

High Phosphorus Nickel Alloy Deposition by Brush Plating Process

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Abstract. Nickel (Ni) alloy coating with high phosphorus (P), P >10wt.%, is usually deposited by electroless and electrolytic plating processes and has been widely used for corrosion and wear resistance applications. However, the deposition rate is low and plating tanks with temperature control are required, and not viable for on-site coating and coating repair. The tank-free brush plating is usually controlled by constant voltage and featured with high deposition rate due to high current density (>100 A/dm²), while the current density of conventional tank plating is usually lower than 10 A/dm². However, the high current density of brush plating leads to a challenge to deposit a high phosphorus (Hi-P) Ni alloy, as the P content in the nickel phosphorus (NiP) alloy coating is inversely proportional to the operating current density based on the tank plating practices. In this paper, we report a brush plating process to deposit high phosphorous nickel thin film on carbon steel coupons. Design of experiments (DOE) was used to optimize the brush plating process, including plating bath formation, and plating parameters. It is found that low pH value and high phosphorous acid (H₃PO₃) concentration in the plating bath are beneficial for high P content in the NiP deposit. High pH value and low 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) concentration are beneficial for high current efficiency. By using the optimized bath chemistry and plating parameters, NiP coating with P content of 13.7 wt.% was deposited on carbon steel coupons with a current efficiency as high as 19.4 %.

Keywords: Brush plating, Nickel alloy plating, High phosphorus nickel plating, Nickel bath formulation, High current density plating

1 Introduction

NiP alloy coating has found its applications in various industry sectors such as aerospace, oil & gas (O&G) and marine & offshore (M&O) due to the excellent performance in wear and corrosion resistance. The physical and chemical properties of NiP alloy coatings are significantly influenced by the phosphorus content in the coating and the post heat treatment. Based on the P content, NiP alloy coatings are generally grouped into three categories, namely low phosphorus (LP), medium phosphorus (MP), and high phosphorus (HP) with P content of 2-5 wt%, 6-9 wt% and 10-13 wt%, respectively [1]. As a general guideline, LP coating shows high hardness and better wear resistance. With increasing P content, the hardness of NiP coating reduces, but the corrosion resistance drastically increases.

To deposit NiP alloy coatings, both electroless and electrolytic plating processes are widely used. Since developed by Brenner and Riddell [2], the electroless plating process is well known for the excellent corrosion and wear resistance of the resulted coating, in particular, it is comparable with that of hard chromium in hardness after heat treatment [3]. However, electroless NiP alloy coating processes suffer many drawbacks, such as an expensive reducing agent required, a high operating temperature, and more bath control than chromium plating. Furthermore, the deposition rate of electroless plating is very low. To overcome these difficulties, Brenner et al [4] proposed electrolytic deposition of NiP coating.

Compared with electroless nickel (EN) plating, electrolytic approach for NiP alloy coating has attracted more attentions recently because of its easy maintainability, high deposition rate, low operation cost, as well as a possibility of changing the properties and adapting them to many applications.

However, like EN coating process, the tank-based electrolytic deposition process is also not viable for plating on large work pieces such as those in M&O and O&G industries. To address this challenge, brush plating has been proposed, which also known as selective plating, or swab plating, is a very useful and portable method of contact plating [5-8].

In its simplest form, brush plating process resembles painting, as shown in Fig. 1. Brush plating equipment includes power packs, solutions, plating tools, anode covers, and auxiliary equipment. The power pack has two leads. One is connected to the plating tool and the other is connected to the workpiece to be plated. The anode is covered with an absorbent material which holds the solution. The operator dips the plating tool in the solution and then brushes it against the surface of the workpiece that is to be finished. When the anode touches the work surface a circuit is formed and an electrodeposit is produced. Plating occurs only where the anode contacts the workpiece. During the brush plating process, the plating tool is always kept in motion whenever it is in contact with the work surface. The movement will apply even plating on the entire area being plated and ensure a quality finish.

