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Effect of Rare Earth Salt and Perpendicular Magnetic Field on Corrosion Resistance and Microstructure of CoMoP Film in Chloride Solution

Li Jiang, Jianbiao Lu, Shanshan Pan, Yundan Yu, Guoying Wei, Hongliang Ge[*]

College of Materials Science and Engineering, China Jiliang University, Hangzhou, China.
[*]E-mail: hongliang_ge@cjlu.edu.cn

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In order to improve the corrosion resistance of CoMoP film in 3.5% NaCl solution, rare earth(lanthanum) salt and perpendicular magnetic field(PMF) were adopted in the film deposition process. The corrosion of modified CoMoP film was studied using electrochemical techniques, and the microstructure of film was investigated using scanning electron microscopy(SEM), X-ray diffraction(XRD) and energy-dispersive X-ray spectroscopy(EDX). The results indicated that the introduction of La element in CoMoP film promoted the cathodic polarization of corrosion process, shifted the corrosion potentials to more negative values and decreased the corrosion current densities. Moreover, as the PMF intensity increased from 0.1T to 0.5T in the deposition process, the corrosion potential of CoMoP film in 3.5% NaCl solution showed a shifting towards positive values and the corrosion current density decreased. The addition of La salt or introduction of PMF in the deposition process can refine the grains of film and make surface more compact.

Keywords: Corrosion, rare earth, magnetic field, CoMoP film

1. INTRODUCTION

Cobalt(Co)-phosphorus(P) films are focused particularly with regard to their magnetic properties and the barrier metallisation for copper in ultralarge scale integration[1,2]. Molybdenum (Mo) has many advantages, such as high melting point, high thermal stability, good electrical conductivity, low diffusivity and varied workability for the pattern fabrication. Introduction of Mo to the Co-based coating not only can produce materials with good soft magnetic properties[3], but also improve the property of deposits as barriers against the copper diffusion into substrate [4,5]. CoMoP films are usually produced by electrodeposition[6,7]. It is known as an induced co-deposition process, since Mo cannot be deposited by itself from aqueous solution and the only possibility is co-deposition with the iron group metals[1,8].

Corrosion of magnetic film in environmental conditions is usually an electrochemical process which requires the presence of water at the surface of film[9]. With ample supply of oxygen and the presence of inorganic contaminants dissolved in the adsorbed water, an electrolyte capable of enhancing the corrosion rates substantially is formed. In the literatures, several researches on increased corrosion resistance of CoMoP film have been reported[6,7]**.** From the previous work of our research, it was found that if CoMoP film was exposed to humid air at room temperature for several days, the bright film surface were oxidized and lose metal luster. As the corrosion of CoMoP film progressed in humid air, the magnetic property weakened, as well as, the capability of impeding interdiffusion between eutectic and Cu elements gradually diminished in the following several months. Therefore, improving the corrosion resistance and lengthening service lift of CoMoP film is the issue that catches people's attention. Preparing CoMoP film with good corrosion resistance should be fully considered during the deposition process.

Rare earth(RE) can form alloy with other metals and is widely used in magnetic materials, magnetic light storage materials, catalytic materials and hydrogen storage materials. RE salts, especially cerium(Ce) and lanthanum(La) salts, are known to inhibit the corrosion processes and improve mechanical property effectively on several substrates such as steel[10], galvanised steel[11], aluminium and its alloys[12]. RE salts can also be used to deposit surface conversion films or incorporated in the alloys[13-15]. The improvement on property is mainly attributed to the formation of meta-stable RE-containing phases along the grain boundary, which increases the creep resistance significantly. In addition, some impurity elements in alloys that severely deteriorate the corrosion resistance, can be removed by formation of intermetallic compounds with RE[16]. Mercer and Hill[17] found that RE can trap deleterious elements and decrease the activity of cathode during the film deposition process.

