Crystallization and electrochemical corrosion behaviors of nanometer amorphous Ni-P alloys

Zhizhen Li 1, Mengfei Luo 2, Hui Mao 1 and Chaoqun Bian 1

1 Pharmaceutical and Material Engineering School, Jinhua Polytechnic, 321000, Zhejiang Province, People’s Republic of China
2 Institute of Physical Chemistry, Zhejiang Normal University, 321000, Zhejiang Province, People’s Republic of China
E-mail: lizhizhen307@126.com

Keywords: electroless plating, nanocrystalline, corrosion resistance, uniform corrosion, diffusion control

Abstract
Ni-P alloy coatings with a phosphorus content of 11.65 wt% were deposited by electroless plating. The as-plated nano-amorphous Ni-P alloy coatings were heated in air for 1 h at 200–500 °C. By using an atomic force microscope and the x-ray diffraction method, the nanocrystalline morphology and the crystallization phase identification of the coatings were studied. The corrosion behavior of the coatings in the 3.5 wt% NaCl solution was analyzed using polarization curves and impedance spectroscopy. It was observed that the corrosion behavior of the coatings was affected by the change in the nanocrystalline structure; during the heat treatment, the nanocrystalline structure of the coating alloy undergoes sequential changes from amorphous → the adjustment of amorphous → precipitated phase → crystalline. Meanwhile, the corrosion behavior of the coating alloy has also changed from uniform corrosion controlled by charge transfer → uniform corrosion controlled by diffusion → grain boundary corrosion. The Ni phase and the Ni3P phase developed a compact and dense nanocrystal layer on the surface of the coating alloy, in which the best performance by the corrosion resistant coating can be found.

1. Introduction

There has been no systematic research on the influencing factors and mechanism of the corrosion resistance of the nano-amorphous electroless Ni-P alloy coating. Nanocrystalline materials are highly reactive because of the presence of many grain boundaries [1–3]. According to the typical theory of metal corrosion, grain boundaries are the active areas for corrosion, and nanocrystalline materials are prone to corrosion because of the presence of grain boundaries. However, in recent years, several studies have proved that the nano-amorphous electroless nickel coating displays better corrosion resistance than crystalline nickel. The nano-amorphous structure does not have grain boundaries and is highly homogeneous, and thus, there are no defects or preferential corrosion paths [4–7]. The aforementioned views are contradictory to each other. Therefore, nano-amorphous electroless nickel coating has attracted many types of research in understanding the corrosion resistance and its mechanism.

Iman et al [8–10] studied the corrosion resistance of amorphous, nanocrystalline, and tempered nanocrystalline Ni-P alloys. Among these alloys, the amorphous alloy shows the best corrosion resistance. Youssef et al [11–13] attributed the findings to the formation of the corrosion surface passivation film, which is mainly controlled by diffusion. The diffusion of solute atoms in nanocrystals is faster than that of coarse grains, and the nanocrystalline surface is more beneficial for the nucleation of the passivation film because it has many grain boundaries. Ankita et al [14–16] attributed the improvement of the nano-crystalline resistance to the change in its corrosion mechanism. When the grain size reaches the nanometer scale, the crystal structure on the surface of the coating is fine and uniform, which causes the uniform corrosion on the surface. However, the grain boundary corrosion is often seen in coarse-grained materials. Anijdan et al [17–19] investigated the
corrosion behaviour of Ni-P-Cu nano-composite coating, and found that the corrosion resistance of the nano-composite coating substantially reduces during the crystallisation, which reduced the P content of the coating as it formed different phases.

Other studies have suggested [20, 21] that a certain content of a solute in the nanocrystalline layer has a critical grain size, that forms a complete passivation film. When the grain size is less than the critical value, the solute element with the self-passivation property can easily form a complete protective film on the surface because the grain refinement can reduce the critical solute content of the protective oxide film on the surface of the alloy and improve the corrosion resistance of the crystal layer. In recent publications [22–25], the authors used the same grain boundary diffusion channel theory to explain the effect of the corrosion resistance of the Ni-P alloy coating.

In this study, the nano-amorphous coating with a phosphorus content of 11.65 wt% was prepared, and a heat treatment was carried out. The microstructures and electrochemical properties were studied using an atomic force microscope (AFM) and electrochemical measurements. The two-dimensional and three-dimensional morphological changes of the coated nanocrystals were investigated, and the corrosion behavior of the nano-amorphous coating alloy in the Cl\(^{-}\) corrosion environment was analyzed. The result not only includes the classical theory of atomic diffusion and grain boundary corrosions but also explains how the formation of crystal phase and the increase in grain boundaries affect the corrosion properties of the coating alloy during crystallization.