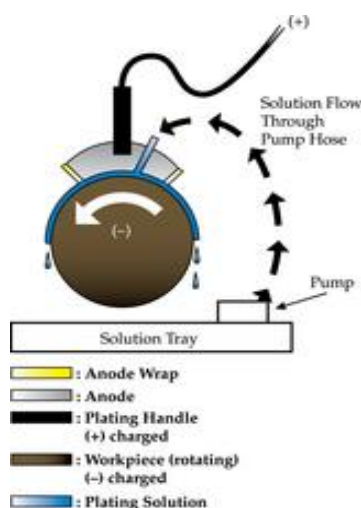


Fig. 1. Illustration of brush plating on outer surface of round work piece [8].

The tank-free brush plating is usually controlled by constant voltage and featured with high deposition rate due to high current density ($>100 \text{ A/dm}^2$), while the current density of conventional tank plating is usually lower than 10 A/dm^2 . The high current density of brush plating leads to a high deposition rate, but also results in a challenge to deposit a high phosphorus ($>10 \text{ wt.}\%$) nickel alloy, as the phosphorus content in the NiP alloy coating is inversely proportional to the operating current density based on the tank plating practices. In this paper, we report a brush plating process, including bath chemistry, and plating parameters, such that uniform NiP coating with a higher P content more than $10 \text{ wt.}\%$ can be deposited with a current efficiency of about 20% .

2 Experimental

2.1 Methodology

The formulation of plating bath and the operating voltage are identified as the critical factors which have significant influence on the P content in NiP coating, in particular, with high current efficiency. At the first, the compounds for making the plating solution were chosen basing on the demands, experiences and references. Secondly, orthogonal experiment was used to determine the optimized content of each chemical in the plating solution and the effect of each ingredient was investigated. Thirdly, the operating voltage was varied to obtain higher P content and current efficiency.

2.2 Bath formulation

The chemical bath formulation for brush plating of high phosphorus nickel alloy was carried out based on nickel sulfate and phosphorous acid with complexing agents. For example, nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) was chosen as the source of Ni in brush plating. Nickel chloride (NiCl_2) was not being considered, as Cl^- is a well-known element causing the tensile stress of the coating. Phosphorous acid (H_3PO_3) was chosen as the source of P in brush plating. Phosphoric acid (H_3PO_4) was chosen as a pH buffer rather than a source of P because it was too difficult to be reduced into P under the plating condition applied in this study. A further and important role of the H_3PO_4 is to suppress the oxidation of H_3PO_3 on the anode and weaken the reduction ability of Ni ions on cathode to benefit increasing P content in the deposit. It also can act partly as complexing agent. Hypophosphorous acid (H_3PO_2) was not being considered, because it is

relatively unstable in brush plating. An organic phosphorus compound, HEDP was chosen as buffering and complexing agent as well, because it has 4 hydrolysable H⁺ and strong complexing due to the chelation. Boric acid (H₃BO₃) was not being considered, because it is prone to precipitation at room temperature. So, the chosen ingredients were NiSO₄·6H₂O, H₃PO₄, H₃PO₃ and HEDP. The pH value was adjusted by potassium hydroxide (KOH) and sulfuric acid (H₂SO₄).

2.3 Design of Experiments (DOE)

In order to make the design of orthogonal experiments more accurate, some preliminary experiments were conducted in the basis of experience and references to test the boundary of the bath ingredient concentration and pH value (refer to Table 1).

After that, orthogonal DOE (refer to Table 2) was designed with five factors and four levels based on the results of the above preliminary experiments. These experiments were expected to find out the optimized content of each ingredient in the plating solution and the pH value for higher P content in the coating with higher current efficiency. The optimized bath formulation was further tested at different plating voltages.

