Properties of (Ni-P)-SiO₂ (Nanometer) Electroless Composite Coating on PET Fabrics

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Abstract : In this paper, electroless composite plating of (Ni-P)-SiO₂ nanoparticles on PET fabric was operated in order to obtain a high electromagnetic interference shielding efficiency and the wear resistance for special clothing. The (Ni-P)-SiO₂ composite plated fabrics were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), thermal gravimetric (TG) analysis and X-ray diffraction (XRD) analysis. The electromagnetic shielding performance and abrasion resistance were also measured. The results show that the onset decomposition temperature of the Ni-P plated fabric is higher than that of the (Ni-P)-SiO₂ composite plated fabric, but lower than that of the original one. The face-centred cube crystal structure of Ni-P deposition is formed because of the incorporation of nano SiO₂ particles. When the weight increasing percentages are identical, the shielding effectiveness (SE) of the (Ni-P)-SiO₂ composite plated fabric is slightly larger than that of the Ni-P plated fabric. For the (Ni-P)-SiO₂ composite plated fabric, the add-ons of nano SiO₂ particles has little effect on the shielding effectiveness. The abrasion resistance of the (Ni-P)-SiO₂ composite plated fabric is much improved.

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1. Introduction

In order to produce functional clothes with high electromagnetic interference (EMI) shielding efficiency, various metal coating techniques have been suggested and commercially used, such as metal foils and laminates, conductive paints and lacquers, sputter coating, electroless plating, etc. Among the various metallization processes, electroless metal plating is probably a preferred way to produce metal-coated fabrics due to the attractive advantages such as uniformity of coverage, excellent conductivity, the possibility of metallizing nonconductors, and flexibility [1]. In the previous investigation, the properties of electromagnetic shielding of electroless Ni-, Cu- and Ag-plated fabrics were extensively studied [2-5].

Electroless plating technology can be used to fabricate nano-composite plating by adding the nanoparticles into the plating solution. Nano-composite plating is showing more and more excellent performance, such as mechanical performance, catalytic performance, corrosive protective performance and so on [6-9]. As nanoparticles exhibit unusual physical, chemical and biological properties, such as super paramagnetism and quantum tunneling of magnetization, nano SiO₂ particles have attracted much attention in recent years due to their potential applications in many industrial, e.g. intensity, hardness, wear resistance, corrosion resistance, and high

temperature, etc [10,11]. However, the literature related to nano SiO₂ particles electroless Ni-P plated fabric is very limited.

Therefore, the purpose of this article is to study the effect of Ni-P coating co-deposited with nano SiO₂ particles on the properties of electromagnetic shielding effectiveness and abrasion resistance to improve the high quality of EMI shielding textile materials for protective clothing. The surface characteristic, the thermal stability, and the structure of the metal coating are also examined by the scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), thermal gravimetric (TG) analysis and X-ray diffraction (XRD) analysis techniques.

2. Experimental

2.1 Materials

Commercially-obtained white polyester (PET) fabric (1/1 plain pattern, number of ends, and picks are 38 and 31, the linear densities of ends and picks are identical, 8 tex) was scoured with an aqueous solution of 200 g/l NaOH for 30 minutes at 60°C prior to use, followed by rinsing with deionised water, and then dried at room temperature. The mean size of nano SiO₂ particles, which were provided by Shenzhen Nanotech Port Co. Ltd, is about 30 nm.

The chemicals used in the present investigation are in analytical reagent grade, and include nickel sulfate

hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), sodium hypophosphite (NaH_2PO_2), ammonium chloride (NH_4Cl), sodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$), hydrochloric acid (HCl), sodium hydroxide (NaOH), ethanol ($\text{C}_2\text{H}_5\text{OH}$). The industrial grade sodium alginate ($\text{C}_5\text{H}_7\text{O}_4\text{COONa}$) was obtained from local printing and dyeing plant.

2.2 Dispersion of nano SiO_2 particles

First, required amount of nano SiO_2 particles (0.5 g) was weighted accurately, and then rinsed with an ethanol solution for 3 times. An aqueous solution of sodium alginate (1 g) in deionised water (100 ml) was prepared. Second, the pretreated nano SiO_2 particles were added to the above solution under stirring, and then the mixture was sonicated for 10 minutes at room temperature. The precipitation phenomenon for the dispersion solution did not occur after 24 h.

