Journal of Electrochemistry

Volume 4 | Issue 4

1998-11-28

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Recommended Citation
Yue Zeng, Hongxin Huang, Xiaoming Xiao, Shixun Lian. Corrosion Characteristics of Electrodeposited Ni Mo P Alloy Immersed in NaCl Solution[J]. *Journal of Electrochemistry*, 1998 , 4(4): Article 10.
DOI: 10.61558/2993-074X.3145
Available at: https://jelectrochem.xmu.edu.cn/journal/vol4/iss4/10

第4卷 第4期
1998年11月
电化学
ELECTROCHEMISTRY
Vol.4 No.4
Nov. 1998

Corrosion Characteristics of Electrodeposited Ni-Mo-P Alloy Immersed in NaCl Solution ①

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Abstract The corrosion characteristics of electrodeposited Ni-Mo-P alloy immersed in 5wt.% NaCl solution were investigated using immersion, anodic polarization curves, XPS and AES analysis. The corrosion rates of amorphous Ni-Mo-P alloys are lower than that of crystalline Ni-Mo-P alloys. Anodic polarization curve experiments show that for the electrodeposited Ni-Mo-P alloys, the nickel mol fraction of which has in between 0.719 and 0.868, the corrosion potential moves to positive with the increase of P content, and the peak current value of active region increase with the increase of Mo content in alloys, though the effects of P content on the peak current of active region and of Mo content on the corrosion potential are insignificant. XPS and AES analyses indicate that after immersion in 5wt.% NaCl solution, an oxidation film of about 50 nm in thickness is formed on the surface of Ni-Mo-P alloys. This oxidation film is composed of Ni_2O_3, MoO_3 and PO_4^{3-}, and acts as a barrier between the alloy and the electrolyte.

Key words Ni-Mo-P alloy, Corrosion, Anodic polarization curve, XPS, AES

1 Introduction

The corrosion characteristics of crystalline nickel have been studied extensively. According to Dougll and co-worker[1~3], nickel passivates in acidic Na_2SO_4 solution through the formation of a NiO layer about 1 nm in thickness. Flis and Duquette[4] examined the effect of phosphorus on anodic dissolution and passivation of nickel in near-neutral solution. Addition of phosphorus enhanced the dissolution rate comparing to that of pure Ni, but as the phosphorus concentration increased the dissolution rate decreased. Auger Electron Spectroscopy (AES) showed that passive

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① Received 11 July, 1996, accepted 31 October, 1996

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oxide films on the Ni-P alloys were thinner than those on nickel. Diegle et al[5] studied the anodic behavior of amorphous Ni-20P alloy in H_2SO_4 and HCl electrolytes. They found that Ni-20P alloy passivates in 0.1 mol/L H_2SO_4 over a range of potentials where nickel is active, and that it dissolutes rapidly at higher potentials where nickel is passive. Kawashima et al[6] found that amorphous Ni-Mo-P alloys prepared by melting nickel phosphide with molybdenum are not passivated by anodic polarization in sulfuric acid. Instead, the alloys form thick porous surface films and suffer pitting corrosion in acidic chloride solution. X-ray Photoelectron Spectroscopy (XPS) analysis on Ni-18P alloy after polarization in 1 mol/L HCl showed phosphorus concentrated in the surface films, relative to nickel[7]. Sheng-long Lee[8] reported corrosion resistance of electroless Ni-Mo-P alloys using potentiodynamic polarization curves and immersion weight loss.

The aim of this paper is to investigate the effect of both molybdenum and phosphorus on corrosion behavior of electrodeposited Ni-Mo-P alloys in 5% NaCl solution using anodic polarization curve, the X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) analysis. Some X-ray diffraction (XRD) of the alloys was also performed.