Moreover, magnetic field also plays a greatly role during the deposition process of magnetic film. Remsen[18] was the first to investigate the effect of magnetic field on the course of chemical reactions, and the effect of magnetic field on the electrode potential has been reported by Gross[19]. An applied permanent parallel magnetic field has a large influence on the mass transport and the deposit morphology[20,21]. In the absence of permanent perpendicular magnetic field(PPMF), the mass transport factors which can control the electrode process are diffusion, ionic migration and convection(natural and forced). With the application of a PPMF forces such as paramagnetic force(F_p), field gradient force(F_B), Lorentz force(F_L), electrokinetic force (F_E) and magnetic damping force(F_D) can become prominent in an electrode reaction[22], and the current efficiency of system increase. In addition, with the presence of magnetic field, Co electrodeposition rate is clearly enhanced due to an increase magnetic moment of Co^{2+} ions in solution in the field gradient force and paramagnetic force. Many researches found that holes on the surface of the Co deposit from the effect of hydrogen evolution reaction has disappeared with the application of magnetic fields[23,24]. Furthermore, corrosion measurements showed that the electrodeposits of the Co-based alloys in the presence of a PPMF had larger polarization resistance R_p[25]. Studies on the influence of magnetic field on the migration, refinement and distribution behavior of precipitated phase showed that the the introduction of magnetic field improved the corrosion resistance of materials.

In view of the advantages of RE salts and perpendicular magnetic field(PMF) on the anti-corrosion performance of alloys, in this paper, their effects on the improvement of corrosion resistance for electrodeposited CoMoP film were investigated simutaneously. In addition, the relationship between microstructure and corrosion performance was also discussed.

2. EXPERIMENTAL

2.1 CoMoP film electrodeposition

Electrodeposition was performed on copper substrate with size of 2×2cm^2. Prior to the deposition, the substrate was degreased in alkaline solution (12 g/L NaOH, 60 g/L Na_2CO_3 and 60 g/L Na_3PO_4) , then pickled in diluted H_2SO_4(10%) solution for 30s to remove the native oxide layer from the copper sheet surface. For electrodeposition of Co alloy, the components of electrolyte were summarized in Table 1. After deposition, the samples were washed with distilled water and dried.

Table 1. Components and operating conditions of CoMoP film electroplating solution

Component	Concentration
$CoCl_2 \cdot 6H_2O$	0.1 mol/L
$C_6H_{14}N_2O_7$	0.2 mol/L
Na_2SO_4	0.32 mol/L
$NaH_2PO_2 \cdot H_2O$	0.075 mol/L
$(NH_4)_6Mo_{24} \cdot 4H_2O$	0.0014 mol/L
Temperature	60℃
pH	6.0
$La(NO_3)_3$	0.6-1.4 g/L
Current density	0.17 A
Magnetic field	0.1-0.5 T
Ultrasonic	60 W
Time	20 min

2.2 Electrochemical methods

Electrochemical measurements, including potentiodynamic polarization curves and electrochemical impedance spectroscopy(EIS) were performed on electrochemical working station(PARSTAT®2273) with the conventional three electrode cell. The CoMoP film specimen was used as the working electrode, a platinum foil as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The test solution was 3.5% NaCl aqueous solution. EIS was carried out at range of 10mHz~100kHz with 5mV perturbation signal at the corrosion potential. To test the reliability and reproducibility of the measurements, duplicate experiments were performed.

2.3 Microstructure analysis

The phase structure of the films was characterized by X-ray diffraction analysis (XPert Philips PW1830) using a CuKα radiation as an incident beam at 40kV and 150mA. Surface morphology of each specimen was examined using scanning electron microscopy (SEM, Hitachis-4800), attach to energy-dispersive X-ray spectroscopy (EDX, GENE SIS2000 XMS 60 S, EDAX, Inc.) operated at 10 kV to analyze the composition.

3. RESULTS AND DISCUSSION

3.1 Effects of La salt addition in the plating solution

3.1.1 Corrosion resistance of modified CoMoP film by La element

In the deposition process, addition different content of $La(NO_3)_3$ in the plating solution can prepare different CoMoPLa films. Within a certain addition range, the more $La(NO_3)_3$ addition in the plating solution, the more content of La element was brought into CoMoP film, proven by the EDX analysis results shown in Table 4.

