EFFECT OF pH ON THE CHARACTERISTICS OF ELECTROLESS Ni-P COATINGS

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Abstract

In this study electroless Ni-P coatings were deposited on W302 steel substrates. The effects of bath pH and heat treatment at 400 °C were investigated on the surface morphology, phase structure, phosphorus content, thickness and microhardness of the coatings. It was observed that both the phosphorus content and coating thickness are dependent on the bath pH. In an acidic/neutral bath, low and medium phosphorus coatings with thickness of 13.9-19.8 μm were synthesized, while in an alkaline bath, high phosphorus, 4.8-5.8 μm-thick coatings were formed. Coatings containing medium or high P seemed to be amorphous, while low P coatings had microcrystalline structures. Hardness was also dependent on the composition of the coating. After heat treatment, the structure of the coatings transformed into crystalline Ni with the precipitation of Ni_3P phases, which resulted further increases in hardness.

Keywords: Ni-P coating; P content; Hardness; Effect of pH; Heat treatment.

1. Introduction

In many fields of industry, tools, machines, parts and other devices with high hardness and proper wear and corrosion resistance are required to resist the load of environmental and technological influences. These properties can be achieved efficiently and economically by producing electroless nickel-phosphorus (Ni-P) coatings. Ni-P coatings are widely used in the aerospace, automotive and chemical industries, and also in oil production. In order to facilitate solderability as well as a protective sub-layer of certain assets (eg. memory disks), they are also preferred for use in the electronic industry.

Electroless deposition process is an autocatalytic method, driven by chemical reactions without the need of external electric current. When applying sodium hypophosphite as a reducing agent, Ni-P alloy coatings can be synthesized. Thus obtained Ni-P coatings have a non-equilibrium phase structure that can be amorphous, microcrystalline or a combination of the two phases [1-2]. After heat treatment, equilibrium phase structure can be obtained by the formation of crystalline Ni and the precipitation of nickel-phosphide (Ni_3P) [3-4].

The electroless deposition process can be expressed by two overall reactions, which describe the reductions of the Ni and P elements:

$$2H_2PO_2^- + Ni^{2+} + 2\ H_2O \rightarrow 2H_2PO_3^- + H_2 + 2\ H^+ + Ni^0 \quad (1)$$

$$2H_2PO_2^- + 2\ H \rightarrow 2\ P + 2\ OH^- + 2\ H_2O \quad (2)$$

This method has the advantage that the geometric roughness of the surface to be coated does not affect the thickness of the deposited coating [5]. By controlling bath parameters (bath composition, pH, temperature), the physical and mechanical properties of the coatings can be modified within a certain range [6]. Ni-P coatings can be deposited effectively on steel [7-9], aluminium and aluminium alloys [10, 11], other metals and alloys [12-13], plastics [14-15] and ceramics as well [16-17].

One of the most important requirements for electroless coatings is to achieve proper adhesion between the substrate/coating interfaces [18-19]. In case of steel substrates, the adhesion improving effect of nitriding process has also been reported [20].

In the electroless plating technique, the use of stabilizers is also recommended, e.g. thiourea [21-22], Pb-acetate [23], maleic acid [24], etc., by which the lifetime of the bath can be increased. The applied stabilizer and its concentration also influence the deposition rate, surface morphology and microstructure of the coatings [25-26].

The phosphorus content affects the phase structure of the formed coating. Fundo et al. [2] found that the

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increase of phosphorus content results in a more amorphous structure. For coatings with low P content (4 at%) the structure was still crystalline, in medium P coatings (6.9 at%) amorphous structure incorporating microcrystallites was observed, while high P content (13.8 at%) resulted in amorphous structure. The surface morphology was also affected by the P content.

Surfactants may also be added to the Ni-P bath, which can influence the properties of the coatings, and the conditions of deposition [27-28]. Chen et al. investigated the effects of using different types of surfactants. With their use, it was observed that the deposition rate of the coatings can be increased up to 25%, the porosity of the coatings can be reduced, and the corrosion resistance of the coatings can be significantly increased [29].