2 Experimental Procedure

The Ni-Mo-P alloys were electrodeposited on copper substrates. The bath compositions and operating condition were reported in our previous paper[9]. The chemical compositions of the alloys were assayed by an Energy Dispersion Spectrometer (EDS, X-650 9VP, Japan). The structures of the alloys were determined by an X-ray diffractometer (XRD, 2038 X-ray diffractometer, Japan) with Fe-K_α target. The qualitative elemental characterization has been carried out via the use of X-ray Photoelectron Spectroscopy (XPS, PHI-5100 ESCA, USA) and Auger Electron Spectroscopy (AES, PHI 610/SAM, USA).

Corrosion behavior tests were conducted under the following conditions:

(1) Corrosion resistance in solution consisting of 5 wt.% NaCl at pH 8 at room temperature was determined by measuring weight loss. Reported corrosion rates are steady-state values determined from slop of weight loss vs. time (300 hours).

(2) Anodic polarization behaviors were measured in 5 wt.% NaCl solution at pH 6.5 at room temperature.

(3) Corrosion potentials (E_c) of the alloys immersed in 5 wt.% NaCl solution at pH 6.5 at room temperature were measured against a saturated calomel electrode (SCE).

3 Results and discussion

In correlating composition and structure (Fig. 1), it is evident that an amorphous structure is characteristic of alloys with high phosphorus or high molybdenum content. As far as the binary nickel-base alloys are concerned, the amorphous area ranges about more than 10 at.% phosphorus or 24 at.% molybdenum, respectively. The ternary amorphous Ni-Mo-P alloys lie on right side of dash line in Fig. 1 on the whole.

Weight loss data resulting from immersion for 300 hours in 5 % NaCl show relatively good resistance to corrosion for the alloys with a high phosphorus or molybdenum content, which are amorphous alloys. The amorphous alloys lie on right side of dash line in Fig. 1, that is, region for $24X_p + 10X_{Mo} - 2.4 > 0$ (X the mol fraction). Fig. 2 shows that the relationship between the weight loss data and X_A ($X_A = 24X_p + 10X_{Mo} - 2.4$). The amorphous alloys show more resistance than the crystalline ones in this environment. This may be the fact that the amorphous structure is free of phase boundaries[10]. After immersion test in 5 % NaCl over 300 hours, the surfaces of some amorphous Ni-Mo-P alloys retain original metallic luster, although weight losses occur, and the surfaces of crystalline alloys with low amount of P and Mo become irised or dusky.

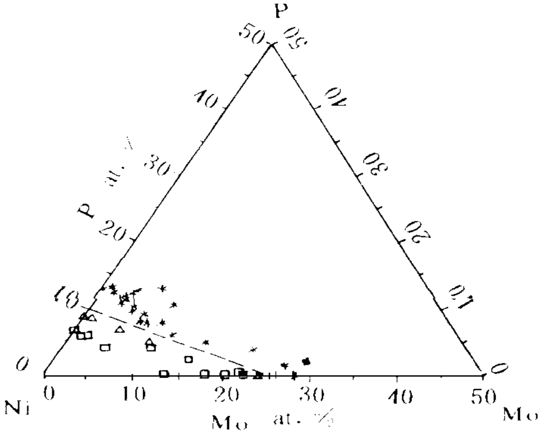

Fig. 1　Amorphization map of electrodeposited Ni-Mo-P alloys

* - Amorphous; □- Crystaline;

