



ELECTROLESS NI-P DEPOSITION PLUS NICKEL PROSPEROUS COATING ON AZ91D MAGNESIUM ALLOY

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ABSTRACT

An electroless Ni-P deposition procedure has been advanced to treat the AZ91D magnesium alloy surfaces against corrosion. Magnesium alloy AZ91D became first sulfated in a nickel sulfate bath containing thiourea-molybdate. Then an electroless Ni-P deposition became performed on the sulfate coating from a sulfate answer. The stages in the sulfate coatings had been analyzed by way of XRD. Microstructures of sulfate coatings and electroless Ni-P depositions have been located by using SEM and EDS. It was located that there has been metal nickel inside the sulfate coating and the addition of thiourea-molybdate in the sulfating bathtub resulted within the boom of nickel in the coating. Quite a few disperse steel nickel particles acted because the catalyst nuclei for the succeeding Ni-P deposition. Therefore, the Ni-P depositions with dense and first-rate microstructure have been acquired on the sulfate coatings received from the sulfating bath in which 10.0~12.5g/l thiourea molybdate turned into introduced. The Ni-P plus nickel sulfate coatings at the AZ91D magnesium alloy exhibited ideal corrosion resistance as shown via the effects of the salt spray corrosion test.

Keywords: magnesium alloy, sulfating, electroless deposition, corrosion resistance.

1. INTRODUCTION

Magnesium alloy has low density, excessive energy-to-weight ratio and different properly physical and mechanical characteristics, which makes it viable for structural packages within the aerospace, electronics and automobile fields. But, the usage of magnesium alloys has been limited because of their undesirable houses that encompass bad corrosion and occasional wear resistance. Consequently, formation of anticorrosion and excessive wear-resistance coatings at the floor of Mg or Mg alloys is vital in realistic programs [1-3]. On the grounds that magnesium is one of the maximum electrochemically active metal, regular coatings, such as nickel, copper and nickel coatings, can most effective provide a physical barrier in opposition to the corrosion assault of magnesium substrate. So, any coatings on magnesium alloys have to be uniform, adherent and porosity loose as viable. Electroless deposition technique of ni and Ni-P alloy coatings has been a well-known commercial method that has determined numerous programs in many fields because of its manufacturing of outstanding coatings which can be corrosion-resistant, excessive put on-resistant and own properly lubricity, high hardness and appropriate ductility [4-8].

There were a few reviews on the electroless plating Ni and Ni-P on magnesium alloys [9-14]. However, it's far stated that in those reviews on the electroless plating on magnesium, the nickel ions have been provided by means of basic nickel carbonate in the plating bathtub. Also, in the electroless in plating process on magnesium alloy [13], the samples have been etched first in an answer of chromate and nitric acid after which

soaked in HF way to form a conversion film before electroless nickel deposition happened. However chromium compounds are carcinogenic materials that must be used with caution. In our preceding work, an electroless Ni-P deposition on AZ91D magnesium alloy from a plating tub containing sulfate nickel was proposed [15].

In this study, AZ91D magnesium alloy samples had been first pretreated in a nickel sulfating bath to gain a sulfate coating. Then, the electroless Ni-P deposition at the sulfate coating was undertaken via using the plating bathtub containing sulfate nickel. The influences of thiourea molybdate (Na₂MoO₄) inside the sulfating tub at the microstructure of sulfate coating and the microstructure and corrosion resistance of the final electroless Ni-P deposition were studied.