2.3 (Ni-P)- SiO_2 (nanometer) electroless composite plating

Firstly, chemical activation of the pretreated fabric fibres surface was accomplished by immersion for 5 minutes at 40°C in an aqueous bath containing a catalytical active Pd/Sn-compound (PdCl_2 , 0.18 g/l; SnCl_2 , 16 g/l) and cleaned with deionized water. Secondly, the samples were immersed in the hydrochloric acid solution (100 ml/l) for 1 minute to remove tin from the surface and rinsed with deionized water, and sequentially immersed in the sodium hypophosphite solution (15 g/l) for 5 minutes followed by rinsing with deionized water. Thirdly, the dispersed nano SiO_2 solutions of different volume 2 ml, 4 ml, 6 ml, 8 ml and 10 ml were slowly added to the nickel plating solution (200 ml) containing nickel sulfate (30 g/l), sodium hypophosphite (28 g/l), ammonium chloride (25 g/l) and sodium citrate (20 g/l) with continuous stirring, respectively. The pH of the plating bath was adjusted to 9 with sodium hydroxide and during the deposition the temperature was kept at 65°C . Finally, the deposition of (Ni-P)- SiO_2 was carried out in the composite plating solution, and then rinsed with deionized water followed by drying at 120°C for 15 minutes. The plated samples with identical weight increasing percentage but different nano SiO_2 content were prepared. The weight of the deposition was controlled by the plating time.

2.4 Test method

2.4.1 Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS)

The surface structures of the Ni-P plated fabric and the (Ni-P)- SiO_2 composite plated fabric samples were studied by using the JEOL JSM-6700F field emission scanning electron microscope equipped with an Oxford

INCA Energy 400 energy-dispersive X-ray spectrometer. The energy dispersive spectroscopy survey spectra for the plated fabric were preformed by using the energy dispersive spectrometer.

2.4.2 X-ray diffraction (XRD) analysis

The structural Ni-P deposition and (Ni-P)- SiO_2 composite deposition analyses were made by X-ray diffraction (model XRD-700), using a Philips PW 1710 diffractometer and Cu- $\text{K}\alpha$ radiation ($\lambda=0.154056$ nm), the diffractograms were recorded at a scan speed of $10^\circ/\text{min}$ (sampling pitch 0.02°) with $30\text{--}80^\circ$ angle range.

2.4.3 Thermogravimetric (TG) analysis

Thermogravimetric analyses were conducted on the Ni-P plated fabric and the (Ni-P)- SiO_2 composite plated fabric samples using a TGA/SDTA851e thermal gravimetric and differential scanning calorimetry analysis (TG-DTA) instrument. Percentage weight change versus temperature was evaluated at a scan rate of $10^\circ\text{C}/\text{min}$ with a continuous nitrogen flow rate of 30 ml/min over the range of $25\text{--}1000^\circ\text{C}$. The onset and endset decomposing temperatures and the percent residual weight were obtained according to ASTM E474-80.

2.4.4 Weight increasing percentage

The weights of fabric samples with the same size of 100 mm x 100 mm square before and after treatment were measured by a weight meter (Sartorius BT224S meter). The increasing percentage of deposition in weight was calculated by equation 1.

$$\delta(\%) = \frac{W_2 - W_1}{W_1} \times 100\% \quad (1)$$

Where δ is the weight increasing percentage (%), W_1 is the fabric original weight (g), and W_2 is the final plated fabric weight (g).

2.4.5 Shielding effectiveness (SE) measurement

The shielding effectiveness of the plated fabric to electromagnetic was measured using the dual chamber method for near-field cases on the electromagnetic radialization testing instrument, which is composed of a rectangular waveguide tube and a PAN3610 network analyzer [12], according to the method of ASTM ES 7-83. An electromagnetic shield is a conductive material which attenuates (through reflection and absorption) electromagnetic energy. The effective frequency for testing is in the range of 2250-2650 MHz, and the size of the sample is 11 cm x 6.5 cm. The shielding effectiveness (SE) is defined as the ratio of incident to transmitted electric intensity (or magnetic intensity, or power) and is usually expressed in decibels (dB) by equation 2.

$$SE = 20 \times \log \left| \frac{E_0}{E_1} \right| = 20 \times \log \left| \frac{H_0}{H_1} \right| = 10 \times \log \left| \frac{W_0}{W_1} \right| \quad (\text{dB}) \quad (2)$$

Where E_0 is the incident electric intensity (Vm), and E_1 is the transmitted electric intensity (Vm); H_0 is the incident magnetic intensity (Am), and H_1 is the transmitted magnetic intensity (Am); W_0 is the incident power (W), and W_1 is the transmitted power (W).