Δ - Amorphous and Crystaline

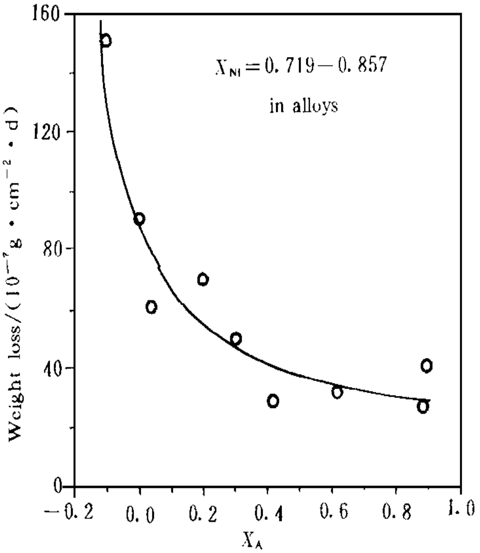

Fig. 2　Weight loss rate of Ni-Mo-P alloys

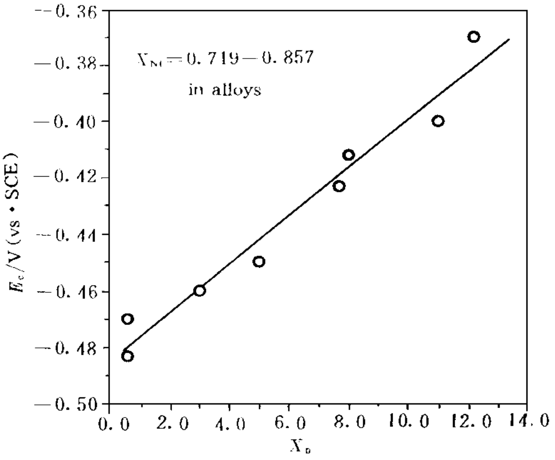

Fig. 3　Effect of P content on corrosion potential

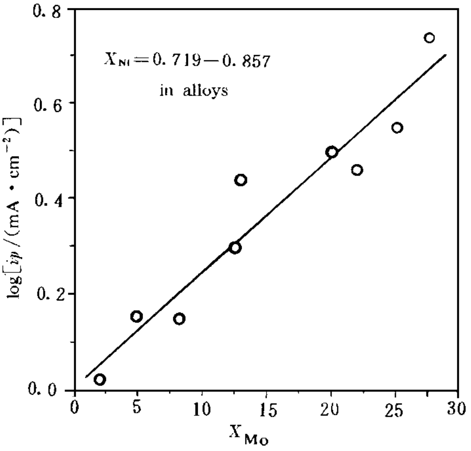

Fig. 4　Effect of Mo content on peak current

The studies on the anodic polarization curves of some alloys in 5 wt. % NaCl solution at pH 6.5 show that the binary Ni-Mo alloys have a narrow passive region and an active region, and that the binary Ni-P alloys have not an active region in this environment[9]. The larger phosphorus content in Ni-Mo-P alloys, the more positive the corrosion potential, and the larger molybdenum content in Ni-Mo-P alloys, the larger the peak current value of the active region. Fig. 3 and Fig. 4 show the effects of P and Mo content on the corrosion potential (E_c) and on the peak current value (i_p) of active region, respectively. It may be seen from Fig. 3 and Fig. 4 that when X_{Ni} is in between 0.719 and 0.868, the corrosion potential moves to positive with the increase of P content, and the peak current value of active region increase with increase of Mo content in alloys, though the effects of P content on the peak current of active region and of Mo content on the corrosion potential are insignificant. The corrosion potential of the binary Ni-Mo alloy is about - 0.485 V, and the active regions of the binary Ni-P alloys disappear, i. e., the peak current of active region is very small.

