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Research on the Solution and Properties of Ni-P/n-Al_2O_3 Electroless Composite Plating

Huang Yan-bin†, Liu Fei-fei, Zhang Qi-yong, Ba Guo-zhao, and Liang Zhi-jie

Department of Equipment Remanufacturing,
Academy of Armored Forces Engineering, Beijing 100072

In order to further improve the corrosion resistance and wear resistance of the Ni-P coatings of electroless plating, electroless Ni-P/n-Al_2O_3 composite deposits were prepared by adding some nano Al_2O_3 particles in Ni-P plating bath. The bath composition and proproties were studied in this paper. The orthogonal test was applied in order to get the new composite solution, taking the initial stable potential as evaluation standard and considering the elements correlation at the same time. The processing parameters have been optimized by single factor experiment in which the depositing speed was chosen as the evaluation standard. The results showedthat the process is stable and the composite Ni-P/n-Al_2O_3 deposits werebright and smooth, whose hardness and corrosion resistance are much better than simple Ni-P coatings. Furthermore the surface appearance and structure of the composite Ni-P/n-Al_2O_3 coating were investigated by SEM and XRD method. It was proved that the coating surface is typical cystiform cells and its structure is amorphous. All test results ofcomposite coating showed that all various physical coating properties had been improved by adding nano-particles. The hardness of optimal coating is more than 600HV and increases to 1000HV after heat-treating, and its hardness is 20~50% higher than Ni-P coating. The rust points appeared in 200 hour by immersing the coating into the 10%HCl solution and the corrosive speed is 3×10^{-3} mg/(cm^2·h)which was obtained after 300 hour. In the same condition Ni-P coating is 5.6×10^{-3} mg/(cm^2·h). The salt spray resistance of the layers can exceed 600h with the thickness 20μm.

Keywords: *electroless plating; Ni-P/n-Al_2O_3; corrosion resistance; wear resistance*

1. Introduction

Nano composite deposits is a kind of Nano composite material by composite deposits technique. In order to further improve the performance of the Ni-P electroless plating coatings, Ni-P/n-Al_2O_3 composite deposits were prepared by adding n-Al_2O_3 particles in Ni-P plating bath to achieve co-deposition with Ni-P. The shape of n-Al_2O_3 particle is usually global(spiculate or sheet), its surface is smooth and its diameter is only 20～40 nm. In recent years, much research is reported about Ni-P/n-Al_2O_3 composite deposits, but the bath stability and stir process still need to be improved. In order to improve the bath stability and obtain better composite deposits, the authors have studied the bath composition and processing parameters.

2. Experiment

2.1 substrate and Instruments

Substrate: 45 steel 50 mm × 25 mm × 1 mm

Experimental instruments: electronic thermostat water bath DK-98-I, pHS-2 acidity meter, PZ26b direct current voltage meter, Nano test 600 equipment, Quanta 200 scanning electron microscope, D8 Advance X-ray diffractometer

2.2 Plating Process

Plating process: chemical degreasing → flushing → activating by hydrochloric acid → rinsing → salt bath further degreasing → washing → activating by dilute sulphuric acid → flushing by deionized water → amorphous state plating → flushing by cold water → post treatment → blowing

† Corresponding author: hyb102@sina.com

2.3 Property Test

2.3.1 Measurement of the Corrode Potential

The corrode potential is evaluated by PZ26b direct current voltage meter, compared with SHE. The final potential was the average of two parallel values.

2.3.2 Measurement of the Structure and Surface Appearance

The structure of the composite Ni P/n Al_2O_3 coating was tested by D8 Advance XRD, and the surface appearance by Quanta 200 SEM.

2.3.3 Measurement of the Corrosion Resistance

Composite coatings are immersed into the 3.5% NaCl, 10% HCl and 10% H_2SO_4 solution respectively. After 300 hours, corrosion resistance was valued by measuring the decreased mass of the samples.

2.4 Experimental Design

The nano-dispersed solution was prepared by the laboratory of equipment surface engineering. Orthogonal test was designed to get the optimal coating, in which the function of each ingredient and processing parameters were studied.

Table 1. Level and factor (g/L)

Factor	$NaHPO_2 \cdot H_2O$ A	$Na_3Cit \cdot 2H_2O$ B	Complexant 1 C	Complexant 2 D	n-Al_2O_3 E
1	30	14	6	3	4
2	27	17	8	5	6
3	24	20	10	7	8
4	21	23	12	9	10

3. Results and Discussion

3.1 Orthogonal Test

In this research we adopt 5 factor and 4 level orthogonal test, which is shown in Table 1. The other factors keep the same: $NaH_2PO_2 \cdot H_2O$ 25g/L; stabilizer 0.8 mg/L; temperature 85~90 ℃; pH 4.5~5; time 2 h.