2. Experimental

Mild steel comprising (in wt%) 0.12%–0.20% C, 0.30%–0.70% Si, 0.30% Mn, 0.045% P, \(\leq 0.045\)% S and Fe balance was applied as a substrate. Abrasive papers (200–1000 grades) were used to polish steel substrates, and the polished substrates were further electro-cleaned with periodic reverse current in 10 wt% NaOH activated by the acid dip in 25 wt% HCl. The steel substrates were immersed in the plating bath with different compositions, which are presented in table 1. The deposition was done in a 1000-ml bath, which was maintained at a pH of 4.5–5.0 and a temperature of 88 °C–90 °C. The steel substrates were then plated for 3.5 h.

Based on the weight, density, and area, the thickness of the resulted Ni-P film was 35 \(\mu\)m. Using the energy dispersive spectrometry, the chemical compositions of the Ni-P amorphous alloy were determined as Ni\(_{88.35}\)P\(_{11.65}\). The Ni-P alloy coating was given heat treatment in air for 1 h at 200, 300, 400, and 500 °C for each composition.

X-ray diffraction (XRD; KY-2000) was used to identify the amorphous structure of the particles. The surface morphology and the particle size of the materials were analyzed using a scanning electron microscope (SEM; LEO-438-VP) and an atomic force microscope (AFM; SII-SPI-3800N). Electrochemical measurements were performed on the electrochemical analysis system (PS-16A), the sweeping rate was 2 mV·s\(^{-1}\), and the corrosive medium was 3.5 wt% NaCl aqueous solution. Before the electrochemical test, the Ni-P alloy sample was polished in acetone, and the exposed area for the analysis was obtained from the double coating of epoxy resin (EP 651), leaving an uncovered area of \(\sim 1.0\) cm\(^2\). All operations were carried out at room temperature.

3. Results and discussions

3.1. Composition and microstructure of the coating alloy

Figure 1 presents the amorphous structure of the Ni-P alloy, which was analyzed by XRD. Only one broad peak around 2\(\theta = 45^\circ\) was observed, indicating the complete amorphous character of the Ni-P alloy [26–29], as shown in figures 1(a)–(c). With an increase in the heating temperature, both the number and the strength of the
diffraction peaks increased, suggesting that the existing crystallization of the Ni-P amorphous alloy increased gradually. Two kinds of crystalline diffraction peaks in agreement with Ni and Ni$_3$P were observed simultaneously in the XRD patterns, which implied that both Ni and Ni$_3$P were formed at the same time during the crystallization process. However, it was reported that the position and strength of Ni$_{12}$P$_5$ and Ni$_5$P$_2$ were similar to those of Ni$_3$P, and their crystal structures were easy to convert into Ni$_3$P. Therefore, the existence of Ni$_{12}$P$_5$ and Ni$_5$P$_2$ cannot be completely excluded (figure 1(d)). As shown in figure 1(e), except for the increase in the strength of the diffraction peaks, there were no further changes in the XRD patterns when the heating temperature was above 400 °C, suggesting the completion of the crystallization process.

### 3.2. AFM representation of the coating alloy

The nano-amorphous morphology of the Ni-P alloy was investigated using AFM. Figure 2 shows the three-dimensional AFM images of the as-plated sample scanned over the areas of 20 μm × 20 μm and 1 μm × 1 μm. In figure 2(a), the smooth topography of the Ni-P amorphous alloy shows flat hill-like structures without obvious grain boundaries, representing the amorphous characteristics of the film; the average roughness of the surface is ~200 nm. Figure 2(b) shows the topography of the scanned area of 1 μm × 1 μm. The Ni-P amorphous alloy is made up of a large number of small needle-shaped particles that are distributed homogeneously on the surface. The average roughness of the needle-shaped particles is ~5.20 nm.

The topography of the Ni-P nano-amorphous alloy during heat treatment at different temperatures is shown in figure 3. As observed in the AFM images, the surface morphology of the Ni-P nano-amorphous alloy exhibits a beach-like shape that includes many small rounded particles distributed homogeneously on the surface (figures 3(a) and (b)). After the completion of the crystallization process, the small particles assembled into big
blocks, which looked like valleys; the average roughness of these big lumps is \( \sim 100 \) nm (figure 3(c)). The blocks were a mixture of Ni phase and Ni\(_3\)P phase, which was clearly observed in the XRD patterns (figure 1). Both obvious grains and grain boundaries were observed when the heating temperature was 500 °C, indicating the completion of the crystallization process (figure 3(d)).