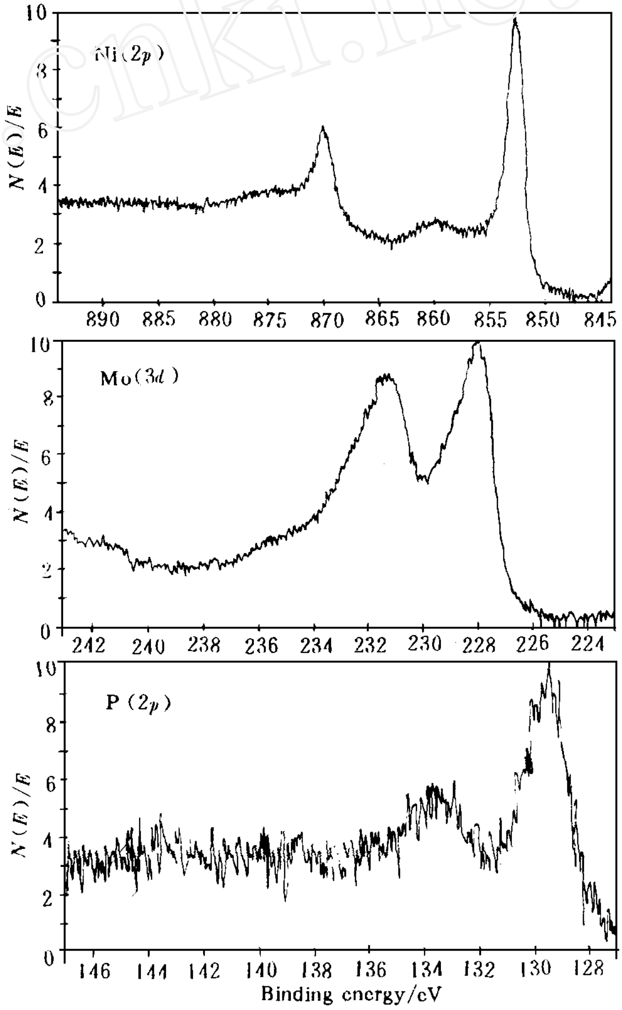

Fig. 5　XPS spectra for Ni, Mo and P in Ni-Mo-P alloys

The XPS allows to identificate the phosphorus, molybdenum and nickel species within the Ni-Mo-P alloys. After the sputter by Ar$^+$ for 20 min (about 4 nm, in order to minimize problems with surface contamination) the XPS spectra of Ni (2p), Mo (3d) and P (2p) for the Ni-Mo-P alloy is shown in Fig. 5. As determined from the P (2p) spectral region (Fig. 5), two chemically distinctive types of phosphourus are in the alloy, the low binding energy peak at 129.5 eV is consistent with zero-valence phosphours, while the peak at about 133.6 eV is probably P(V) as PO_4^{3-} in accordance with Diegle at al[11]. There is one chemical species of Mo as observed from the Mo(3d) spectral region(Fig. 5). The binding energy peaks at 227.9 eV and 231.0 eV are associated with Mo($3d_{5/2}$) and Mo($3d_{3/2}$) of zero-valence molybdenum[12]. The Ni($2p_{3/2}$) peak shown in Fig. 5 is at 852.7 eV, corresponding to zero-valence nickel. Besides the peaks of Ni, Mo and P, two small peaks are present: the first at 532.5 eV and the second at 286.2 eV, corresponding to O(1s) and C(1s), respectively, which show a low of oxygen and carbon exist in the Ni-Mo-P alloy. Before sputter the Ni(2p) and Mo(3d) regions shown a peak at 856.5 eV and 235.6 eV corresponding to NiO and MoO_3, and after sputter carbon and oxygen peak were greatly descend, which indicate the that polluted carbon existed on the surface of the alloys and that the surface was partly oxidized when the alloy was exposed to the atmosphere.

After immersion in 5 wt. % NaCl solution and the sputter by Ar^+ for 20 min the XPS spectra of Ni(2p), Mo(3d) and P(2p) for the alloy are shown in Fig. 6. As seen from Fig. 6, the Ni has a peak at 855.8 eV corresponding to Ni_2O_3 (855.7 eV[12,13]). The three peaks at 228.05 eV, 231.66 eV and 235.58 eV for Mo($3d_{5/2}$) and Mo($3d_{3/2}$) correspond to the mixture of Mo (228.0 eV and 231.6 eV) and MoO_3 (232.6 eV and 235.6 eV)[13]. Fig. 7 shows the XPS spectra fitted for Mo and MoO_3. And P has two species [P and P(V)] on the surface, but it exists mainly in P(V) (133.6 eV, probably PO_4^{3-}). The same re-