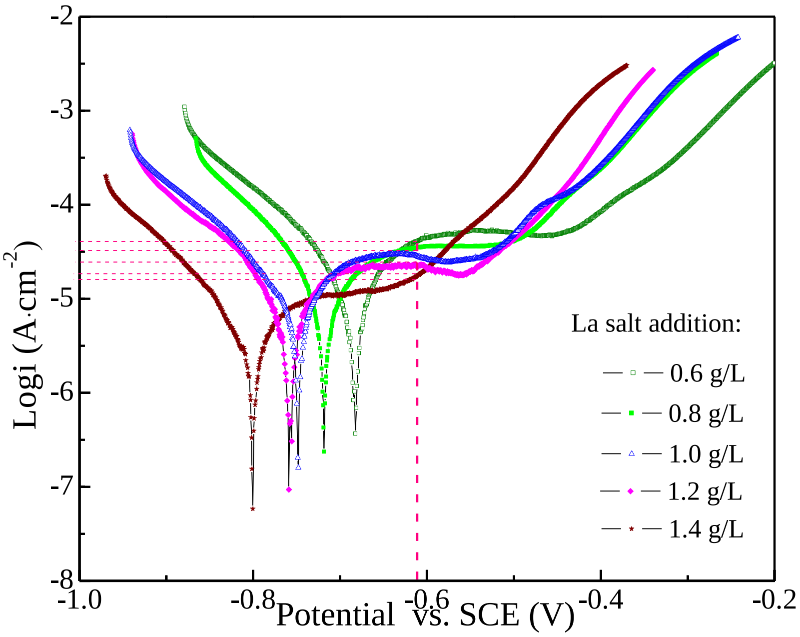


Figure 1. Polarization curves of modified CoMoP films by La element in 3.5%NaCl solution

Table 2. Electrochemical corrosion data related to polarization curves of modified CoMoP films by La element in 3.5%NaCl solution

$La(NO_3)_3$(g/L)	**0.6**	**0.8**	**1.0**	**1.2**	**1.4**
Corrosion Potential(V)	-0.683	-0.718	-0.748	-0.759	-0.800
Corrosion Current Density(10^{-6}A/cm^2)	31.62	25.12	15.85	10.12	6.31

Fig.1 and Table 2 show the polarization curves and electrochemical corrosion data of modified CoMoP films by La element in 3.5%NaCl solution. The introduction of La element in CoMoP film promoted the cathodic polarization of corrosion process. As La content in CoMoP film increases, the cathodic polarization effect increased, where corrosion potential moved towards more negative values (corrosion potential slightly changed from -0.683V to -0.800V). The corrosion current intensity in Table 2 was calculated by Tafel extrapolation method. Subsequently, the corrosion rate (CR) was determined using the relationship：

$$CR = \frac{0.13 \times I_{corr} \times eq.wt}{\rho} \qquad (1)$$

where ρ is the density of modified CoMoP film(g·cm^{-3}) and I_{corr} was the current density (10^{-6}A·cm^{-2}) which also representative of the degradation of film. As the increase of La element in CoMoP film, I_{corr} calculated from polarization curve was lower; furthermore, the anode dissolution currents of modified CoMoP film by La element were declined at the same potential (shown in Fig.1). Thus, from the equation (1), it indicats that corrosion rate for film containing high content of La element is lower.

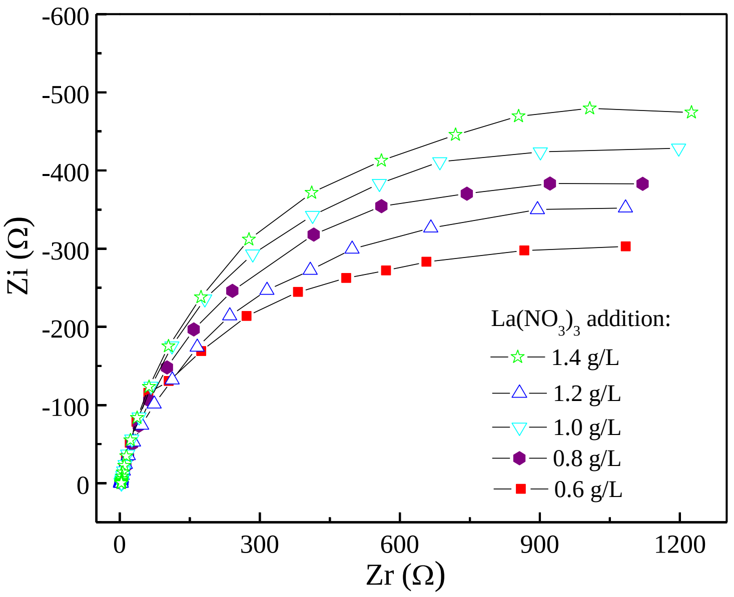
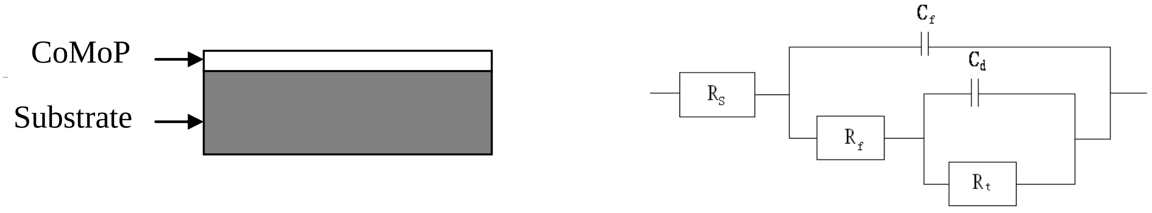


