy formation of continuous and uniform coating on surface of substrate with complex shape, and capability of depositing on either conductive or nonconductive parts, which have attracted a lot of interests in both academia and industry[13-15]. Therefore, electroless plating has been widely employed to deposit metallic thin film on surface of electrically nonconductive three-dimensional substrates.

In this work, electroless plating method was applied to deposit a layer of Ni-P alloy on surface of HGMs. Then morphology, composition, structure, infrared radiation and magnetic property of HGMs before and after plating were characterized by means of

SEM, EDS, XPS, IR, XRD and VSM.

EXPERIMENTAL

Pretreatment of HGM

HGM is a kind of nonmetal material whose main ingredient is $3Al_2O_3 \cdot 2SiO_2$, so they must be pretreated before electroless plating. Washing, etching, sensitization and activation are included in pretreatment process. Firstly, HGMs were cleaned, degreased and polished with ethanol (C_2H_5OH), 0.1mol/L sodium hydroxide (NaOH) solution and 0.3mol/L sodium carbonate (Na_2CO_3) solution at 40¡ æ for 10min. Secondly, HGMs were etched in 1mol/L hydrofluoric acid (HF) solution and 0.05mol/L sodium fluoride (NaF) solution at 40¡ æ for 2min. Thirdly, HGMs were sensitized in 0.5mol/L stannum chloride ($SnCl_2$), 0.1mol/L sodium stannate (Na_2SnO_3) and 0.5mol/L hydrochloric acid solution at 40¡ æ for 3min. Fourthly, HGMs were activated in 0.01mol/L palladium chloride ($PdCl_2$) and 0.5mol/L hydrochloric acid solution for 10min at room temperature. At last, HGMs were fully washed in distilled water.

Electroless plating of HGM

The pretreated HGMs were put into alkaline bath. The composition of electroless bath and the operating conditions are listed in TABLE 1.

TABLE 1 : Compositon and operation conditions of electroless plating

Chemicals	Concentration (mol/L)
$NiSO_4 \cdot 6H_2O$	0.12
$NaH_2PO_2 \cdot H_2O$	0.28
$Na_2P_2O_7 \cdot 10H_2O$	0.23
NH_4Cl	0.06
$(NH_2)_2CS$	4×10^{-5}
pH	10
Tempreture (°C)	55
Time (min)	20

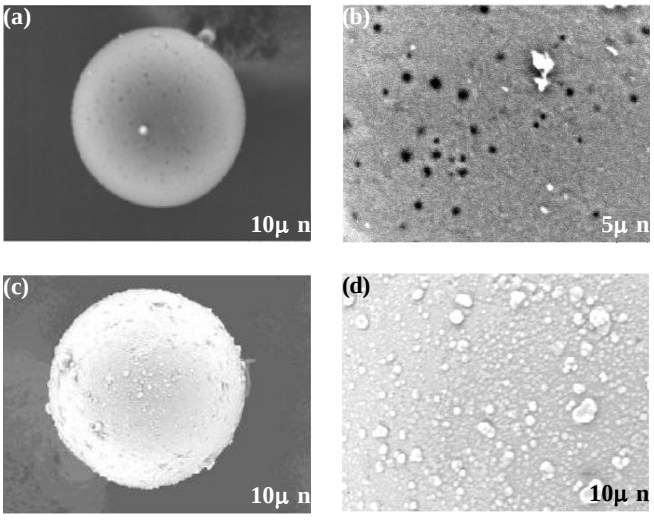
Characterization of HGM

Morphology of HGMs before and after plating was investigated by scanning electron microscopy (STEREOSCAN-440, 20kV, U.K., Leica Cambridge Co. Ltd). Energy dispersion spectrometry (NSS300, USA, Thermoelectricity Co. Ltd) and X-ray photoelectron spectroscopy (XSAM800, U.K., KRATOS Co. Ltd) were performed to identify chemical composition of the plating on surface of HGMs. Structure analysis was carried out by X-ray diffractometer (D/max- ‡ UA, Japan, Rigaku Co. Ltd, Cu Kα, 45 kV, 40 mA). Infrared spectrum was recorded on spectrometer (Nicolet5700, USA, Nicolet Co. Ltd). Magnetic property was tested by vibrating sample magnetometer (LakeShore 7400, USA, LakeShore Co. Ltd).