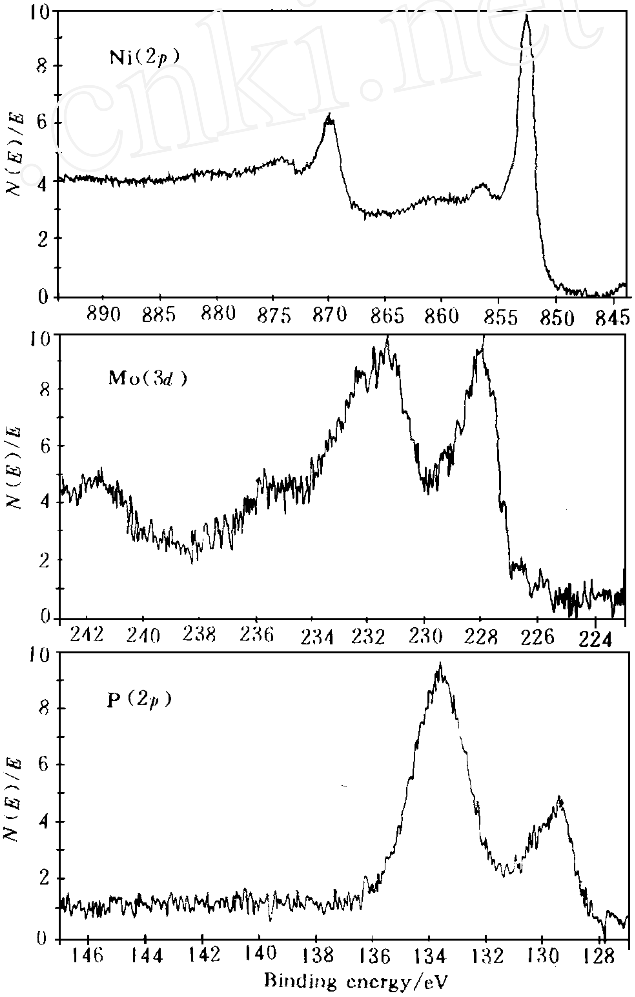

Fig. 6 XPS spectra for Ni, Mo and P in Ni-Mo-P alloys after immersion

sults were obtained from Auger Electron Spectroscopy (AES).

AES profile (Fig. 8) of the alloy after immersion in 5 wt. % NaCl solution shown after sputter (about 40 nm/min) for about 1.2 min (about 50 nm) the interior of the alloy was reached, which indicates the Ni-Mo-P alloy form oxidation films with thickness of about 50 nm in the environment of 5 wt. % NaCl solution. The concentration of Mo and P in the surface film after immersion is lower than those of Mo and P before immersion, which is different from the fact that Ni-P alloys in HCl solution exhibit an enrichment of elemental P on the alloy surface[7].

4 Conclusion

The addition of molybdenum and phosphorus to Ni-base alloy affects greatly on the corrosion characteristics of electrodeposited Ni-Mo-P alloys in 5 wt. % NaCl solution. The corrosion rate of amorphous Ni-Mo-P alloys is lower than that of crystalline Ni-Mo-P alloys. The anodic polarization curve experiments show that the corrosion potential moves to positive with the increase of P content, and the peak current value of active region increase with the increase of Mo content in alloys, though the effects of P content on the peak current of active region and of Mo content on the corrosion