Chang et al. [30] studied the effects of bath pH in acidic (pH4-pH6) and in alkaline (pH8-pH10) ranges. In acidic medium their coatings were amorphous, while in alkaline medium coatings with crystalline structure were formed. The highest degrees of hardness were exhibited by coatings prepared using a pH5 (701 $HV_{0.05}$) and a pH8 bath (803 $HV_{0.05}$). After heat treatment, a further increase in hardness was achieved.

The aim of our study is a systematic investigation of the effects of bath pH altered over a wide range (pH 4.2-pH 9.2) on the properties of electroless Ni-P coatings, including the phosphorus content of the coating, which is less mentioned in literature. In most papers, mild steel is being used as a substrate. In our study, for this purpose a medium-chromium steel was used (W302), which is less frequently investigated. Furthermore, the effect of thiourea in our system is also discussed.

2. Experimental

Ni-P coatings were deposited on W302 steel (Böhler-Uddeholm Hungary Ltd.) substrates. The chemical composition of the steel is given in Table 1. Samples with dimensions of 17 mm x 8 mm x 3 mm were cut. Prior to the deposition process, the steel samples were grinded with emery paper (600, 800) then were polished to finish their surface. Next, they were ultrasonically cleaned in acetone bath for 15 minutes, followed by alkaline degreasing in a 10 wt% NaOH solution at 80 °C for 25 minutes. Finally, the surface of the specimens was activated in 35 wt% HCl solution for 1 min. After each step a distilled water rinse was applied.

Nickel sulphate ($NiSO_4 \cdot 6H_2O$) was purchased from VWR Chemicals Ltd., while sodium acetate ($NaH_2PO_2 \cdot H_2O$) and sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$) were obtained from Molar Chemicals Ltd. Sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) was bought

Table 1. *Chemical composition of W302 steel*

Element	Composition [%]
C	0.39
Si	1.1
Mn	0.4
Cr	5.2
Mo	1.4
V	0.95
Fe	90.56

from Spectrum 3D, and thiourea was purchased from Reanal Private Ltd. The bath compositions and the operating conditions used for the experiments are listed in Table 2. Nickel sulphate was the source of Ni ions, sodium hypophosphite served as the reducing agent and thiourea was used as a stabilizer. The Ni-P bath was divided into acidic/neutral and alkaline baths. The difference was in the applied complexing agent. In the acidic/neutral bath sodium acetate was used, while in the alkaline bath sodium citrate was applied. The pH adjustment was carried out with a Thermo Scientific Orion 3 Star pH meter using 10 wt% sulfuric acid and 10 wt% sodium hydroxide. Adjusting an acidic/neutral medium could be done using Na-acetate complexing agent. However, with the use of this agent, precipitation of nickel-hydroxide inhibited the adjustment of alkaline pH value. For this purpose, Na-citrate proved to be more appropriate.

Table 2. *Bath compositions and operating conditions used for electroless Ni-P deposition*

Bath pH	Bath composition	Concentration	Conditions
Acidic/neutral (pH 4.2, 5.2, 6.2, 7.2)	$NiSO_4$	15 g/l	Temperature: 80 °C Stirring rate: 200 rpm Deposition time: 60 min Bath volume: 50 ml
	CH_3COONa	13 g/l	
	NaH_2PO_2	14 g/l	
	Thiourea	1 mg/l	
Alkaline (pH 8.2, 9.2)	$NiSO_4$	15 g/l	
	$Na_3C_6H_5O_7$	50 g/l	
	NaH_2PO_2	14 g/l	
	Thiourea	1 mg/l	

The as-plated steel samples were sealed in a stainless steel tube containing argon shield gas. After that they were heat treated in a LT-S/1200 model furnace, at 400 °C for 1 h, followed by air cooling to room temperature.

The thickness of the deposited coatings was measured with a Zeiss optical microscope and its software. Images of the surface morphology and cross

section of the coatings were captured and studied by Scanning Electron Microscopy (ZEISS EVO MA 10 and HITACHI S-4800 models). The phosphorus content was analysed using energy dispersive spectroscopy (EDS).