Orthogonal test results are shown in Table 2. In this research, there are two factors to evaluate coating quality: the initial stable potential and depositing speed. Both are important, so we treat them equally.

The sum of the initial stable potential and depositing speed value, that is *y*, is the final evaluation standard. By means of mathematics, analysis of orthogonal test results is shown in Table 3. As the result of the potential difference is (328)-(375)=47 and the deposits speed is 13.70-7.31=6.39, we take-0.375 as the potential benchmark and 7.31 as deposits speed benchmark. The result adds 1 per adding 4.7 and 0.639 respectively.

Deduced from Table 3, the influence of factors is arranged as the following sequence: $Na_3Cit \cdot 2H_2O$ > $NaHPO_2 \cdot H_2O$ > n-Al_2O_3> Complexant 2> Complexant 1. The optimal formulation is $A_4B_1C_4D_2E_3$, that is, NO. 13.

Table 3. Analysis of orthogonal test results

Ⅰ	8.698	13.563	9.660	9.255	8.920	T= 41.255
Ⅱ	8.877	8.360	9.643	11.127	10.337	
Ⅲ	10.082	8.730	11.287	10.287	11.133	
Ⅳ	13.598	10.602	10.665	10.585	10.865	
R	4.900	5.203	1.644	1.872	2.213	

Table 2. Orthogonal test results

Factors	$NaHPO_2 \cdot H_2O$ (g)	$Na_3Cit \cdot 2H_2O$(g)	Complexant1 (g)	Complexant2 (g)	n-Al_2O_3 (g)	potential (v)	depositing speed (μm)	y
1	A1	B1	C1	D1	E1	−0.353	7.77	10.25
2	A1	B2	C2	D2	E2	−0.335	12.28	6.91
3	A1	B3	C3	D3	E3	−0.337	7.31	8.88
4	A1	B4	C4	D4	E4	−0.367	12.27	10.16
5	A2	B1	C2	D3	E4	−0.364	12.18	11.98
6	A2	B2	C1	D4	E3	−0.346	13	7.36
7	A2	B3	C4	D1	E2	−0.363	7.94	6.61
8	A2	B4	C3	D2	E1	−0.361	8.15	9.56
9	A3	B1	C3	D4	E2	−0.351	12.72	14.60
10	A3	B2	C4	D3	E1	−0.369	9.50	7.06
11	A3	B3	C1	D2	E4	−0.375	10.56	9.21
12	A3	B4	C2	D1	E3	−0.355	9.12	9.46
13	A4	B1	C4	D2	E3	−0.337	13.70	18.83
14	A4	B2	C3	D1	E4	−0.328	8.66	12.11
15	A4	B3	C2	D4	E1	−0.354	10.88	10.22
16	A4	B4	C1	D3	E2	−0.339	10.25	13.23

3.2 Single Experiment of Processing Parameters

In order to further study the function of processing parameters, we take the method of changing one factor and keep others the optimal level.

3.2.1 Influences of Bath Temperature

Influences of temperature on the potential of composite coating are shown in Fig. 1. The potential value reach the peak at 85 ℃. As the polymer in the solution, the solution will possibly decompose at the high temperature. so we choose the temperature 85~90 ℃.

3.2.2 Influences of pH Value

Influences of pH value on potential of composite coating are shown in Fig. 2. The potential of composite coating was stable between the value 4.5~5. When the pH value is less than 4, the potential increase. But the deposits speed is low and the coating is very brittle. so, we choose the pH value as 4.5~5. Usually ammonia is used as regulator.

3.2.3 Influences of Stir

The stir is the key factor in the composite plating. Stir can remove the air bubble adsorbing in the surface of sample. On the other hand, it can make nano particle suspend enough in the solution to avoid nano reuniting. Mechanical stir is asymmetry so that the coating is not even. Gaseous stir overcomes the disadvantage of the mechanical stir, but the process is incomplete. It needs to be studied in the future.