RESULTS AND DISCUSSION

SEM analysis

SEM photographs of HGM before and after plating are shown in Figure 1. From Figure 1 (a) and Figure 1(b), it can be seen that HGM before plating is a high spherical pellet, with diameter of 50μm or so. There are also a lot of pores on the surface of HGM before plating. As shown in Figure 1(c) and Figure 1(d), there is no obvious change in its sphericity when HGM is plated. The diameter of HGM after plating is bigger than that before plating. The plating on surface of HGM is uniform. The pores on surface of HGM disappear when a layer of plating is coated. Furthermore, it can be found that the plating is composed of particles with 1~2 μm diameters at high magnification as shown in Figure 1(d). According to mechanism of electroless plating, particles in plating are assembled with atoms reduced during electroless plating process. Therefore, the morphology of surface layer may be more smooth if the



(a) (b) before plating; (c) (d) after plating.

Figure 1 : SEM photos of HGM

electroless plating is composed of smaller particles. How to achieve smooth and magnetic coating on the surface of HGM is being studied.

Figure 2 is SEM photograph of cross-section of HGM after plating. The top layer is the coating of electroless plating, and the down layer is the wall of HGM. It shows that the thickness of the plating is about 3μm, and the thickness of the wall of HGM is 8μm or so. The joint between the plating and the wall of HGM is very tight.

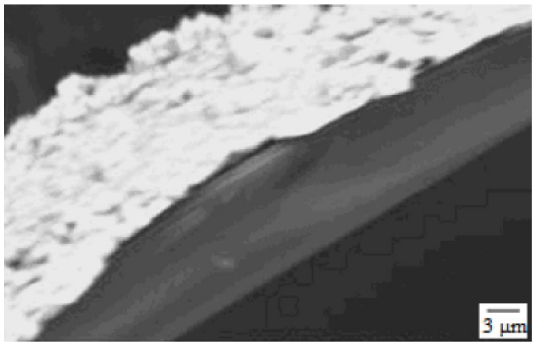


Figure 2 : SEM photo of cross-section of HGM after plating

EDS analysis

EDS analysis of the plating on surface of HGM is shown in Figure 3. It indicates that the plating on surface of HGM is composed of Ni and P. The weight percentage of Ni in the plating is 94.8%, and that of P is 5.2%. Compared with the content of Ni, the content of P is rather low.