The phase structure of the coatings was investigated with X-ray diffractometry (XRD), using a Bruker diffractometer (D8 Advance model) with Co Kα radiation. Microhardness measurements on the cross sections of the coatings were carried out using a Mitutoyo MVK H1 hardness tester, applying a load of 10 g, with a holding time of 10 s.

3. Results and Discussion
3.1 Chemical composition and thickness of the Ni-P coatings

The P content of Ni-P coatings as a function of the bath pH is shown in Fig. 1. Initially, P content decreases with increasing pH value. Upon reaching pH 6.2 and 7.2, the P contents are 3.67 and 3.75 wt% respectively, which are the minimum P contents in our system. This phenomenon is attributed to the P reduction reaction (1.2) which is retarded with increasing pH, as the amount of OH⁻ ions increases, agreeing with results in the literature [31]. However, upon reaching pH 8.2 there is a sharp increase in the amount of phosphorus. The coating deposited at pH 8.2 has the maximum P content of 13.48 wt%. This increase is probably due to the presence of thiourea, and the change of the complexing agent. In lower concentrations ($\leq$ 1 mg), thiourea promotes the reduction of Ni^{2+} ions in acidic solution [32-33]. However, in alkaline bath, it might decompose and form urea [34]. This behaviour can influence the Ni-P reduction process, and inflict a change on the coating composition. As Figure 2 shows, the thickness of the electroless deposited coatings increases with increasing pH in the acidic range. The thickest coating (19.8 µm) was formed at pH 6.2. For a neutral pH, the thickness of the coating starts to decrease, and at alkaline pH (8.2 and 9.2) the thinnest coatings were formed with 4.8 and 5.8 µm thickness, respectively. In acidic range, the increase of bath pH favours the reduction of Ni^{2+} (1.1), which results in higher deposition rate. When reaching alkaline pH, the effect of changing the complexing agent and the decomposition of thiourea might also cause a decline in deposition rate.

The pH 6.2 sample with the thickest coating was chosen for further studying the rate of formation of the coating. The change of the coating thickness as function of deposition time is shown in Fig. 3. A quadratic equation passing through zero was fitted through the experimental points with R^2=0,9995. Therefore, the deposition rate can be estimated as:

$$v = \frac{d\mathrm{d}}{d\mathrm{t}} = 0.1342 \ + \ 0.00656t$$

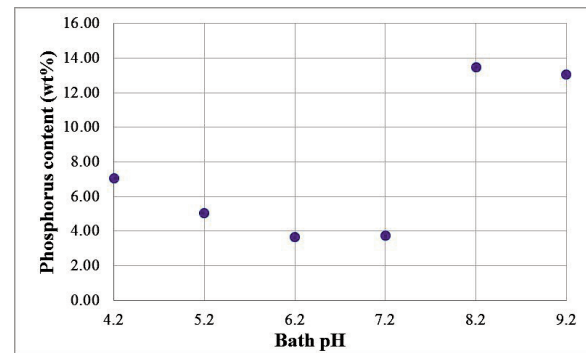where d = coating thickness (µm), t = deposition time (min).

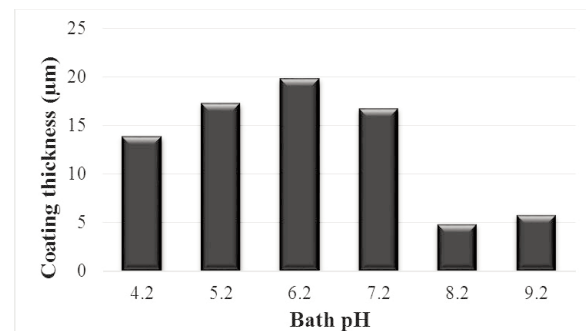**Figure 1.** *P content of the Ni-P coatings as a function of the bath pH*

Figure 2. *The thickness of Ni-P coatings as a function of the bath pH*
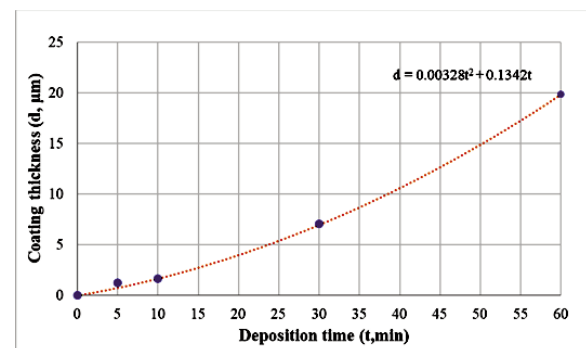

