Study on Preparation and Property of Ni-Co-P Coatings of AZ31B Magnesium Alloy

Xianguang Zeng[1,2 a *], Xingwen Zheng[1,b], Hong Luo[1,c], Xiuzhou Lin[1,2,d], and Xiaolang Jiang[1,e]

[1] Institute of Material and Chemical Engineering, Sichuan University of Science and Engineering, Zigong, Sichuan, 643000, China

[2].Material Corrosion and Protection Key Laboratory of Sichuan Province, Zigong 643000, China

[a*] hnzxg1979@126.com, [b] zxwasd@126.com, [c]luohong28@163.com, [d]linxiuzhou@163.com, [e]1252585567@qq.com

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Abstract. AZ31B was used as the basic material in electroless Plating of Ni-Co-P, The optimium formula and process conditions were obtained by using the orthogonal experiment methods. XRD, SEM and EDS were used to characterize phase structure,compositon and morphology of Ni-Co-P coating. The morphology,corrosion resistance, composition ,hardness,thickness and binding force of coating are measured and analysed. The optimum formula and the technological conditions were gained as follows：26.0g/L $NiSO_4 \cdot 6H_2O$，28.0g/L $CoSO_4 \cdot 7H_2O$，24.0g/L $NaH_2PO_2 \cdot H_2O$，80.0g/L $Na_3C_6H_5O_7 \cdot 2H_2O$，60.0g/L NH_4F ,temperature of 90.0℃,0.001g/L KI, 0.05g/L SDBS ,the plating time of 2.0 h and pH of 8.0.Under this condition, the coating had stronger corrosion resistance, drop time for $KMnO_4$ solution was 272s; The hardnesses was 229.60HV ;the deposition rate was faster, up to 53.33 $g \cdot m^{-2} \cdot h^{-1}$;thickness was 12.43 μm;the surface of the coating was uniform;the distribution of porosity was smaller;there was well-bonded with the substrate.

Introduction

The electroless plating of Ni-P was controlled by auto-catalytic reduction of metallic salt complexes occurring on the substrate. Electroless deposition offered an alternate and attractive methods of producing a thin and uniform coating ,and it had been known to obtain a Special performance coating when compared to electroplating.Electroless Ni-Co-P alloy had advantages from both Ni-P alloy and Co-P alloy . Ni-Co-P alloy coating possed unique properties such as high coercive force, the smaller residual magnetism, high wear resistance, high corrosion resistance and high density magnetic that were widely used in compact disk, MEMS, surface anti-corrosion, aerospace and other fields[1-6]. In the present,main preparation methods consisted of electroless plating method, electroplating method and sputtering method, etc., in which the electroless plating was a common method for obtaining Ni-Co-P alloy.Although the plating rate, stability and bath life subjected to certain restrictions, but because of its simple operation, uniform coating, high density and hardness characteristics, it had been widely used in many fields [7-11].In this paper, the AZ31B magnesium alloy was used as matrix to make electroless Ni-Co-P alloy under the alkaline conditions. the formula and process conditions of Ni-Co-P were systematically studied. Furthermore, it could improve the existing problems such as slow plating speed and coating corrosion resistance, and lay a good foundation for the development and application in the future.

Experimental

Materials and Experiment Reagent

Die-casted AZ31B magnesium alloy that were purchased from Dongguan Yuelute Industries Co., Ltd (China) was the experimental materials used for the investigation. Samples with sizes 50×25×2mm were cut and the substrate was metallographically ground with sand paper with different grits (180, 320, 600, 800, 1200) step by step before the pretreatment processed. The chemical compositions were shown in Tab.1. $NiSO_4 \cdot 6H_2O$, $NaH_2PO_2 \cdot H_2O$,SDBS,KI , $Na_3C_6H_5O_7 \cdot 2H_2O$ were supplied by Chengdu Kelong Chemical Reagent Factory. C_2H_5OH, H_3PO_4, $(NH_4)HF_2$, Na_2CO_3 and NaF were purchased from Chongqing Chuandong Chemical (Group) Co., Ltd. Other chemicals were purchased from Chongqing Beibei Chemical Reagent Factory. All chemicals were of analytical grade and used as received without further purification. Distilled water was used throughout the work.