Figure 2. Nyquist plots for modified CoMoP films by La element in 3.5%NaCl solution



(a) (b)

Figure 3. (a) Model of modified CoMoP film; (b) Equivalent circuit used to fit the EIS data (R_s is the solution resistance; C_f and R_f is the surface film capacitance and resistance; R_t is the charge transfer resistance; and C_d is the double layer capacitance)

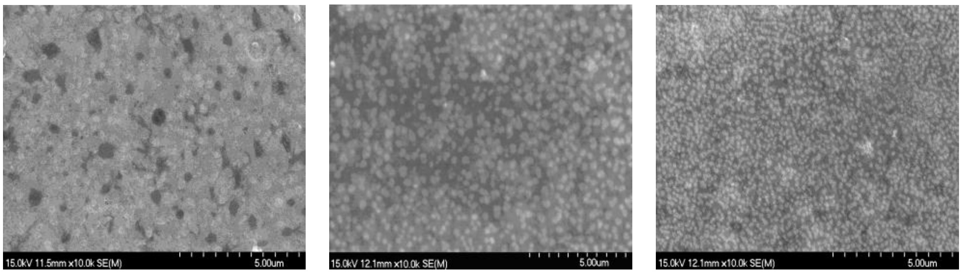
Table 3. Values of the elements in equivalent circuit required for fitting the EIS of modified CoMoP films by La element

$La(NO_3)_3$(g/L) Parameters	0.6	0.8	1.0	1.2	1.4
R_s (ohm·cm^2)	3.373	2.298	3.585	3.66	3.41
C_f (10^{-4}F/cm^2)	4.992	3.375	6.535	6.526	4.523
R_f (ohm·cm^2)	104.5	139.7	143.9	219.2	246.5
C_d (10^{-4}F/cm^2)	25.66	18.05	18.23	17.33	13.70
R_t (ohm·cm^2)	669.2	782.8	881.4	909.6	950.9

The EIS measurements were carried out to determine the kinetic parameters for electron transfer reactions at the modified CoMoP film/electrolyte interface and to confirm the data obtained by polarization measurements. The Nyquist plots for modified CoMoP film by La element at an open-circuit potential immersed in 3.5% NaCl solutions for 2h are shown in Fig.2. The corrosion process associated with formation of the electrochemical double layer, film dissolution in 3.5% NaCl solution and the adsorption and deposition of corrosion products on the corrosion surface. The difference in protective efficiency could be obtained from the limit of the impedance, which was a simple parameter used to evaluate the corrosion resistance of electrodes[26]. The impedance spectra of the Nyquist plots were analyzed by fitting to the equivalent circuit model shown in Fig.3, and the values of fitting elements were listed in Table 3. As the La content in CoMoP film increased, both surface film resistance R_f and charge transfer resistance R_t increased. It indicates that within a certain range, corrosion resistance of film with more La element was better.

3.1.2 Microstructure of modified CoMoP films by La element

In alloy deposition process, a small quantity of La salts added into the plating solution can improve the dispersion ability and uniform electroplating behavior, as well as, enhance the plating current efficiency and film hardness[27]. As the amount of La salts in the electrolyte increased, the cathodic polarization of alloy electrodeposition was improved. The reason was that when $Co(H_2O)_n^{2+}$ and $Co(OH)(H_2O)_{n-1}^{+}$ existed in the electrolyte, these metallic ions hydrate may form adsorption film on the surface of cathode;however, the addition of La salt may result in adsorption film of $La(OH)_3$ on cathode surface in place of the hydrate shells of Co or CoMo partially. As reduction of Co and Mo ions in deposition process was hindered, ion exchange rate of discharge between cathode and electrolyte slowed down, as well as, the cathode polarization effect increased[27]. Moreover, the La salts added into plating solution had the effect of refining grains for film surface. The morphologies of modified CoMoP films by La element are shown in Fig.4. As the amount of La salts increased, the structure of films are more compact and characterized with smaller grains.