Figure 3. *Coating thickness of the pH 6.2 sample as a function of deposition time*

3.2 Surface morphology and cross-sectional study of the coated samples

Figure 4 shows SEM images of the surface morphology of the coated samples. It can be seen that the coating at pH 4.2 (Fig. 4a) is smooth with darker pits, which may occur during the synthesis of electroless Ni-P coatings [29]. The surfaces of samples pH 5.2 and pH 6.2 (Fig. 4b,c) as well as

pH 8.2 and pH 9.2 (Fig. 4e,f) are similar; the coatings are made up of small cauliflower-like nodules. Above the value of pH 5, this kind of appearance can be attributed to the presence of thiourea in the bath [24]. In the last two cases, (Fig. 4e,f) finer surface morphology can be observed. The pH 7.2 sample (Fig. 4d) has an interesting morphology: larger spheroidal cauliflower-like clusters have grown on the finer structured surface.

The cross sections of the samples are illustrated in Fig. 5. It can be clearly seen that the coatings were formed uniformly with no visible cracks, which refers to proper adhesion between the substrate and the coating.

3.3 Microstructure and microhardness of the coatings

The results of XRD analysis showed that coatings with medium and high P content were amorphous, while low P content samples had semi-amorphous microstructure. After heat treatment, the microstructure of the coatings transformed into crystalline Ni with precipitated Ni_3P phases in accordance with literature [2-3].

Figure 6 shows the hardness of the Ni-P coated samples before and after heat treatment. The values are the average of three measurements. The hardness of the substrate was 204 $HV_{0.01}$. It can be clearly seen that the coatings reached a higher hardness in all cases.
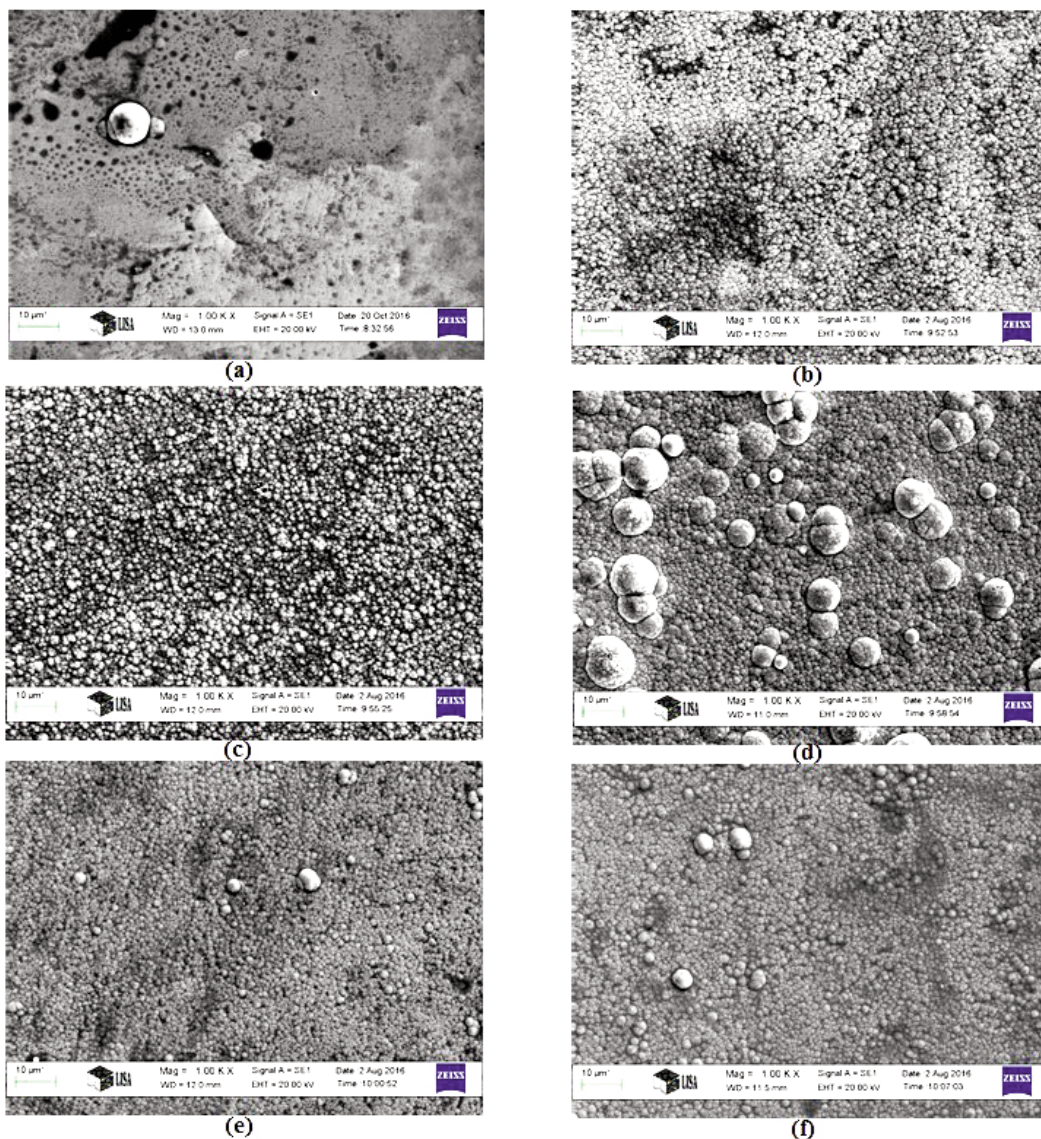