2. MATERIALS AND METHODS

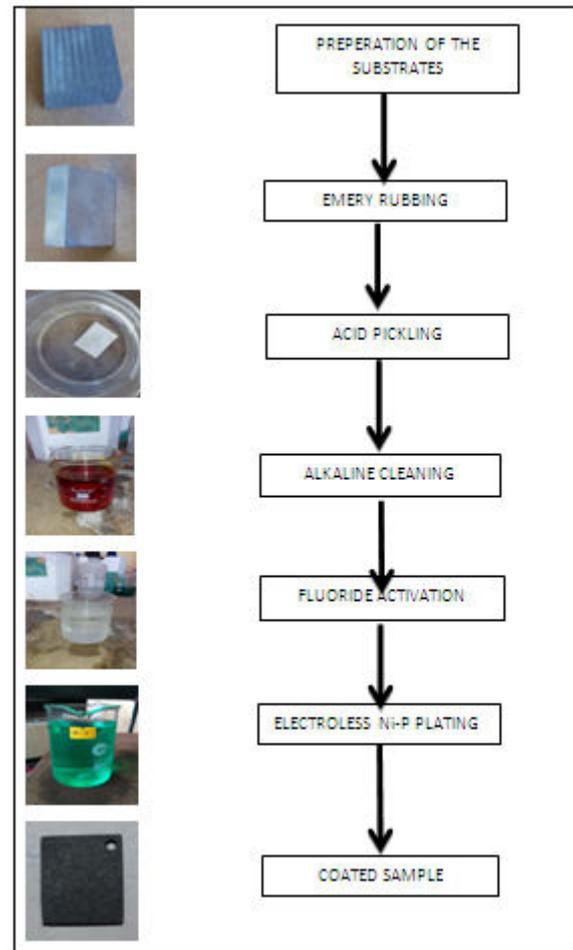
Electroless deposition technique of Ni-P alloy coating has been a well-known industrial method that has found numerous packages in lots of fields due to tremendous residences of coatings, along with high corrosion-resistant, excessive wear-resistant, right lubricity, excessive hardness and suited ductility. Every other benefit of the electroless deposition method is that every uniform coating may be acquired without special necessities for substrate geometries. But, electroless coating on different substrates, which includes magnesium alloys, has many demanding situations within the processing of plating and there are very restrained reports on electroless plating on magnesium alloys. Table-1 depicts the composition of AZ91D magnesium alloy.

**Table-1.** The compositions of the AZ91D magnesium alloy (in wt.%).

| Al | Zn | Mn | Ni | Cu | Ca | Si | K | Fe | Mg |
|------|------|------|-------|-------|-------|-------|-------|-------|---------|
| 8.77 | 0.74 | 0.18 | 0.001 | 0.001 | <0.01 | <0.01 | <0.01 | 0.001 | Balance |

In this experiment, direct electroless Ni-P coating on the AZ91D magnesium alloy is undertaken by using the use of the plating bath containing nickel sulfate. Magnesium and its alloys have highly chemical interest and once they touch with air or water, oxide and hydroxide films might be fashioned on the floor, which might have a determinant impact on the coating adhesion and uniformity. Nonetheless, a totally specific pre-treating method and unwavering experimental situations yield a great shielding coating on AZ91D magnesium alloy. As a consequence the pre-treating processes play a completely critical function in getting a terrific protective coating on magnesium and its alloys.

The deposition coating of electroless Ni-P is typically now not very dense. There are micro-holes or gaps between the micrometer clusters (which are consisted of amorphous or nanocrystalline grains). Consequently, a porosity take a look at changed into proposed to assess the porosity of the Ni-P coating on magnesium alloy. that is, a filter out paper was soaked in a reagent answer of 10 g/l NaCl, 106 g/l ethanol and zero.1 g/l phenolphthalein dissolved in distilled water. Then the clear out paper with the reagent solution became pasted onto the nickel coating for 10 min. After taking the filter out paper away, crimson spots or crimson areas had been stated on the surface of the coating. The porosity of coating is evaluated particularly through the ratio of crimson spot vicinity to the sector vicinity formerly pasted via the filter out paper. The precept of the approach is that, if there are microwaves at the coating penetrating to the base alloy, magnesium within the magnesium alloy is being eroded by means of the NaCl solution. on the equal time hydrogen gives out at the surface and H⁺ ions are fed on, a number of OH⁻ ions collect in answer of the filter paper, which makes the phenolphthalein inside the solution flip crimson. Figure-1; explain the process flow diagram of Ni-P deposition.

**Figure-1.** Process flow diagram.

3. RESULTS AND DISCUSSIONS

A magnesium alloy has excessive chemical reactivity, so fluoride activation of magnesium alloy in a HF solution is commonly used before chemical treatment [16, 17]. The formation of Mg movie at the floor can restrain the corrosion of the Mg matrix. Within the present test, a mixture of sodium fluoride and organic amine (NaF: organic amine = 8.5: 1 in weight) become used as anticorrosion agent and changed into without delay introduced into the sulfating bathtub. Acetic acid changed into employed to reduce the production of the sludge within the sulfating tub. If no acetic acid became delivered in the sulfating bathtub, some insoluble sulfate will precipitate out as sludge in the bathtub. The sludge in the tub could impact the coating fine. Acetic acid can combine with a few insoluble sulfate to shape a solvable complicated compound to be able to stabilize the bathtub. AZ91D magnesium alloy is used as the substrate fabric. The work piece of size 30mm length, 20mm width and 10mm thick (30*20*10) is machined for corrosion testing.