(a) 0.6g/L $La(NO_3)_3$ (b) 1.0 g/L $La(NO_3)_3$ (c) 1.4 g/L $La(NO_3)_3$

Figure 4. SEM images of modified CoMoP films deposited with different $La(NO_3)_3$ addition in the plating solution

The EDX analysis results of the modified CoMoP film by La element are shown in Fig.5 and Table 4. The Co element was the main substance in alloy deposit with content more than 80 wt%, while the content of Mo and P elements were more than 13wt% and 4wt%. For small quantity of La salts added into the electrolyte, the La content in the alloy deposit was little (0.45%~1.19%). In addition, as the content of La salts added to the deposited solution increased, in deposited film, both Co and La element content (wt.%) increased, while the Mo and P element content declined. Higher content of Co element can make the film structure denser by forming cobalt oxide or passive film, which prevented the penetration of external corrosion factors and reduced the release of metal ions[28,29]. More La element in deposited film may form metastable RE-containing phases that significantly increased the corrosion resistance.

Table 4. EDX analysis results of modified CoMoP films by La element

$La(NO_3)_3$(g/L) Element	0.6	0.8	1.0	1.2	1.4
Co (wt%)	80. 41	80.49	80.86	81.12	81.35
Mo (wt%)	14.51	14.25	14.08	13.62	13.31
P (wt%)	4.63	4.59	4.32	4.21	4.15
La (wt%)	0.45	0.67	0.74	1.05	1.19

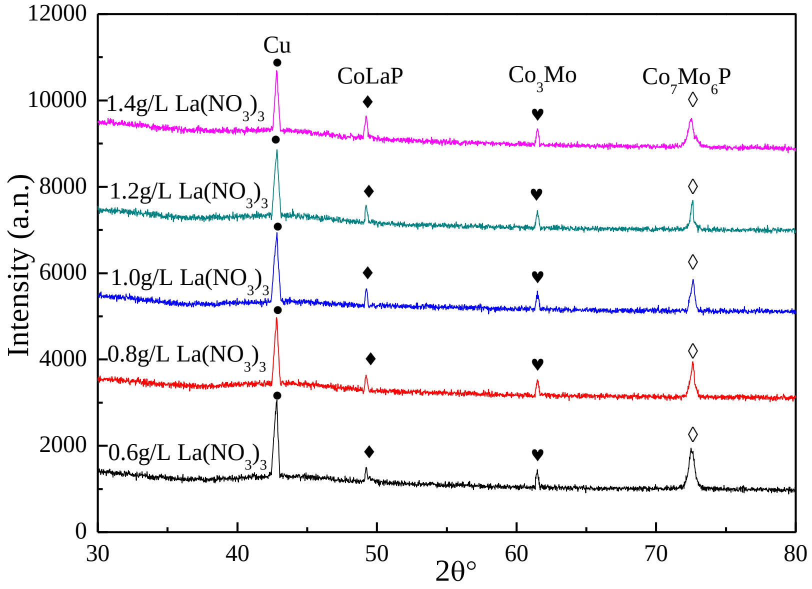


Figure 5. X-rays patterns of modified CoMoP films by La element

Fig.5 shows the diffraction patterns of the modified CoMoP film with different content of La element. The pattern revealed that the deposits were consisted of nanocrystalline phase. Peaks at 43.5° around could be ascribed to metallic copper used as the substrate. Co was the main component of the deposits, at room temperature, the ε-Co phase was able to dissolve substantial amount of Mo forming Co_3Mo solid solution at $2\theta \approx 61°$. No peaks of pure Mo were detected in the deposits, since it didn't form a separate metallic phase in the Co-Mo alloys. In addition, it is worth noting that elecrodeposited Co-Mo alloys containing low Mo percentage feature hexagonal structure[30]. Moreover, as the increase addition of La salt in plating solution, component of CoLaP in deposited film increased, while the Co_7Mo_6P declined comparatively. It was induced that the improved corrosion resistance of modified CoMoP film mainly attributed to the increase of Co compounds and La-containing phases in film.

3.2 Effect of perpendicular magnetic fileds (PMFs)

3.2.1 Corrosion resistance of CoMoP film deposited under different PMFs

Corrosion of CoMoP film deposited under different PMF was investigated in 3.5% NaCl solution. The polarization curves and electrochemical corrosion data are shown in Fig.6 and Table 5. Corrosion was widely studied as an interfacial phenomenon that led to a metal's destruction via electrochemical dissolution reactions and transport phenomena. As the PMF intensity increased from 0.1T to 0.5T in the deposition process, the corrosion potential of deposited film in 3.5%NaCl solution had a positive orientation change and the corrosion current decreased from $29.81\times10^{-6}A\cdot cm^{-2}$ to $3.162\times10^{-6}A\cdot cm^{-2}$.