Tab.1 Chemical compositions of AZ31B magnesium alloy

Element	Mg	Si	Fe	Al	Ca	Mn	Zn	Be
Wt.%	95.52	0.03	0.05	3.10	0.05	0.33	0.82	0.10

Electroless Plating Process

Electroless plating process involved a combination in turn:magnesium alloy samples washing →sanding→acetone degreasing→derusting→washing →pickling →activation →washing →Zincating →electroless plating→washing→drying → weighing → performance testing. What deserved to be mentioned the most was the zincating process which was repeated twice, each one for 20 s.It contributed to improve the plating rate and performance of coating . Zincating process was shown as follows : It was conducted in a $ZnSO_4 \cdot 6H_2O$,$K_4P_2O_7$, NaF, and Na_2CO_3 mixed solution at 80℃ for 1h. Its compositions were fixed as (30 g $ZnSO_4 \cdot 6H_2O$, 100 g $K_4P_2O_7$, 5 g NaF and 5 g Na_2CO_3) in 1 L H_2O. Between the two zincating processes, AZ31B was cleaned in distilled water and 1 M H_2SO_4 solution with each one for 15 s.

Characterization

The surface appearance of as-prepared Ni-Co-P alloy coating was detected by GB/T 11376-1997. Its morphology and composition was examined by SEM (Model VEGA 3, Czech) and EDS (Bruker EDS QUANTAX) respectively. Potentiodynamic polarization technique was applied to study the general corrosion resistance parameters of bare AZ31B and as-deposited Ni-Co-P alloy coating. It was performed using CHI660D electrochemical workstation (Shanghai Chenhua Instruments, China) in a conventional three-electrode system ,AZ31B and Ni-Co-P alloy coating electrode were used as the working electrode.A platinum electrode and a saturated calomel electrode(SCE)were used as the counter and reference electrodes,respectively. The working electrode was immersed in 3.5% NaCl solution at 90 ℃ and left until the steady-state open circuit potential was attained. It was taken as the free corrosion potential. Thereafter, potentiodynamic polarization measurements were recorded at a scan rate of 2 mVs-1, starting from -1000 mV to 0 mV versus reference electrode. Binding force of coating was tested according to GB/T 13913-2008. According to HB5061-77 (magnesium alloy chemical oxidation film layer quality inspection) , $KMnO_4$ drop solution methods was conducted to record the color changing time. Formula of $KMnO_4$ drop solution was shown in Tab.2. In general, drop time for $KMnO_4$ solution became longer, the corrosion resistance of coating appeared to get stronger. Coating porosity was attained according to GB/T 5935-1986 with filter paper method. The thickness of coating was measured by metallographic methods[12]. Crystal structure and crystallinity of as-prepared Ni-Co-P alloy coating was investigated by XRD (DX-2600,China) in a 2θ range from 15 to 75° with a wavelength λ = 0.15406 nm and 35 kV/30 mA.

Tab.2 Formula of $KMnO_4$ drop solution

Experiment Reagent	$KMnO_4$(g)	HNO_3(mL)	H_2O(mL)
Dosage	0.05	5	95

orthogonal experiment method

With reference to domestic and foreign research and a large number of preliminary experiments related to ternary electroless, available concentration range of in basic plating solution and process parameters were determined as follows:$CoSO_4 \cdot 7H_2O$ 24.0- 28.0 g/L,$NiSO_4 \cdot 6H_2O$ 26.0-30.0 g/L,$NaH_2PO_2 \cdot H_2O$ 18.0-24.0g/L,$Na_3C_6H_5O_7 \cdot 2H_2O$ 75.0-85.0g/L,NH_4F 60.0-80.0g/L, plating time 1.5-2.5h and temperature 80-90℃. At the same time, stabilizer KI 0.001g/L, the surfactant SDBS 0.05g/L and PH value of 8.0 were fixed in plating solution throughout the experiment.On the base of preliminary experiment ,an orthogonal test table $L_{18}(3^7)$ was used with seven factors, namely $CoSO_4 \cdot 7H_2O$ concentration, $NiSO_4 \cdot 6H_2O$concentration, $NaH_2PO_2 \cdot H_2O$ concentration, $Na_3C_6H_5O_7 \cdot 2H_2O$ concentration, NH_4F concentration, time and temperature. In addition, $KMnO_4$ drop time for $KMnO_4$ solution were taken as an indicator,This study used $L_{18}(3^7)$ orthogonal table to take orthogonal test was performed to attain optimum formula and process condition.orthogonal test design was shown in Tab. 1[13].