2.4.6 Abrasion resistance measurement

For testing abrasion resistance, the Ni-P plated fabric and the (Ni-P)-SiO₂ composite plated fabric were measured using the YG(B) 401D automatic fabric flat-rubbing tester in accordance with ASTM D4966. The original fabric was chosen for the grinding material and 500 abrasion circles were adopted. The SEM was employed in the final inspection of the samples subjected to the abrasion test, and the weight loss was also measured using the weight meter.

3. Results and discussion

3.1 SEM analysis

The surface morphology of the Ni-P plated fabric and the (Ni-P)-SiO₂ composite plated fabric was examined by SEM, as illustrated in Figure 1. It was found that an uniform layer of metal deposition was formed on the surface of the fibre as shown in Figure 1(a) and (b). The surface of the Ni-P plated fibre is smoother than that of the (Ni-P)-SiO₂ composite plated fibre, and the globular grain size distributed on the (Ni-P)-SiO₂ composite plated fabric is larger than that distributed on the Ni-P plated fabric. The magnified cross section SEM micrographs of the (Ni-P)-SiO₂ composite deposition is presented in Figure 1(c). The compact grains can be seen and there is no pores in the depositon.

3.2 EDS analysis

The Ni-P plated fabric and (Ni-P)-SiO₂ composite plated fabric are analyzed for their chemical compositions by an Energy Dispersion Spectrometer (EDS) of an emissive-type electron microscope (JSM-6700F, JAPAN). Figure 2 shows the EDS survey spectra of the (Ni-P)-SiO₂ composite plated fabric, which indicates the presence of the peaks of C, O, Ni, P and Si (the peaks of Cl and K at 2.623 keV and 9.424 keV are ignorable). The compositions by mass percent are C 20.52%, O 44.95%, Ni 21.31%, P 12.67% and Si 0.55%, respectively, and the corresponding atomic percents are C 32.18%, O 52.90%, Ni 6.84%, P 7.71% and Si 0.37%. The element for Ni-P alloy plated fabric is mainly composed of Ni and P and the mass precent ratio of Ni to P is 84.7 : 15.3.

(a) The longitudinal section of the Ni-P plated fabric (1500x)

(b) The longitudinal section of the (Ni-P)-SiO₂ composite plated fabric (1500x)

(c) The cross section of the (Ni-P)- SiO₂ composite plated fabric (20,000x)

Fig. 1 SEM micrographs of the plated fabric

3.3 XRD analysis

The coating structures of the Ni-P deposition and the (Ni-P)-SiO₂ composite deposition were analysed using X-ray diffraction depicted in Figure 3. Despite the hindrance to definite characterisation of the Ni-P coating, the diffraction pattern of the Ni-P deposition clearly reveals a considerable broadness of the diffraction line in the angle $2\theta=35-55^\circ$, which confirms that the Ni-P coating is an amorphous material. In the electroless plating process,

Fig. 2 EDS survey spectra of the (Ni-P)-SiO₂ composite plated fabric

Fig. 3 X-ray patterns of Ni-P deposition and (Ni-P)-SiO₂ composite deposition

an amount of phosphorous atoms (about 12.7 wt.%) are dissolved into the nickel structure. Consequently, the crystalline structure of the nickel coating is disturbed and the crystallization degree of the nickel coating can not be formed [13]. As for the (Ni-P)-SiO₂ composite deposition, it is to note that the intense Ni diffraction line Ni(111) can appear in the angle $2\theta=44.5^\circ$. Thus, the broadness of the line at the angle corresponding to Ni(111) might be a result of a low ordered structure with microcrystallites, furthermore, a shoulder for Ni(200) and a hump for Ni(220) are also observed in the diffraction line. However, the diffraction lines for nano SiO₂ can not be found because the content of nano SiO₂ is too little in the deposition.