The work piece of dimension 8mm diameter and 30mm duration is machined for wear testing.

Pre-treatment method consists of 4 levels of cleansing the substrate surface, they may be emery rubbing, alkaline cleansing, acid cleaning, and fluoride activation. The purpose of these four stages is to clean the substrate floor in order that coating can be carried out simpler and uniformly. Emery rubbing: to get a replicate like clean structure to aid clean coating inspection and to get coating deposition in proper manner. Alkaline cleaning: to put off soil content material and greases. Acid cleansing: to get rid of the oxide layer gift on the floor fluoride activation: to create equipotential movie on the surface of the substrate, additionally eliminates oxide layer persists at the floor.

Magnesium and its alloys have notably chemical hobby and whilst they're in contact with air or water, oxide

and hydroxide movies would be fashioned at the floor, which would have a damaging effect on coating adhesion and uniformity. As a consequence the pre-treating procedure play a very essential function in getting an excellent shielding coating on magnesium and its alloys.

Requisites needed for pre-treatment process includes

- **Emery rubbing-** emery sheets (400, 600, 800, 1000, 2000)
- **Alkaline cleaning-** acetone solution
- **Acid cleaning-** chromium (iii) oxide (cr2o3)
- **Fluoride activation-** hydrogen fluoride (HF)



Figure-2. Emery sheets of grade 400, 600, 800, 1000, 2000.

- Requisites needed for electroless coating process
- **Nickel chloride-** source of nickel
 - **Sodium hypophosphite-** reducing agent
 - **Sodium acetate -** complexing agent
 - **Thiourea-** stabilizer
 - **Ammonia-** for stabilizing ph in the bath
 - **Nano Al₂O₃-** additive (40 - 60 nm)
 - **Nano SiO-** additive (40 - 60 nm)

3.1 Sample treatment of Ni-P alloy

The sample is cut into portions for coating and testing in step with the scale and the sample is cut for the dimension of 30mm diameter and 7mm height. The pattern became then polished with emery sheet (400, 600, 800, 1000, 1200) after which wiped clean with acetone. Later the alkaline cleansing becomes followed. Before placing the samples inside the en tub they have to be treated such alkaline cleaning methodologies. For this an answer was organized by means of dissolving sodium hydro-oxide (45g/l) and tri-sodium orthosulfate (10g/l) in distilled water. It became heated to 65oc and samples have been

dipped in that answer for 20 minutes. Then acid treatment with chromium tri-oxide (125g/l). Fluoride activation with HF ultimately.

3.2 Electroless coating- bath and operating conditions

The composition of the plating bathtub for electroless Ni-P deposits became taken as nickel sulphate because the supply of nickel, sodium hypophosphite because the steel decreasing agent, sodium acetate as a complexing agent, thiourea acts as a solution stabilizer and the ammonia solution (nh3.h2o) is used to adjust pH of the plating bath. The ph of the tub was maintained at 6.4 ± 2 by adding enough quantity of NaOH solution as and whilst required. This tub changed into stored in a water bath and heated. The temperature of the bathtub was controlled and maintained at around 800c and the corresponding temperature of the electrolyte turned into monitored the usage of a thermometer. The coating turned into executed for a length of 1 hour with general volume of the plating tub.

Surface observations of sulfate coating and electroless Ni-P coating were realized with SEM (jms-5310, japan electronics) and EDS (inc250). The phases in sulfate coatings were analyzed by XRD (d/max-2500pc, cuka α). Salt spray exposure of about forty μ m Ni-P coating based on sulfate coating became done in a sf850 salt spray cabinet (atlas electric devices company) in line with astm



b117 general. A five wt.% nacl solution changed into used to create a salt fog within an enclosed chamber. Take a look at temperature of 35 °c turned into maintained.

SEM micrograph of the sulfate coatings formed on AZ91D alloy is shown in Figure-3. EDS evaluation on unique micro regions indicated that the clusters had been the complex of hopeite ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) and metal

nickel debris. There are some micro cracks (Figure-3 (a)) within the sulfate coating that become received from the bath with out Na_2MoO_4 . And the sulfate coating received from the bathtub containing Na_2MoO_4 has less micro cracks, see Figure-3 (b)~(f).