The two-dimensional AFM image of the Ni-P sample heated at 400 °C with a scanning area of 20 \( \mu \)m \( \times \) 20 \( \mu \)m is shown in figure 4. In the figure, the whole crystalline grains were observed, and the grains were round with obvious grain boundaries between them. Many lumps comprising both Ni phase and Ni\(_3\)P phase were distributed homogeneously on the surface of the crystalline grains. The lumps formed a compact and

![Figure 3. AFM images (1 \( \mu \)m \( \times \) 1 \( \mu \)m) of Ni-P amorphous alloy treated at (a) 200 °C, (b) 300 °C, (c) 400 °C, (d) 500 °C.](image)

![Figure 4. Surface grain diagram (20 \( \mu \)m \( \times \) 20 \( \mu \)m) of Ni-P amorphous alloy heated at 400 °C.](image)
dense nanocrystal layer, which was clearly observed in one of the AFM images (figure 3(c)). The nanocrystal layer affects various properties of the Ni-P amorphous alloy, such as corrosion resistance [30, 31]. The electrochemical behavior of the Ni-P amorphous alloy was analyzed by measuring anodic polarization curves and using electrochemical impedance spectroscopy (EIS).

3.3. Electrochemical corrosion behavior of the coating alloy
The anodic polarization curves of the Ni-P nano-amorphous alloys treated under different temperatures in the 3.5 wt% NaCl aqueous solution are shown in figure 5 [32, 33]. The curves signified that the corrosion potential was positively shifted when the heating temperature increased from as-plated to 400 °C; however, the corrosion potential was negatively shifted when the heating temperature was 500 °C. The highest corrosion potential was observed in the Ni-P alloy treated at 400 °C, and there is an anodic passive region in the range of 0–500 mV. The maximum corrosion potential of the alloy treated at 400 °C is attributed to the combination of the following two effects: First, the Ni phase and the Ni₃P phase crystallize and form a dense nanocrystal layer on the surface of the Ni-P alloy, which is clearly observed in one of the AFM images (figure 4). This result is supported by Bai’s report [34]. Second, the heat treatment can effectively eliminate the internal stress and reduce the porosity of the Ni-P alloy, as shown in one of the AFM images (figure 3).

The Nyquist plots of the Ni-P nano-amorphous alloys treated at different temperatures in the 3.5 wt% NaCl aqueous solution are shown in figure 6. In the figure, only a regular semicircle (capacitive loop) was observed in the high-frequency region for the Ni-P amorphous alloys when the heating temperature increased from as-plated to 300 °C, indicating that the corrosion process was controlled by the charge-transfer reaction. The corrosion resistance property mainly depends on the speed of the ion migration and the thickness of the diffusion layer. The impedance is only capacitive, which increased from 1012 Ω to 1200 Ω when the temperature increased from as-plated to 300 °C [35–38]. The heat treatment increased the density of the coating and reduced the rate of charge transfer in the coating. Thus, the corrosion resistance of the coating improved, which was clearly indicated by the anodic polarization curves (figure 4).

The Nyquist plot of the Ni-P nano-amorphous alloy treated at 400 °C comprised a small semicircle at the high-frequency region and a straight sloping line at the low-frequency region, indicating that the corrosion process was controlled by the combined reactions of charge transfer and reactant diffusion. The straight line indicated that an intact passivating film formed on the coating surface, which inhibited the migration of ions. Therefore, the diffusion control is the key influencing factor affecting the corrosion reaction, but not charge transfer. This result is supported by Chang’s report [39]. The Nyquist plot of the Ni-P nano-amorphous alloy treated at 500 °C was disordered and irregular, indicating that the Ni-P amorphous alloy was crystallized and oxidized and that the grain boundaries and oxidation points affected the discharge mechanism of the electrochemical reaction.

Figure 5. Potentiodynamic polarization curves of Ni-P amorphous alloy treated under different temperature.
Figure 6. Nyquist plots of Ni-P amorphous alloy treated at (a) 200 °C, (b) 300 °C, (c) 400 °C, (d) 500 °C.
4. Conclusions

The amorphous nanocrystals in the high-phosphorus Ni-P coating alloy made the surface structure of the coating uniform and compact. Therefore, the corrosion behavior of the coating showed uniform corrosion, and the corrosion resistance improved. Owing to the heat treatment, the corrosion behavior of the coating alloy in the Cl- corrosion environment was analyzed. The nanocrystalline structure of the coating alloy undergoes the sequential changes from amorphous \( \rightarrow \) the adjustment of amorphous \( \rightarrow \) precipitated phase \( \rightarrow \) crystalline. Meanwhile, the corrosion behavior of the coating alloy also changed from uniform corrosion controlled by charge transfer \( \rightarrow \) uniform corrosion controlled by diffusion \( \rightarrow \) grain boundary corrosion. The Ni phase and Ni,P phase formed a compact and dense nanocrystal layer on the surface of the coating alloy, in which the best performance of the corrosion resistant coating can be found.

Acknowledgments

This work was supported by Zhejiang Provincial Natural Science Foundation of China (Grant No. LQ15E010006), National Nature Science Foundation of China (Grant No. 21902065) and Jinhua Science and Technology Bureau (Grant No. 2019–4–165). We also acknowledge the technical support that is given by institute of physical chemistry, Zhejiang normal university.