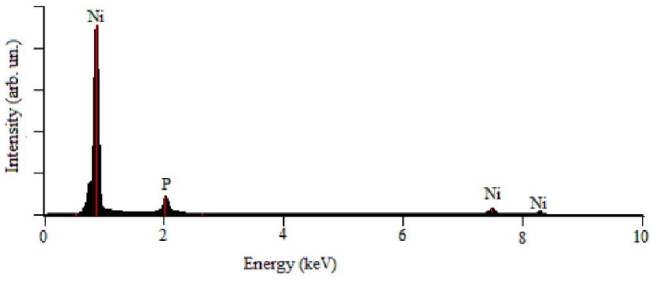
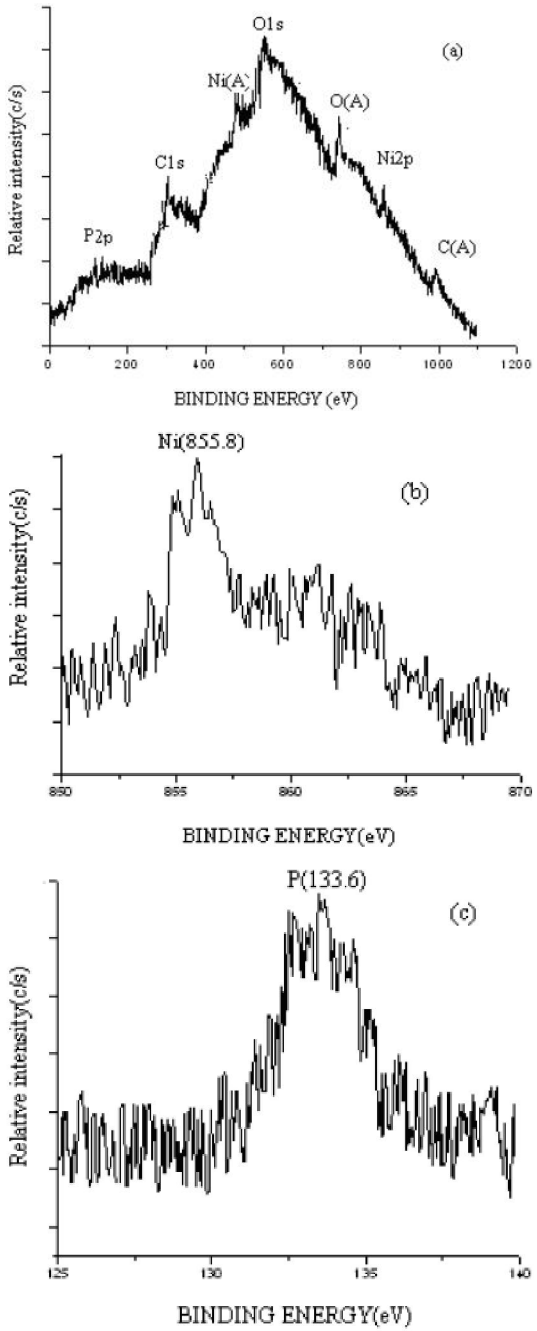


Figure 3 : EDS spectrum of plating on surface of HGM

XPS analysis

XPS measurement was employed to identify surface composition of electroless Ni-P alloy film. The XPS spectra of Ni-P plating are shown in Figure 4. In XPS spectra, peaks at 855.8 eV and 133.6 eV are ascribed to Ni 2p and P 2p, respectively. The result clearly shows that Ni element exists primarily as Ni^0 only with a small quantity of Ni^+, and P element exists as P^{3-}. Therefore, we can deduce that the electroless Ni-P plating is composed of a combination of Ni^0 and a small amount of Ni_3P.



(a) survey spectra; (b) Ni 2p; (c) P 2p.

Figure 4 : XPS spectra of plating on surface of HGM

XRD analysis

XRD patterns of HGM before and after plating are shown in Figure 5. Because the main ingredient of HGM is SiO_2 and Al_2O_3, there are strong diffraction peaks of SiO_2 and Al_2O_3 in XRD patterns of HGM before and

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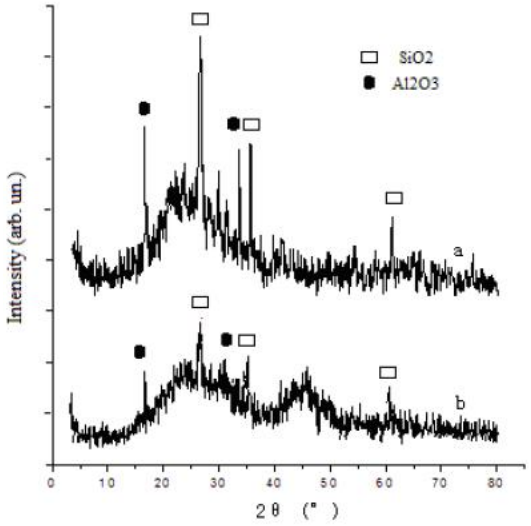
after plating. Three peaks at 28.12°, 35.18°, 60.56° are characteristic peaks of SiO_2, and two peaks at 18.32°, 35.18° are ascribed to Al_2O_3. Comparing XRD patterns shown in Figure 5(a) and Figure 5(b), the characteristic peak intensity of SiO_2 and Al_2O_3 in the plated HGM is decreased obviously. The result shows that the covering degree of Ni-P plating is compact and the thickness reaches at least to μm scale. Furthermore, there is a broad peak at 2θ = 40~50° in XRD of the plated HGM, which indicates that the Ni-P plating on surface of HGM is amorphous.