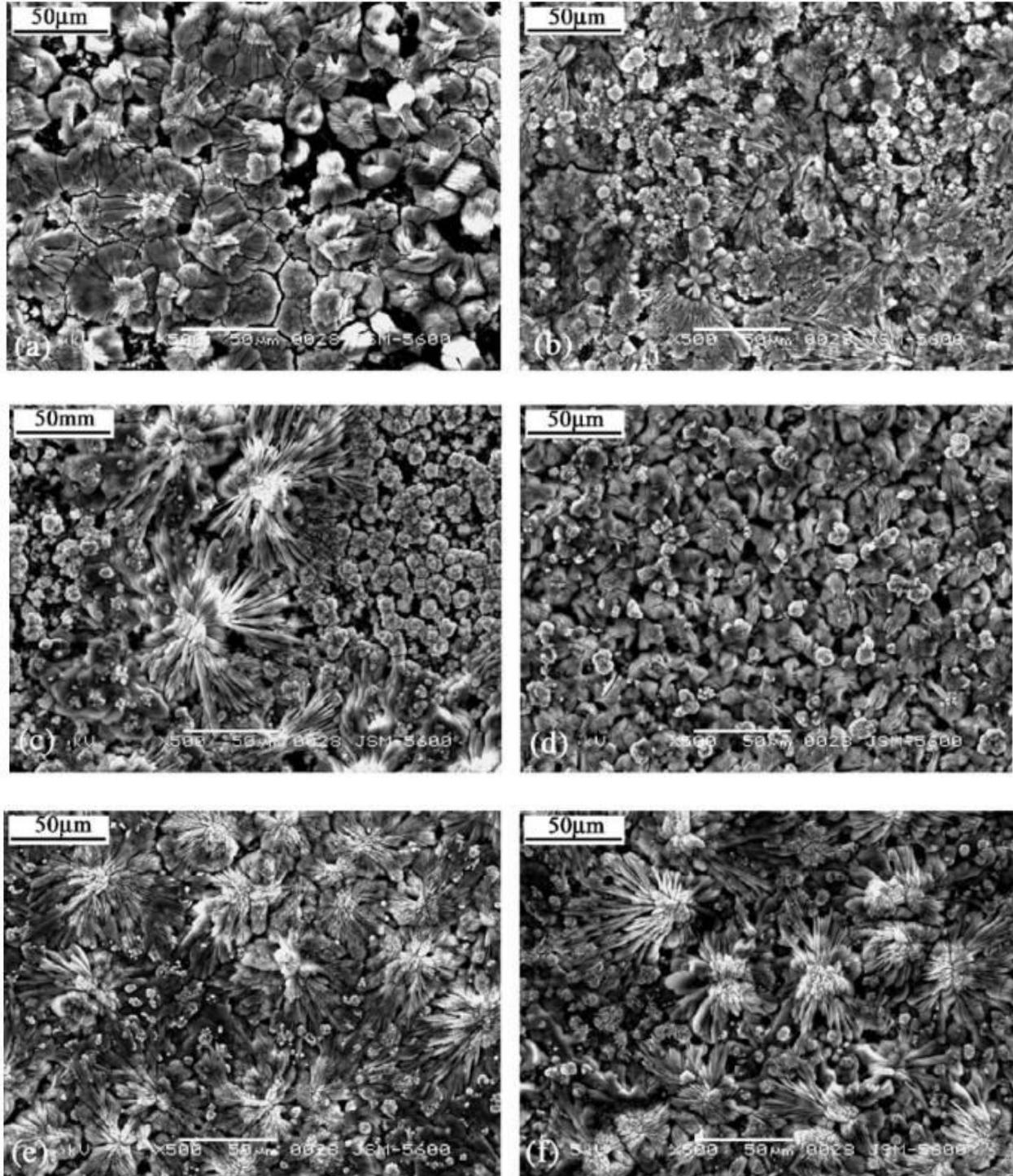


Figure-3. SEM micrographs of the morphologies of the Ni-P depositions deposited on the sulfate coatings of AZ91D magnesium alloy, the sulfate layers were.



Composition of AZ91D sulfate solution

The chemical composition of the bath is optimized as below after adjusting to obtain perfect coating as shown in below.

Table-2. Pre-treatment composition of solution for treatment.

| Chemical | Quantity per (Litre/ no) | Quantity per 200ml |
|--|--------------------------|--------------------|
| Emery sheets (400, 600, 800, 1000, 2000) | 1 | Nil |
| Sodium hydroxide | 45 g | 9g |
| Acetone | Required level | |
| Hydrogen fluoride | 350 ml | 70ml |

Sulfate coating is generally used as pretreatment or base coating for further surface treatment. Short sulfating time is an advantage for its application in industrialization. Therefore, an accelerator should be used. In previous studies [18, 19], it was found that nitrate and nitrite were effective to accelerate the formation of sulfate coating. In the sulfating bath, the nitrate and nitrite ions are strong oxidizing agents. During sulfating, the reduction of nitrate and nitrite resulted in the increase of local pH at metal-solution interface, which facilitated the precipitation of insoluble sulfate [18]. With the addition of nitrate in the sulfating bath, full sulfate coating on the AZ91D magnesium alloy formed in about 2-3 min.