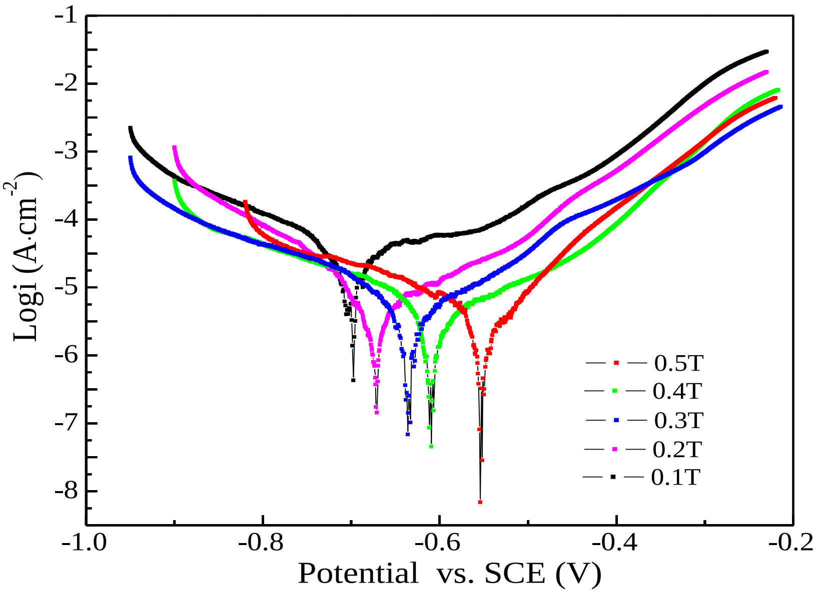


Figure 6. Effect of PMF on the polarization curves of CoMoP film in 3.5%NaCl solution

Table 5. Electrochemical corrosion data related to polarization curves of CoMoP films deposited under different PMFs in 3.5%NaCl solution

PMF field intensity(T)	0.1	0.2	0.3	0.4	0.5
Potential(V)	-0.554	-0.609	-0.636	-0.671	-0.698
Corrosion Current Density (10^{-6}A·cm^{-2})	29.81	12.59	9.772	7.943	3.162

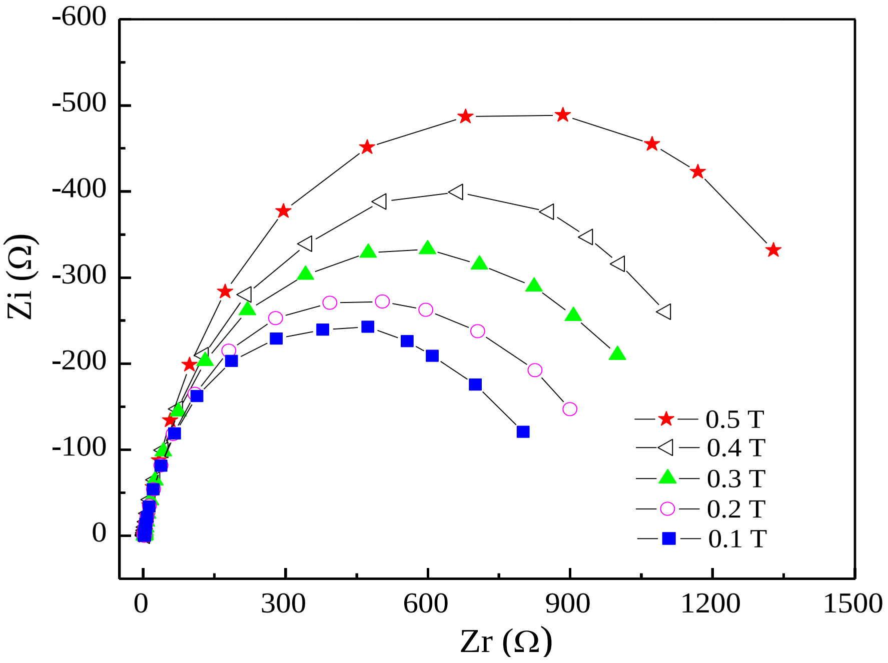


Figure 7. Nyquist plots for CoMoP films deposited under different PMFs in 3.5%NaCl solution