2.4 Materials and experimental methods

Carbon steel was used as the substrate material of testing coupons in this work. The electrolytes for surface cleaning and activating were obtained from a chemical supplier (Sterling Impreglon Asia Pte Ltd). The samples were electro-cleaned by 15 V for 0.043 Ah, and then activated using activator-2 under -10 V for 0.01 Ah and activator-3 under -15 V for 0.02 Ah. Brush plating was conducted under 12 V for 0.5 Ah. The P content was detected by EDS. The current efficiency was calculated based on the measurement of sample mass change.

3 Results and Discussion

3.1

Preliminary experiments with the formulations of different compositions and pH value, and resulted P contents in NiP coating, as well as current efficiency were summarized in Table 1.

Table 1. The formulation of plating baths and plating test results at plating voltage of 12V.

Exp. No	NiSO ₄ ·6H ₂ O	H ₃ PO ₄	H ₃ PO ₃	HEDP	pH	P content (wt%)	Current efficiency (%)
1	200 g/L	10 g/L	20 g/L	30 g/L	0.91	7.7	21.8
2	200 g/L	10 g/L	50 g/L	0 g/L	0.96	8.5	10
3	200 g/L	10 g/L	50 g/L	20 g/L	1.35	6.6	19.8
4	200 g/L	10 g/L	60 g/L	0 g/L	1.50	5.6	12.5
5	200 g/L	50 g/L	60 g/L	0 g/L	1.35	10.3	15.1
6	200 g/L	50 g/L	40 g/L	0 g/L	1.50	7.3	17.1
7	200 g/L	50 g/L	60 g/L	0 g/L	1.50	7.4	17.9
8	200 g/L	50 g/L	80 g/L	0 g/L	1.50	9.9	17.4
9	200 g/L	50 g/L	100 g/L	0 g/L	1.50	11	7.6

The experiments 1-5 were conducted based on literature, and the results do not meet the expectation of the project, i.e., higher P content than 10 wt.% and current efficiency of about 20%. H₃PO₃ was the source of P in brush plating. The experiments 6-9 were used to test the effect of H₃PO₃ concentration on P content and current efficiency. The results are shown in Fig. 2.