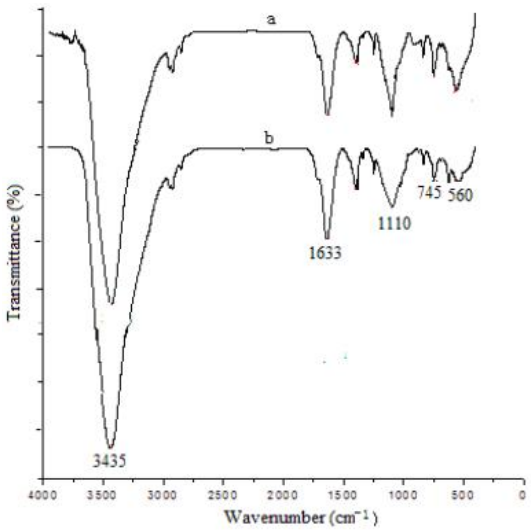


(a) before plating; (b) after plating.

Figure 5 : XRD spectra of HGM

IR analysis

IR transmission spectra of HGM before and after plating are shown in Figure 6. Due to adsorped H_2O on surface of HGM, there are characteristic peaks of H_2O in IR patterns of HGM before and after plating. Peaks at 3435cm-1 and 1633cm-1 are attributed to hydroxy(O-H) stretching vibration and bending vibration, respectively. Because the main ingredient of HGM is SiO_2 and Al_2O_3, there are characteristic absorption peaks of SiO_2 and Al_2O_3 in IR patterns of HGM before and after plating, too. The Si-O stretching vibration of SiO_2 is observed at 1110cm^{-1}, and the Al-O stretching vibration and bending vibration of Al_2O_3 are observed at 745cm^{-1} and 560cm^{-1}, respectively. Comparing Figure 6(a) with Figure 6(b), the intensity of peaks in the plated HGM is lower than those before plating. The result shows that the plated HGM carries anti-infrared radiation property because of Ni-P plating on surface of HGM.



(a) before plating; (b) after plating.

Figure 6 : IR spectrum of HGM

VSM analysis

Figure 7 shows magnetic hysteresis loop of the plated HGM at 300K. As shown in Figure 7, the saturation magnetization(Ms), the remnant magnetization(Mr) and the coercivity(Hc) of the plated HGM are 3.587×10^{-3}emu/g, 6.462×10^{-3}emu/g and 11.93 Oe, respectively. The result shows that the plated HGM is magnetic and can be used in broad areas.

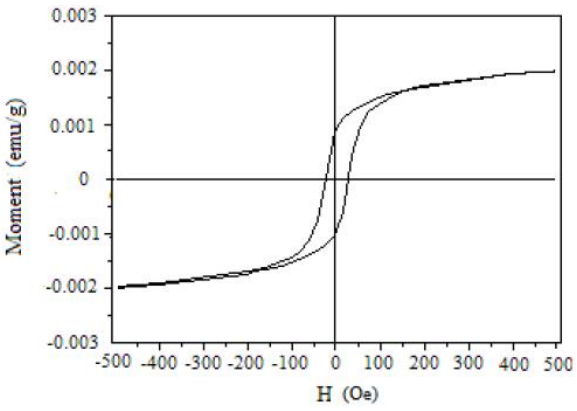


Figure 7 : Hysteresis loops of HGM after plating

CONCLUSIONS

Ni-P alloy plating was successfully coated on surface of HGM by electroless plating technique. The Ni-P plating on surface of HGM is composed of particles with diameters of about 1-2 μm and the phase is amor-

phous. EDS and XPS spectra show that the plating is composed of the combination of Ni with a small quantity of Ni3P. Compared with those before plating, the peak intensity of the plated HGM in XRD and IR decrease obviously, which suggest that plated HGM own anti-infrared radiation property. VSM test shows the plated HGM owns magnetic property. With these two properties, its application range can be broadened.

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