Table-3. Electroless bath composition for treatment.

| Chemical | Quantity per liter | Quantity per 200ml |
|-----------------------------|----------------------|--------------------|
| Nickel chloride | 26g | 5.2g |
| Sodium hyposulfate | 30g | 6g |
| Hydrogen fluoride | 12ml | 2.4ml |
| Sodium acetate | 16g | 3.2g |
| Amonium hydrogen difluoride | 8g | 1.6g |
| Thiourea | 1ppm | 1ppm |
| Ammonia | Added to maintain pH | |

3.3 Electroless Ni-P deposition on the sulfating coating and its performance

A further electroless Ni-P deposition turned into found out at the sulfate coating on AZ91D alloy through the sulfate tub. The influence of Na₂MoO₄ attention in the sulfating bathtub on the microstructures of very last electroless Ni-P coatings become proven in fig. four. traditional microstructure of electroless Ni-P coating includes many “nodular-like” clusters. The phosphorus awareness inside the Ni-P deposition layer is about three.7 wt.% and the XRD diffraction taken at the electroless Ni-P coating indicated that the coating become a aggregate of

amorphous and nanocrystalline grains [15]. It's far visible that the cluster size reduced because the Na₂MoO₄ awareness in the sulfating bath will increase. This need to be attributed to the boom of nickel awareness within the sulfate coatings with the increase of Na₂MoO₄ in the sulfating bathtub. Due to the fact zn₃(po₄)₂· 4h₂o is a nonconductor section, throughout electroless deposition, nickel have to first deposit preferentially on nickel crystals and then enlarge to zones without nickel crystals. The growth of nickel crystals within the sulfate coating furnished extra nuclei for the deposition of ni and boom of Ni-P. Consequently, the cluster length decreases as the Na₂MoO₄ attention within the sulfating bathtub will increase. Because of the lower of cluster size, extra dense microstructures with much less micro-holes or gaps have been obtained.

The porosity (represented via the red location) of approximately 20, 40, and 60 μm thickness Ni-P coating became envisioned by using the porosity test proposed within the experiment part and the outcomes have been proven in Figure-5. It's far seen that for the 20 μm Ni-P coating the crimson area decreased hastily as the concentration of Na₂MoO₄ in the sulfating tub accelerated, and relatively dense Ni-P coatings had been received with the attention of Na₂MoO₄ within the sulfate tub being 2.0~2.5 g/l. The porosity of forty μm Ni-P coating on the sulfate coating rapidly decreases with increasing Na₂MoO₄ concentration within the sulfating tub (in tenths to 0) while the awareness within the bathtub is extra than 1.zero g/l. consequently, a thickness of Ni-P coating of about forty μm is vital to lower porosity to 0 and to guard the substrate from corrosion.

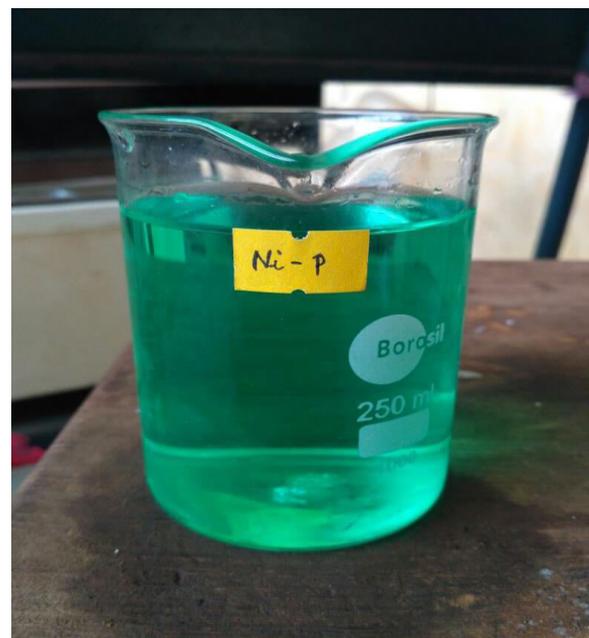


Figure-4. Preparation of electroless Ni-P bath.