ORCID iDs

Zhizhen Li @ https://orcid.org/0000-0003-2538-3311
Chaoyun Bian @ https://orcid.org/0000-0001-5949-8737

References

[1] Liu H, Guo R X and Liu Z 2013 Surf. Coat. Technol. 219 31–41
[2] Wu Y Z, Xie K N, Liu L and Li M 2014 Hot Work. Tech. 43 23–9
[3] Latha N, Raj V and Selvar M 2013 Bod Mater. Sc. 36 719–27
[4] Keong K G, Sha W and Malinov S 2002 J. Alloys Compd. 334 192–9
[5] Marshall G W, Lewis D B and Dodds B E 1992 Surf. Coat. Technol. 53 223
[6] Hur K H, Jeong J H and Lee D H 1990 J. Mater. Sc. 25 2573–84
[7] Georgiza E, Novakovic J and Vassiliou P 2013 Surf. Coat. Technol. 232 432–9
[8] Mafi I R and Daghianian C 2011 App. Surf. Sc. 257 8655–8
[9] Rahiazezeh T, Allahkaram S R and Zarebidakj A 2010 Mater. Des. 31 3174–9
[10] Lyu X and Zhang G 2013 J. Shenying Ligong Univer. 32 131–3
[11] Yousef K M S, Koch C C and Fedkiw P S 2004 Corros. Sc. 46 51–64
[12] Li N, Huang J M and Ma J J 2015 Mater. Sci. Eng. Pow. Metal. 20 244–8
[13] Alishahi M, Hosseini S M and Monirvaghefi M S M 2013 Mater. Corros. 64 212–7
[14] Ashassi-Sorkhabi H and Eshghahi M 2011 Central Eur. J. Eng. 1 234–43
[15] Ashassi H and Moosaei E 2013 Corros. Sc. 77 185–93
[16] Sudagar J, Lian J S and Sha W J 2013 Alloys. Compd. 571 183–204
[17] Mousavi Anijian S H, Sabit M, Moghani Zadeh M and Farzam M 2018 Mater. Res. 21 1–9
[18] Sabit M, Mousavi Anijian S H, Moghani Zadeh M and Farzam M 2018 Can. Metall. Quart. 57 150–7
[19] Mousavi Anijian S H, Sabit M, Moghani Zadeh M and Farzam M 2018 Tribol. Int. 127 108–21
[20] Yang S I and Wang F H 2000 Acta Matell. Sin. 36 985–9
[21] Gao Y, Zheng Z J, Zhu M and Lu C P 2004 Mater. Sci. Eng. 38 98–103
[22] Mazaheri H and Allahkaram S R 2012 App. Surf. Sc. 258 4574
[23] Jappes J T W, Ramamoorthy B and Kesavan Nair P 2005 J. Mater. Process. Technol. 169 308–13
[24] Ashassi-Sorkhabi H and Rafighi S H 2004 Surf. Coat. Technol. 176 318–26
[25] Zhou Z J, Xie H and Li H 2012 Mater. Mech. Eng. 36 30–4
[26] Wang A C and Hu C C 2003 Mater. Chem. Phys. 79 69–75
[27] Hosseini I and Bodaghi A 2013 Surf. Eng. 29 183–9
[28] Yao H L, Wang H J, Wang S S, Zhao Z K and Liu H 2014 Heat Treat. Met. 39 58–64
[29] Iranipour N, Khosrosahhi R A and Ahmadi N P 2010 Surf. Coat. Technol. 205 2281
[30] Li Z Z, Wei Y H, Hou L F and Yang L J 2009 Rare Metal Mater. Eng. 38 52–5
[31] Kesawan R, Dey P P and Khare A 2019 RSC Adv. 9 7967–74
[32] Liu H, Guo R X, Zong Y, Liu, H, Biao J S and Li S 2010 T. Met. Soc. China 20 1028–31
[33] Zhang S Y, Zhang L W, Wei X Q, Yang Y F and Yang X K 2017 Surf. Technol. 264 229–34
[34] Bai A and Hu C C 2003 Mater. Chem. Phys. 79 69–75
[35] Qin T, Ma L Q, Yao Y, Xie R and Ding Y 2012 Rare Metal Mater. Eng. 41 1586–91
[36] Merinova M C, Pardo A, Arrabal R, Merinov S, Casajús P and Mohedano M 2010 Corros. Sc. 52 1696–704
[37] Fan Y, Wu G H and Gao H T 2006 Acta Metall. Sin. 42 35
[38] Yang F F, Kang H J, Guo E Y, Li R G, Chen Z N, Zeng Y H and Wang T M 2018 Corros. Sci. 139 333–45
[39] Chang J, Chen J and Huang A 2017 Heat Treat. Metal. 42 175–7