Figure 4*. SEM (SE) images of the surface of electroless coated samples prepared from baths with different pH: (a) pH 4.2 (b) pH 5.2, (c) pH 6.2, (d) pH 7.2, (e) pH 8.2, (f) pH 9.2*
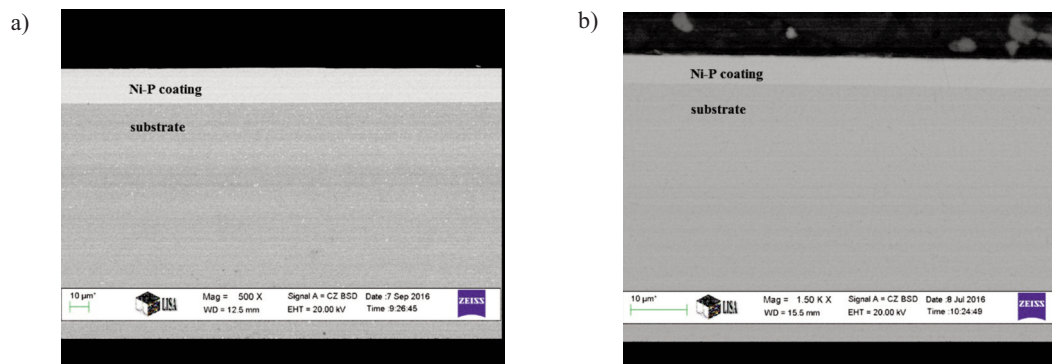
a)

b)

Figure 5. *SEM images of the cross sections of two coated samples: (a) pH 4.2 (M500x); (b) pH 8.2 (M1500x)*

As shown, the hardness of the as-received coatings increases with decreasing P content. The coating (pH 6.2 sample) with the lowest P content (3.67 wt% P) has the highest degree of hardness: 634 HV0.01, while 363 HV0.01 of the coating (pH 8.2 sample) with the highest (13.48 wt%) P content.

After heat treatment, the hardness values of the samples increased in all cases. In the case of low (pH 5.2–pH 7.2) and middle (pH 4.2) P content, the hardness increased and reached nearly the same value of 685 ± 10 HV$_{0.01}$. Nevertheless, in the case of higher P content (pH 8.2-9.2) the hardness reached 745-774 HV$_{0.01}$. This increase is presumably due to the higher P content, which resulted in a higher amount of Ni$_3$P compound formation in the coating. The hardness of the coatings obtained from alkaline bath reached double of their initial value after heat treatment, while in the case of samples prepared from acidic/neutral bath this increase was much lower.