Tab.3 Factor and level of orthogonal experiment

Level	Factor						
	A(g/L) $CoSO_4 \cdot 7H_2O$	B(g/L) $NiSO_4 \cdot 6H_2O$	C(g/L) $NaH_2PO_2 \cdot H_2O$	D(g/L) $Na_3C_6H_5O_7 \cdot 2H_2O$	E(g/L) NH_4F	F（℃） T	G（h） Plating Time
1	24.0	26.0	18.0	75.0	60.0	80.0	1.5
2	26.0	28.0	22.0	80.0	70.0	85.0	2.0
3	28.0	3 0.0	24.0	85.0	80.0	90.0	2.5

Results and Discussion

Optimium technological parameters of electroless

Arranged the tests based on $L_{18}(3^7)$ orthogonal test design table, Orthogonal experiment results were shown in Tab. 4.

Tab. 4 Orthogonal experiment results

Level	Factor							Drop time (s)
	$CoSO_4 \cdot 7H_2O$ (g/L)	$NiSO_4 \cdot 6H_2O$ (g/L)	$NaH_2PO_2 \cdot H_2O$ (g/L)	$Na_3C_6H_5O_7 \cdot 2H_2O$ (g/L)	NH_4F (g/L)	T (℃)	Plating time (h)	
1	24.0	26.0	18.0	75.0	60.0	80.0	1.5	94
2	24.0	28.0	22.0	80.0	70.0	85.0	2.0	92
3	24.0	30.0	24.0	85.0	80.0	90.0	2.5	210
4	24.0	26.0	22.0	85.0	60.0	85.0	2.5	133
5	24.0	28.0	3	75.0	70.0	90.0	1.5	172
6	24.0	30.0	18.0	80.0	80.0	80.0	2.0	141
7	26.0	26.0	24.0	80.0	60.0	90.0	2.0	188
8	26.0	28.0	18.0	85.0	70.0	80.0	2.5	152
9	26.0	30.0	22.0	75.0	80.0	85.0	1.5	121
10	26.0	26.0	18.0	75.0	60.0	80.0	1.5	221
11	26.0	28.0	22.0	80.0	70.0	85.0	2.0	198
12	26.0	30.0	24.0	85.0	80.0	90.0	2.5	251
13	28.0	26.0	22.0	85.0	60.0	85.0	2.5	132
14	28.0	28.0	24.0	75.0	70.0	90.0	1.5	201
15	28.0	30.0	18.0	80.0	80.0	80.0	2.0	197
16	28.0	26.0	24.0	80.0	60.0	90.0	2.0	272
17	28.0	28.0	18.0	85.0	70.0	80.0	2.5	215
18	28.0	30.0	22.0	75.0	80.0	85.0	1.5	178
K1	842.0	1098	1020.0	1088.0	1098	1020.0	987.0	
K2	1131.0	1030	854.0	1093.0	1077.0	854.0	1093.0	
K3	1195.0	1040	1294.0	987.0	1040.0	1294.0	1088.0	
R	353.0	68.0	274.0	106.0	58.0	440.0	106.0	

Plating solution generally consisted of main salt, reducing agent, complexing agent, buffer, stabilizing agent, accelerating agent and Surfactant. Functions of various additives in the plating solution were not the same.To be specific, $CoSO_4 \cdot 7H_2O$and $NiSO_4 \cdot 6H_2O$ were main salt, $NaH_2PO_2 \cdot H_2O$, $Na_3C_6H_5O_7 \cdot 2H_2O$,KI and SDBS were reducing agent , complexing agent ,stabilizing agent and surfactant respectively,NH_4F were both buffer and accelerating agent. It was worth mentioning that the buffer property rised When a certain amount of NH_4F was added in plating solution. Meanwhile ,Mechanism of NH_4F in the the electroless mainly was that F^- accelerated H-P bond rupture for $H_2PO_2^-$to reduce the activation energy of electroless nickel plating reaction on substrate surface and chemical reaction producted with the solvent. Moreover， NH_4^+also played the role of chelating metal ion.In general, the greater range R indicated that the factor was more important. Tab. 3 showed the size of range are that: RF> RA > RC >RD = RG > RB >RE,so the orders of several