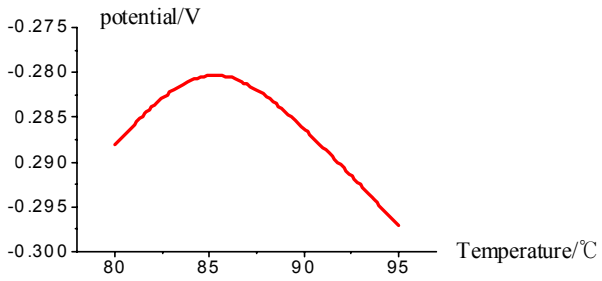

Fig. 1. Influences of bath temperature on potential of composite coating

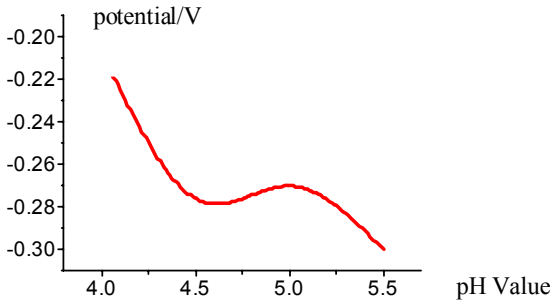

Fig. 2. Influences of pH value on potential of composite coating

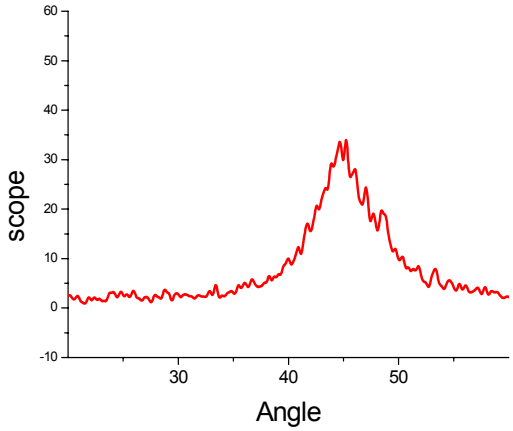

Fig. 3. XRD of composite coating coatings

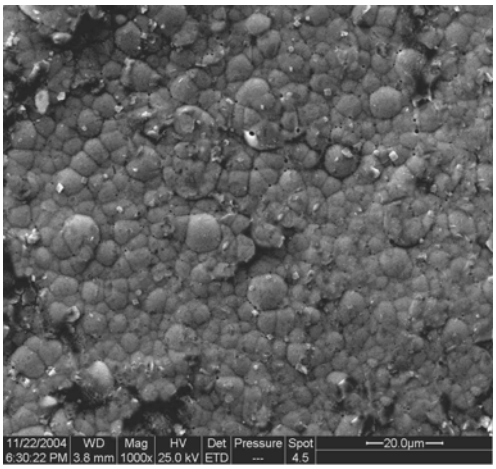

Fig. 4. XRD of composite coating coatings×1000

3.3 Composite Coating Properties

3.3.1 Composite Coating Appearance and Structure

Fig. 3 shows its XRD diagram and Fig. 4 is its micro-appearance by SEM. The coating structure is amorphous by x-ray diffraction. Compared with Ni-P coating, composite coating diffraction have several peaks which are possibly caused by nano particles. SEM photograph shows that the micro-appearance of optimal coating is typical cystiform cells. The content of nano particles reach to 4.8% (mass percent)by the analysis of EDS.

3.3.2 Corrosion Resistance Test

At room temperature, composite coatings are immersed into the 3.5% NaCl, 10% HCl and 10% H_2SO_4 solution respectively. After 300 hours the samples are dried and the corrosion resistance is valued by measuring the decreased mass of the samples. Immersing test results are

Table 4. immersing test results

Corrosive medium	air bubble time /h	Rust point time / h	Corrosive speed mg / (cm^2·h)	
	composite	composite	composite	Ni-P
3.5%NaCl	no	16	8.0×10^{-4}	2.4×10^{-3}
10%HCl	7	no	3×10^{-3}	5.6×10^{-3}
10%H_2SO_4	2.5	no	2.59×10^{-3}	4.6×10^{-3}

shown in Table 4:

Seen from Table 4, composite coating corrosion resistance is improved comparing with Ni-P coating. The number of nucleus increases by adding nano paticles, so the coating became more compact. The corrosion resistance of the coating was improved for the low porosity.

4. Conclusions

(1) Orthogonal tests bring the best plating formulation and the influencing sequence of factors, that is, $Na_3Cit \cdot 2H_2O$ > $NaHPO_2 \cdot H_2O$ > n-Al_2O_3 > Complexant 2 > Complexant 1.

(2) Single experiments bring the best processing parameters: temperature 85~90 ℃, pH 4.5~5; Gaseous stirring 80L/h.

(3) The coating surface is typical cystiform cells and the coating structure is amorphous.

(4) The corrosive speed of the optimal coating is 8.0×10^{-4} mg/(cm^2 · h), 3×10^{-3} mg/(cm^2 · h) and 2.59×10^{-3} mg/(cm^2 · h) when the coating is immersed into the 3.5% NaCl., 10% HCl and 10% H_2SO_4 solution respectively. The corrosion resistance of composite deposits is better than that of Ni-P.

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