3.4 Coated samples

This heat remedy also provided a advantage effect at the adhesion of the Ni-P coating to the base alloy.



The Ni-P coatings with and without the warmth treatment had been soaked in water (25 °C) for 240 h, a few blisters formed on the floor of the coatings. The blister vicinity on the coating surface was used to estimate the adhesion of the Ni-P coating to the base. The results had been shown in fig. 8. it is thrilling to look that after the heat remedy, the blister vicinity at the coatings greatly reduced. The

separation and diffusion-out of hydrogen atoms from the coatings can also take location throughout the warmth remedy at a hundred and eighty °C, which reduces the tensile or bulging strain of hydrogen in the coating and complements the adhesion of the coating to the bottom. The micro blisters fashioned in the coating had been visible in Figure-5.

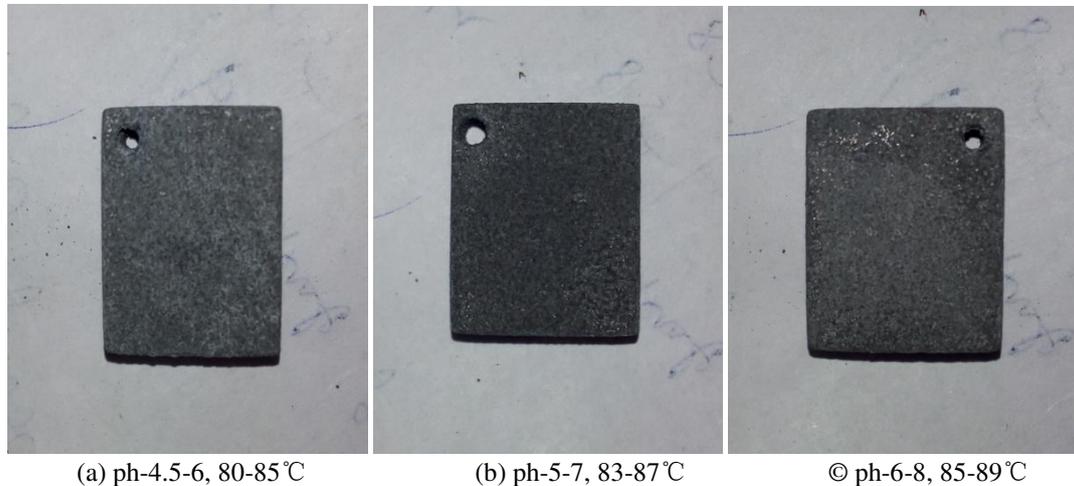


Figure-5. Coated samples by varying the time and pH.

The porosity (represented through the crimson vicinity) of approximately 20, 40, and 60 µm thickness Ni-P coating changed into anticipated by means of the porosity take a look at proposed in the test component and the consequences had been shown in Fig. five. it is seen that for the 20 µm Ni-P coating the crimson area reduced hastily as the awareness of Na₂MoO₄ in the sulfating tub expanded, and comparatively dense Ni-P coatings have been obtained with the concentration of Na₂MoO₄ in the sulfate bath being 2.zero~2.5 g/L. The porosity of 40 µm Ni-P coating on the sulfate coating rapidly decreases with increasing Na₂MoO₄ attention inside the sulfating bath (in tenths to 0) while the awareness in the bathtub is extra than 1.0 g/L. consequently, a thickness of Ni-P coating of about forty µm is necessary to lower porosity to zero and to protect the substrate from corrosion..

4. CONCLUSIONS

The sulfate coating at the AZ91D magnesium alloy turned into received from the bathtub containing in particular phosphoric acid and nickel oxide. There has been nickel inside the sulfate coatings and the addition of Na₂MoO₄ inside the sulfating bath resulted within the increase of nickel in the coating. The life of metallic nickel in the sulfate coating makes it possible to be because the pretreatment layer for further electroless Ni-P deposition. The Ni-P coatings with dense and satisfactory microstructure have been located on the sulfate coatings at the AZ91D alloy that turned into acquired from the sulfating tub in which 2.0~2.5g/l Na₂MoO₄ became introduced. The Ni-P plus sulfate coatings on the AZ91D magnesium alloy exhibited true performance. The salt spray check showed that they might face up to about 150 h

without corrosion. The surface hardness of the Ni-P coating is ready 670 HV, and its hardness become extended to approximately 915 HV thru the warmth treatment of two H at temperature of 180 °C.

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