Table 6. Values of the elements in equivalent circuit required for fitting the EIS for CoMoP films deposited under different PMFs

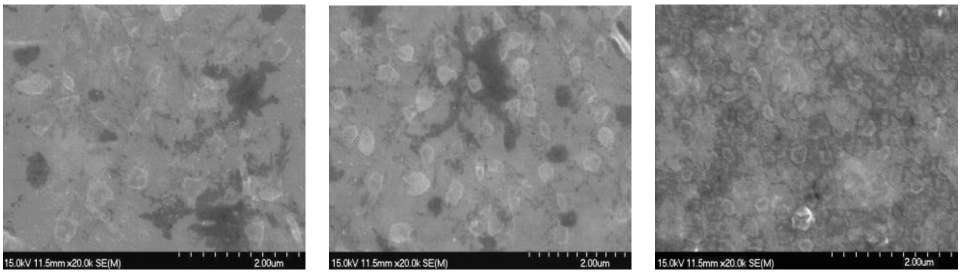
PMF intensity(T) / Parameters	0.1	0.2	0.3	0.4	0.5
R_s (ohm·cm^2)	2.858	2.947	3.335	2.627	2.685
C_f (10^{-4}F/cm^2)	3.961	6.241	6.381	7.519	4.412
R_f (ohm·cm^2)	139.9	148.3	152.1	155.7	157.6
C_d (10^{-4}F/cm^2)	16.521	12.64	11.14	10.61	6.41
R_t (ohm·cm^2)	538.6	595.1	693.7	813.4	1104

Nyquist plots for CoMoP film deposited under different PMFs in 3.5%NaCl solution for 2h are shown in Fig.7. The general trend of the impedance measurements is in agreement with the expectation. As magnetic intensity increased from 0.1T to 0.5T, the semidiameter of semi-circle increased. The impedance spectra of the Nyquist plots were analyzed by fitting to the equivalent circuit model shown in Fig.3. As PMF intensity increased, the double layer capacitance C_d declined, which indicated that it was influenced by the state of electrode/solution interface and the real contact area between electrode and solution; while the surface film resistance R_f increased from 139.9 ohm·cm^2 to 157.6 ohm·cm^2 and charge transfer resistance R_t increased from 538.6 ohm·cm^2 to 1104 ohm·cm^2(shown in table 6). These changes demonstrated that the modified CoMoP film by PMF was denser and compact, as well as, had better property of preventing the penetration of external corrosion factors.

3.2.2 Microstructure of CoMoP film deposited under different PMFs

The main effect of a magnetic field applied on an electrochemical system was the introduction of additional forces on the ions in the electrolyte[31]. Generally the force is Lorentz force. It acted on moving charges by accelerating them in the direction perpendicular to the current and the flux density ,leading to a stirring of the electrolyte. This effect can enhance the mass transport significantly[31,32]. Another force was the field gradient force. It pulled paramagnetic ions in regions of high flux density and diamagnetic ions in regions of low flux density respectively[31]. Moreover, a still controversially discussed force was the paramagnetic concentration gradient force. It was expected to balance the concentration of paramagnetic ions in a homogeneous magnetic field and thus, was directed towards higher concentration gradients and points in the same direction as diffusion[33].

A PMF applied during the preparation of CoMoP films can influence the precipitation mode and the film morphology. The morphology of CoMoP film deposited under different PMF were shown in Fig.8. It was very conspicuous to observe that higher PMF intensity resulted in CoMoP film with smaller grains and more compact surface. The reason was that the existed PMF restrained the convection and diffusion of ions in electrolyte, thus the diffusion of ions reduced and the structure of deposits refined. More compact surface with smaller grains was benefit to reduce the contacted area of corrosion and improve corrosion resistance better.