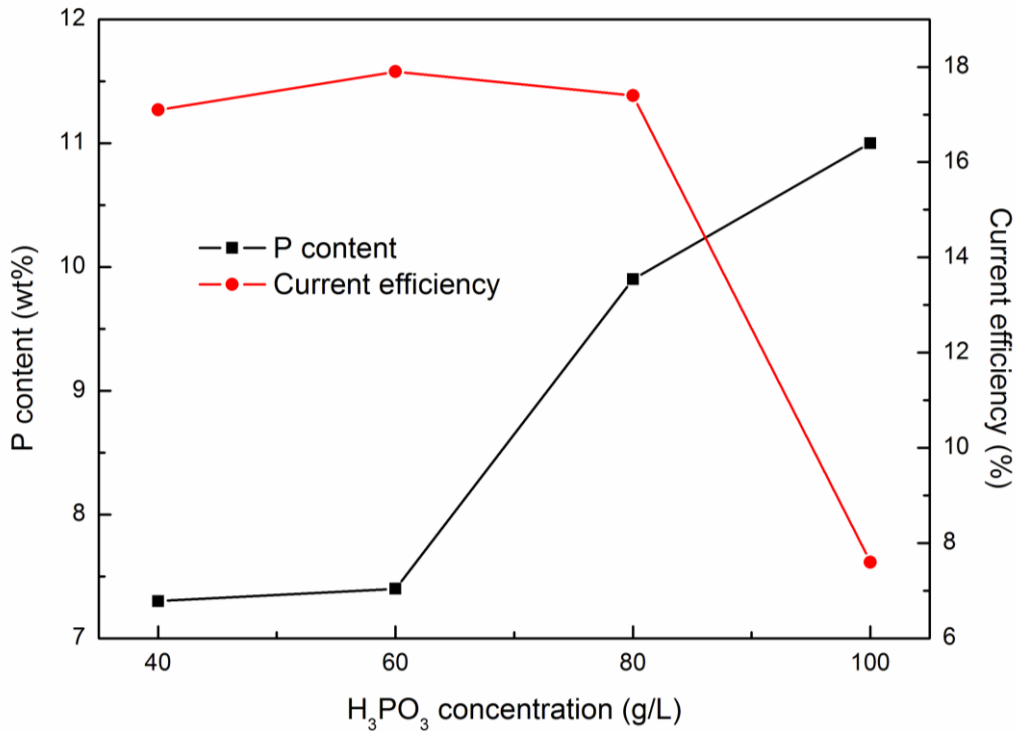


Fig. 2. The effect of H₃PO₃ concentration on P content and current efficiency.

As shown in Fig. 2, with the increase of H₃PO₃ concentration, the P content in NiP coating increases to 11 wt.%, and the current efficiency decreases down to 7.6 %. As described above, H₃PO₃ was the only source of phosphorus for NiP deposit in this study, therefore, the increased H₃PO₃ concentration would promote the deposition of phosphorus. On the other hand, H₃PO₃ is a weak complexing agent of Ni²⁺ due to the existence of P-O- species. The increase of H₃PO₃ in the plating bath would suppress the deposition of Ni, and therefore, lower down the current efficiency. The results show that an optimization of the bath formulation is required. In this study, DOE (orthogonal experiments) was used for this purpose, as shown in Table 2.

Furthermore, the H₃PO₄ was used to suppress the oxidation of H₃PO₃. HEDP was used as pH buffering agent and complexing agent of Ni²⁺. It is noted that low pH value and high H₃PO₃ are beneficial for high P content. On the contrast, high pH value and low HEDP were beneficial for high current efficiency. The design of orthogonal experiments, DOE results and scores are shown in Table 2, Table 3, and Table 4, respectively.

Table 2 Design of orthogonal experiments with five factors and four levels

Level	1	2	3	4
Factors				
NiSO ₄ .6H ₂ O (g/L)	100	150	200	250
H ₃ PO ₄ (g/L)	10	30	50	70
H ₃ PO ₃ (g/L)	30	50	70	90
HEDP (g/L)	0	20	40	60
pH	1	1.3	1.6	2

According to the results given in Table 3, the pH value and H₃PO₃ concentration have greater impact on P content and current efficiency. Low pH value and high H₃PO₃ concentration were beneficial for high P content. High pH value and low HEDP concentration were beneficial for high current efficiency. Based on the score of orthogonal experiments given in Table 4, three optimal bath formulations were selected and

shown in Table 5, which meet the requirements for phosphorous content (>10 wt%) and current efficiency (>19%).

Table 3 Testing results of orthogonal experiments

Level Exp. No	NiSO ₄ . 6H ₂ O	H ₃ PO ₄	H ₃ PO ₃	HEDP	pH	P content (wt%)	Current efficiency (%)	Score
1	1	1	1	1	1	7.0	18.8	0+2 (2)
2	1	2	2	2	2	7.8	13.7	0+1 (1)
3	1	3	3	3	3	13.0	4.5	3+0 (3)
4	1	4	4	4	4	15.9	-2.4	3+0 (3)
5	2	1	2	3	4	11.2	19.9	2+2 (4)
6	2	2	1	4	3	10.2	8.7	1+0 (1)
7	2	3	4	1	2	15.5	2.3	3+0 (3)
8	2	4	3	2	1	16.4	-7.7	3+0 (3)
9	3	1	3	4	2	12.4	9.6	3+0 (3)
10	3	2	4	3	1	15.3	-16.5	3+0 (3)
11	3	3	1	2	4	5.8	18.0	0+2 (2)
12	3	4	2	1	3	9.3	21.6	0+3 (3)
13	4	1	4	2	3	10.7	23.5	1+3 (4)
14	4	2	3	1	4	10.5	31.8	1+3 (4)
15	4	3	2	4	1	9.4	-2.2	0+0 (0)
16	4	4	1	3	2	7.4	22.0	0+3 (3)