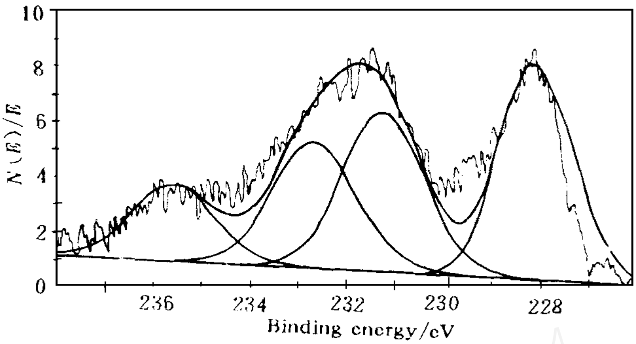

Fig. 7　XPS spectra fitted for Mo and MoO$_3$

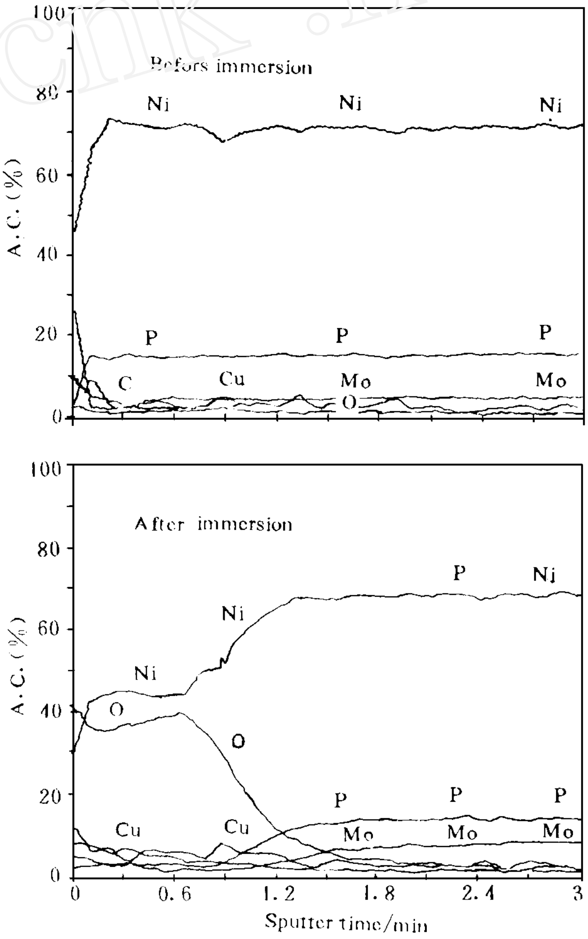

Fig. 8　AES profile of the Ni-Mo-P alloys before and after immersion

potential are insignificant. XPS and AES analyses indicate that after immersion in 5 wt. % NaCl solution an oxidation film is formed about 50 nm in thickness on the surface of Ni-Mo-P alloys. This oxidation film is composed of Ni_2O_3, MoO_3 and PO_4^{3-}, and acts as a barrier between the alloy and the electrolyte.

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电沉积 Ni-Mo-P 合金镀层在 NaCl 溶液中的腐蚀特性

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摘要　用失重法、阳极极化曲线、X-光电子能谱(XPS)以及俄歇电子能谱(AES)研究了电沉积 Ni-Mo-P 合金镀层在 5%NaCl 溶液中的腐蚀特性. 非晶态 Ni-Mo-P 合金镀层比晶态 Ni-Mo-P 合金镀层有较低的腐蚀速度. 阳极极化曲线表明, Ni-Mo-P 合金镀层中, 镍的摩尔分数为 0.719～0.868 时, 随镀层中磷含量的增加, 腐蚀电位正移; 而活化区的峰电流随镀层中钼含量的增加而增加. 磷含量对活化区的峰电流以及钼含量对腐蚀电位的影响均很小. XPS 和 AES 分析指出, 经 5%NaCl 溶液中浸渍后, Ni-Mo-P 合金镀层表面形成厚度约为 50 nm 的氧化膜. 这层氧化膜主要由 Ni_2O_3, MoO_3 和 PO_4^{3-} 等构成, 其在电解质溶液和合金间起着阻挡层的作用.

关键词　Ni-Mo-P 合金, 腐蚀, 阳极极化曲线, XPS, AES