0.1T 0.3T 0.5T

Figure 8. SEM images of CoMoP films deposited under different PMFs

Table 7. EDX analysis of CoMoP films deposited under different PMFs

PMF intensity (T) Element	0.1	0.2	0.3	0.4	0.5
Co (wt%)	80.69	80.94	81.11	81.77	81.84
Mo (wt%)	14.39	14.55	14.70	14.82	14.89
P (wt%)	4.92	4.51	4.19	3.41	3.27

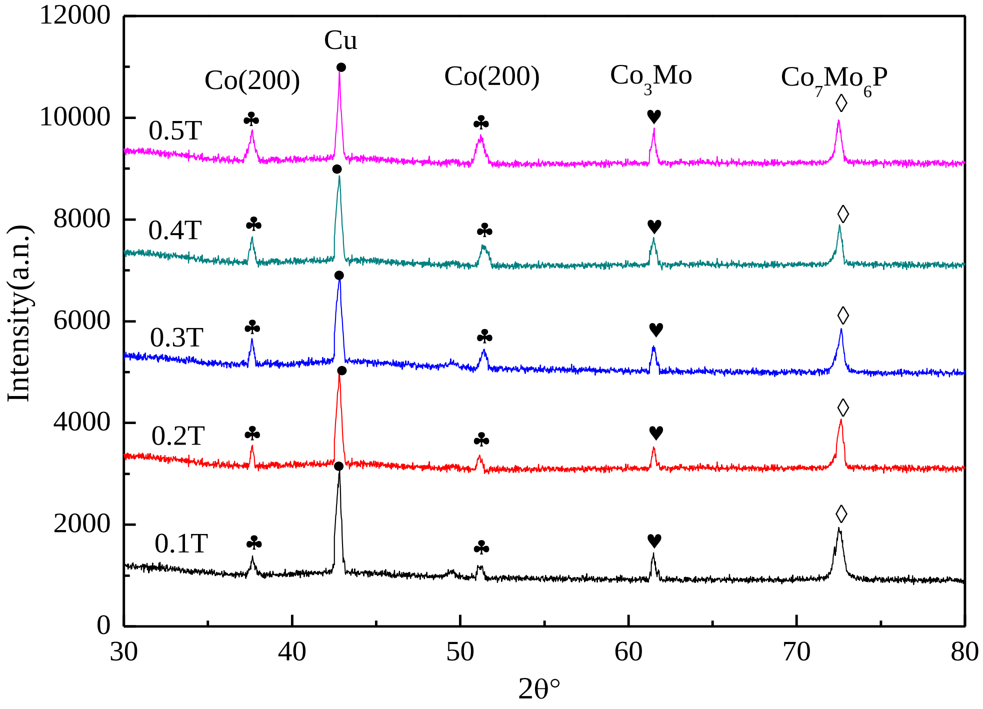


Figure 9. X-rays patterns for CoMoP films deposited under different PMFs

EDX analysis of CoMoP film deposited under different PMFs were shown in Table 7. Co was still the main element in deposits with content more than 80 wt%. As the PMF intensity increased, the content of Co and Mo elements increased, while content of P element declined. It indicated that more Co and Mo contained substances were promoted to be deposited by PMF.

Structural analysis of modified CoMoP film by PMF was performed using XRD, as shown in Fig.9. The components of film are mainly Co_3Mo and Co_7Mo_6P. Compared with diffraction patterns of modified CoMoP film by La element (shown in Fig.4), crystallographic orientation of Co(200) was presented at $2\theta \approx 37.6°$ and 51.2°. As PMF intensity increased, the content of Co element and Co_3Mo in CoMoP film increased obviously, while the content of Co_7Mo_6P slightly declined. The increase of Co and Mo elements were benefit for the corrosion resistance improvement of film. The effect of Co has been explained in the section 3.1.2, and the Mo anion can be used as anodic or cathodic corrosion inhibitor explained by adsorption theory[34]. This results was also approved by Kublanovsky's research[35].

4. CONCLUSIONS

In the electrodeposition process, La salt ($La(NO_3)_3$) and PMF were adopted to improve the corrosion resistance of CoMoP film. The corrosion of modified film was studied by electrochemical techniques. The results showed that the introduction of La element in CoMoP film promoted the cathodic polarization of corrosion process, which made the corrosion potential moved towards more negative values and the corrosion current density declined. In addition, as the PMF intensity increased from 0.1T to 0.5T in the deposition process, the corrosion potential of the modified film in 3.5% NaCl solution were more positive and the corrosion current decreased.

Characterization of the surface of the modified film was performed using SEM, XRD and EDX. The results indicated that the introduction of La element in CoMoP film benefited the deposition of Co and La elements by forming anti-corrosion Co compounds and La-containing phases. Moreover, the increase of PMF intensity facilitated the co-deposition of Co and Mo elements, which can improve the corrosion resistance of CoMoP film obviously. The addition of La salt or PMF in the deposition process can refine the grains of film and make surface more compact.

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