factors affecting the performance of coating were as follows: temperature > $CoSO_4 \cdot 7H_2O$ > $NaH_2PO_2 \cdot H_2O$ > $Na_3C_6H_5O_7 \cdot 2H_2O$= Plating time > $NiSO_4 \cdot 6H_2O$ > NH_4F.Therefore,the best methods could be concluded that: A3B1C3D2E1F3G2, namely the optimun formula and process condition as follows: 26.0g/L $NiSO_4 \cdot 6H_2O$ ， 28.0g/L $CoSO_4 \cdot 7H_2O$， 24.0g/L $NaH_2PO_2 \cdot H_2O$， 80.0g/L $Na_3C_6H_5O_7 \cdot 2H_2O$，60.0g/L NH_4F ，temperature of 90.0℃，0.001g/L KI, 0.05g/L SDBS ,the plating time of 2.0h and pH of 8.0.According to the optimun formula and process conditions for experiments ,the results were obtained that : deposition rate faster, 53.33 $g \cdot m^{-2} \cdot h^{-1}$; drop time of $KMnO_4$ solution for 272 s; thickness of 12.43 μm.

XRD analysis

Fig.1 showed XRD patterns of the Ni-Co-P alloy coating formed by the electroless methods. Mg diffraction peak was not obvious, and It showed that the coating of Ni-Co-P alloy could completely cover the Mg substrate. Obvious characteristic peaks looking like the shape of steamed bread could be observed at about $2\theta = 45°$ so as to explain that as-prepared Ni-Co-P alloy coating was in amorphous structure[14].

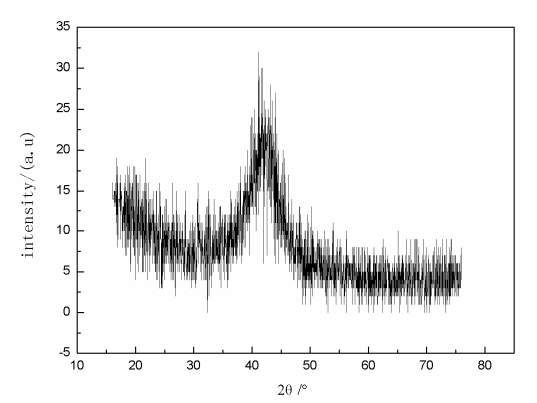

Fig. 1 XRD patterns of Ni-Co-P coating

SEM and EDS analysis

Fig.2 showed surface structures of as-prepared Ni-Co-P coating. From morphologies of Ni-Co-P coating, The results revealed that all the coatings were cellular structures which were similar to the morphology of Ni-P plating coating , and uniform surfaces structure with no cracks were obtained. Due to a dense and compact Ni-Co-P coating on AZ31B substrate, it contributed to reducing porosity, further to enhancing corrosion resistance of Ni-Co-P coating . Due to owing higher activity of atoms on the interface of the cellular organization, it was the easiest position to begin to produce corrosion[15].

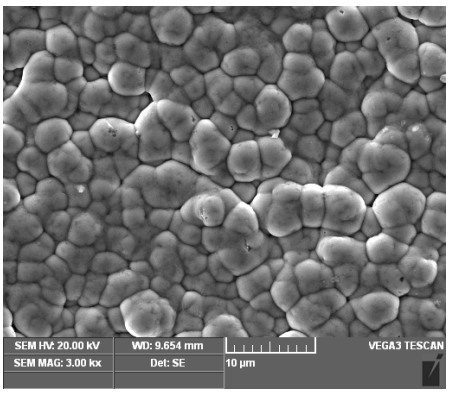

Fig. 2 SEM image of Ni-Co-P coating

To know the presence and weight percentage of Ni,Co and P in the Ni-Co-P coatings, energy dispersive x-ray analyzer (EDX) was used. The results of the Ni-Co-P coating were shown in Fig. 3 and Tab. 5 . The weight percentage of Ni was found to be 71.32, that for Co was 19.29, and that for P was 9.40. The compositional analysis mainly confirmed the presence of Ni,Co and P in the coating.