Table 4 The score of orthogonal experiments

P content (wt.%)	<10	10-11	11-12	>12
Score	0	1	2	3
Current efficiency	<10	10-15	15-20	>20
Score	0	1	2	3

Table 5 The optimized formula of orthogonal experiments

Exp. No	NiSO ₄ .6H ₂ O	H ₃ PO ₄	H ₃ PO ₃	HEDP	pH	P content (wt%)	Current efficiency (%)
5	150 g/L	10 g/L	50 g/L	40 g/L	2	11.2	19.9
13	250 g/L	10 g/L	90 g/L	20 g/L	1.6	10.7	23.5
14	250 g/L	30 g/L	70 g/L	0	2	10.5	31.8

Table 5 shows that HEDP may not be a necessary ingredient in the plating bath. For example, high phosphorus (10.5 wt%) and high current density (31.8%) was obtained simultaneously from bath formula 14, which contains zero HEDP. It should be noted that this chemical bath contains more H₃PO₄ than other two, which implies that HEDP and H₃PO₄ can be exchangeable to some extent. Further study is needed to understand the effects of the two ingredients on the current efficiency and the phosphorus content in the resulted coating.

Table 6 The repeatability evaluation of some tests in orthogonal experiments

Exp. No	NiSO ₄ .6H ₂ O	H ₃ PO ₄	H ₃ PO ₃	HEDP	pH	P content (wt%)	Current efficiency (%)
5	150 g/L	10 g/L	50 g/L	40 g/L	2	11.6	19.7
13	250 g/L	10 g/L	90 g/L	20 g/L	1.6	10.5	19.7

14	250 g/L	30 g/L	70 g/L	0 g/L	2	11.0	25.2
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Repeatability test for the optimal bath formulations were carried out, and the testing results are given in Table 6. Compared with Table 5, it is found that the repeatability is very high. All the three bath formulations can be used to deposit NiP coating with high phosphorus and high current efficiency. However, the max. phosphorus obtained with a current efficiency of about 20% is still less than 12 wt%. To further increase the phosphorus content in NiP coating, the effect of plating voltage was investigated. With decreasing the operating voltage from 12 V to 10 V both P content and current efficiency were changed, as shown in Table 7. It is found that by using bath formula 14 and plating with 10 V, NiP coating containing phosphorus of 13.7 wt.% was deposited with a current efficiency of 19.4 %. It is obvious that the decreased plating voltage significantly increases the P content of NiP coating, with a loss of current efficiency.

Table 7 The repeatability evaluation of some tests in orthogonal experiments

Exp. No	NiSO ₄ 6H ₂ O	H ₃ PO ₄	H ₃ PO ₃	HEDP	pH	P content (wt%)	Current efficiency (%)
5	150 g/L	10 g/L	50 g/L	40 g/L	2	8.6	12.8
13	250 g/L	10 g/L	90 g/L	20 g/L	1.6	15.1	13.9
14	250 g/L	30 g/L	70 g/L	0 g/L	2	13.7	19.4

4 Conclusion

DOE was used to develop brush plating process, including plating bath formulation and plating parameters. More specifically, by varying pH value from 1 to 2, the bath chemistry was optimized by using DOE with five factors and four levels, and the effect of each ingredient was discussed. The effect of operating voltage (10 V and 12 V) on P content was also studied. It is found that low pH value and high H₃PO₃ concentration in the plating bath are beneficial for high P content in the NiP deposit. High pH value and low HEDP concentration are beneficial for high current efficiency. By using the optimized bath chemistry and plating parameters, NiP coating with P content of 13.7 wt.% was deposited on carbon steel coupons with a current efficiency as high as 19.4 %.

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