4. Conclusions

In this research electroless Ni-P coatings were prepared on W302 steel. The coatings were prepared from baths with different pH (pH 4.2–pH 9.2). The as-coated samples were then heat treated at 400 °C. During our study, the following results were obtained:

1. The pH of the bath has an effect on the P content of the Ni-P coatings. P content is lowest, namely 3.7 ± 0.1 wt% at pH 6.2 and pH 7.2; while the highest P content of 13.2 ± 0.2 wt% was obtained at pH values of 8.2 and 9.2.

2. The thickness of the Ni-P coatings depends on the bath pH. The coatings prepared from acidic or neutral baths have a thickness of 13.9-19.8 μm, coatings synthesized from an alkaline bath were 4.8-5.8 μm thick. A connection was also observed between the phosphorus content and the coating thickness: with an increasing amount of P atoms in the
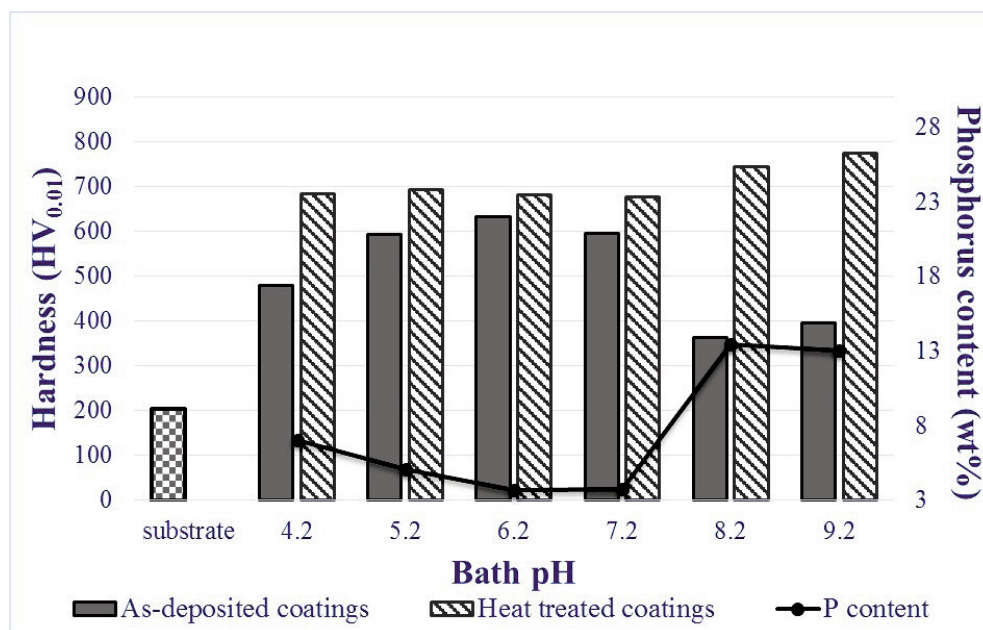
Figure 6. *Hardness of as deposited and heat treated Ni-P coatings as a function of bath pH*

coating, the thickness decreased.

3. The XRD investigation reveals that the coatings with low P content have a semi-amorphous structure, while medium and high phosphorus coatings are amorphous. Due to the heat treatment at 400 °C, Ni_3P compounds precipitated in the coating and crystalline Ni phase was formed.

4. The hardness of electroless Ni-P coating depends on their P content. The hardness decreases with increasing P content. The highest hardness, namely 634 $HV_{0.01}$, was reached at 3.67 wt% P (pH 6.2).

5. After heat treatment at 400°C, the hardness of the samples with high (13.48 wt%) phosphorus content exceeds the hardness of heat treated samples with lower (3.67-7.0 wt% P) phosphorus content, which is presumably due to the formation of a higher amount of Ni_3P compound.

Acknowledgements

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