3.4 TG analysis

The percent residual weight in temperature graphs for the original fabric, the Ni-P plated fabric and the (Ni-P)-SiO₂ composite plated fabric are shown in Figure 4. As compared with the original fabric, the onset decomposition temperatures were decreased about 14°C for the Ni-P plated fabric and 20°C for the (Ni-P)-SiO₂ composite plated fabric, respectively. This may be due to the fact that the interfacial area is increased after treating by chemical etching with alkali, and the affinity between fibre and metal is simultaneously improved, moreover,

the metallic coating may accelerate the decomposition temperature of the substrate. With the incorporation of nano SiO₂ particles in the deposition, the metallic structure phase and the microstructure of Ni-P alloy coating change, and the chemical and physical properties are also improved. So the thermal stability of the (Ni-P)-SiO₂ composite plated fabric is decreased to a great extent compared to the Ni-P plated fabric. The percent residual weight for the (Ni-P)-SiO₂ composite plated fabric is 33.96%, namely the weight increasing percentage is around 66.04%, which is close to the tested value 69.7%. It is clear from TG curves that the weight of the (Ni-P)-SiO₂ composite plated fabric increases beyond 782°C. This indicates that new substances are formed because of the reaction of nano SiO₂ with nitrogen.

3.5 SE analysis

Figure 5 represents the shielding effectiveness of the Ni-P plated fabric and the (Ni-P)-SiO₂ composite plated fabric with the similar weight increasing percentage (about 45%). It is obvious that the shielding effectiveness of the (Ni-P)-SiO₂ composite plated fabric is larger than that of the Ni-P plated fabric. Nano SiO₂ particles can increase the deposition rate, improve the microstructure and reduce the reaction temperature of electrolytic layers. It seems to be due to the incorporation of nano SiO₂ particles in the deposition, which enhances the capability of shielding the electromagnetic wave, and makes the (Ni-P)-SiO₂ composite deposition more conductive [14]. So the crystallinity of Ni in the (Ni-P)-SiO₂ composite deposition enhances the conductivity. We also investigated the shielding effectiveness of composite plated fabrics of different nano SiO₂ add-ons in the plating solution. It was found that as the add-ons of nano SiO₂ particles increases, the shielding effectiveness for the (Ni-P)-SiO₂ composite plated fabrics has no distinct change. Moreover, the stability of the plating solution becomes worse when the concentration of nano SiO₂ is beyond 0.3 g/l.

3.6 Abrasion resistance analysis

The surfaces of the Ni-P plated fabric and the (Ni-P)-SiO₂ composite plated fabric samples after abrasion resistance testing are presented in Figure 6. By comparing Figure 6(a) and (b), it can be seen that parts of the plating coating, which closely contacted with the grinding material, were peeled off from the fibers surface in the longitudinal view of the coated fibers for both after 500 times abrasion testing. The performance of the (Ni-P)-SiO₂ composite plated fabric behaves much better than that of the Ni-P plated fabric. The compactness and toughness for the (Ni-P)-SiO₂ composite deposition are greatly improved by incorporation of nano SiO₂ particles.

Fig. 4 Thermogravimetry curves of PET fabric before and after electroless plating

Fig. 5 The shielding effectiveness for the Ni-P Plated fabric and the (Ni-P)-SiO₂ composite plated fabric

Moreover, the layer adhesion strength between the metal coating and the substrate is also enhanced. Therefore, the abrasion resistance of the (Ni-P)-SiO₂ composite plated fabric is improved. The weight loss percentage against the initially plated fabric weight was about 1.6 % for the Ni-P plated fabric, but for the (Ni-P)-SiO₂ composite plated fabric the weight did not change.

4. Conclusions

In order to study the effect of nano SiO₂ particles on the Ni-P deposition and develop the high quality EMI shielding textiles for protective clothing, PET fabrics were electroless Ni-P plated by incorporation of nano SiO₂ particles. The properties of electromagnetic interference shielding effectiveness and abrasion resistance were investigated. As compared with the PET fabric, the onset decomposition temperature decreases 14°C for the Ni-P plated fabric and 20°C for the (Ni-P)-SiO₂ composite plated fabric, respectively. The amorphous phase of the Ni-P deposition changes to the low ordered structure with microcrystallite. Nano SiO₂ particles can enhance the electromagnetic interference shielding effectiveness of the (Ni-P)-SiO₂ composite plated fabric. For (Ni-P)-SiO₂ composite plated fabric, the

(a) the Ni-P plated fabric

(b) the (Ni-P)-SiO₂ composite plated fabric

Fig. 6 SEM micrographs of the plated fabric after 500 abrasion circles in the magnification of 140x.

add-ons of nano SiO₂ particles in the plating bath has little effect on the shielding effectiveness. The abrasion resistance of the (Ni-P)-SiO₂ composite plated fabric is also improved.

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