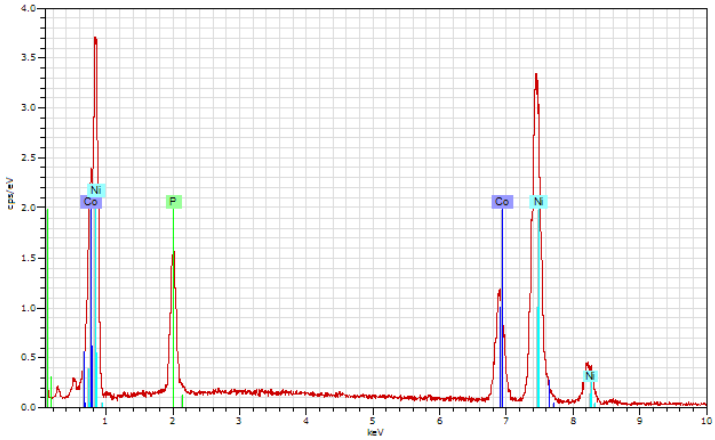

Fig. 3 EDX of Ni-Co-P coating

Tab.5 Composition of Ni-Co-P coating

Element	Ni	Co	P
weight percentage （wt.%）	71.32	19.29	9.40

Corrosion properties

The potentiodynamic polarization measurements were carried out after obtaining the open circuit potential (Eocp). In order to attain the Eocp, the specimens were immersed into the 3.5% NaCl corrosive medium to reach a plateau. the Eocp for a Ni-Co-P coating and AZ31B substrate were -1.237 V and -1.952 V repectively. These results indicated that the Eocp was shifted towards more positive values after Ni-Co-P coating was covered on AZ31B substrate. In other words, the electrochemical stability of the Ni-Co-P coating was much better than the AZ31B substrate without coating in the 3.5% NaCl solution.The potentiodynamic polarization curves of the Ni-Co-P alloy coatings in 3.5% NaC1 solution was illustrated in Fig.4. According to the data of corrosion parameter, the corrosion potential（ Ecorr ）for a Ni-Co-P coating and AZ31B substrate were -1.247 and -1.524V repectively(see Fig.4).the Ecorr of the Ni-Co-P alloy coatings was shifted towards positive values with respect to corrosion potentialof AZ31B substrate. According to the electric potential comparison criterion, the corrosion potential was more positive in the same medium,it was not easier to produce corrosion.Moreover, corrosion resistance of the Ni-Co-P coating was better than AZ31B substrate after plating the Ni-Co-P coating for the electroless.

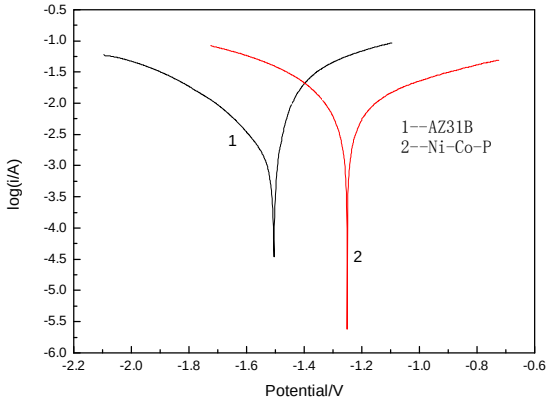

Fig. 4 The potentiodynamic polarization curves of the Ni-Co-P alloy coatings in 3.5% NaC1 solution

Hardness and binding force of the coating

The microhardnesses were measured with HV-5 microhardness tester . The hardnesses of three points were so similar as to be explained for obtained uniform coating. The hardnesses of Ni-Co-P coating and The hardnesses of the blank sample were up to 229.60HV and 128.74HV respectively. Hardnesses and wear resistance were obviously enhanced after the plating.After the coating was rasped by using a rasper along with the coating at 45 ° four times, there are no peeling, shedding and scratches. It indicated the binding forces between the coating and the substrate were better.

Summary

In summary, The optimium formula and process conditions had successfully obtained by orthogonal experiment methods in electroless Plating of Ni-Co-P on AZ31B. Ni-Co-P coating hold compact and uniform surface investigated by SEM. as-prepared Ni-Co-P alloy coating was amorphous by using XRD. The results of drop time for $KMnO_4$ solution and the potentiodynamic polarization measurements indicated that Ni-Co-P alloy coating had better corrosion resistance, so they were expected to become a promising treatment methods of metal surface applied in Many industries of national economy.

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