Effect of Mechanical Attrition on Structure and Property of Electroplated Ni-P Coating on Magnesium Alloy

Chaolei BAN,a,* Fangren WANG,a Jianhai CHEN,a and Shuqin ZHUb

© The Electrochemical Society of Japan, All rights reserved.

ABSTRACT
Mechanical attrition (MA) is applied to assist the electroplating Ni-P coating on a magnesium alloy substrate. The influence of MA on the microstructure and electrochemical performance of the coating was studied with SEM, XRD, electrochemical impedance spectroscopy (EIS) and polarization curves. The results show that under MA, the Ni-P electroplating becomes compact and free of cracks and pores, leading to significant improvement in the coating corrosion resistance. MA promote transformation the coating from amorphous state to crystalline one and produce an obvious transition layer at the coating-substrate interface, which is beneficial to enhancing the coating adhesion strength and other mechanical properties.

Keywords : Magnesium Alloy, Electroplating, Ni-P Coating, Corrosion Resistance

1. Introduction
Magnesium and its alloys are extensively applied in automobile, aerospace, electronic communication, etc., because of their excellent characteristics, such as high strength/weight ratio, low density, high damping, good castability and machinability. However, the electrochemical potential of magnesium is very negative. Owing to their high chemical reactivity and poor corrosion resistance, magnesium alloys’ widespread applications has been greatly limited. It is of great importance to increase the corrosion resistance of magnesium alloys via surface treatment.1–3

Electroless nickel plating is one of most effective ways to protect magnesium matrix and improve the corrosion and wear resistance. Ni/Mg system is a classical example of cathodic coatings on an anodic substrate.4–6 In order to provide adequate protection, the coatings must be uniform, well adhered and pore free. Nevertheless, electroless plating exhibits a certain number of restrictions, especially the weakness of layer adhesion stress, causing poor reliability of the deposit.7 In order to increase the adhesion between the coating and the substrate, a number of technical innovations were reported. Previous works have shown that ultrasound irradiation can improve electroless deposit adhesion strength.8 By the pretreatment procedure of pickling with nitric acid plus phosphoric acid, twice activating with K3P2O7 and NH4HF2, a coarse surface was produced on the Mg substrate and a compact Ni-P alloy coating with better adhesion and corrosion resistance was fabricated.9 Mechanical attrition has been applied during electroless plating to improve the Ni-P coating adhesion and other properties.10

Comparing electroless plating, electroplating generally has the characteristics of simple pretreatments, fast deposition speed, high density and compactness.11 Before electroplating Ni-P deposits on the magnesium alloy, the complex pretreatment processes such as degrease → acid pickle → fluoride activation → zincate immersion has been generally used to remove the residual oxides and hydroxides and to produce a thin layer of zinc to prevent re-oxidation of the magnesium surface.12 Mechanical attrition can help to remove oxides and hydroxides film on the substrate and expose the fresh substrate, eliminating the need for traditional pretreatments and having potential advantages. Mechanically assisted electroplating of Ni-P coatings on carbon steel has been successfully conducted by Ping et al.13 However, mechanical attrition enhanced Ni-P coating on magnesium has hardly obtain comprehensive consideration. The main aim of the presented work is to investigate the impact of mechanical attrition as an additional parameter of the electrodeposition process on Mg substrate, which could modify the structure and properties of Ni-P coating.

2. Experimental
2.1 Electroplating process
The mechanically assisted electroplating set-up is schematically shown in Fig. 1. As shown in Fig. 1, the plating bath was placed on the top of a vibrator. The vibrator provided a sinusoidal vibration of 1 mm amplitude and a 3 Hz frequency in the horizontal direction. Samples to be plated were made of AZ31 die cast magnesium alloy with nominal composition of 2.33% Al, 1.27% Zn, 0.68% Mn, 0.68% Fe, balance Mg. Each sample had dimensions of 20 mm × 10 mm × 2 mm. Two samples were mounted in epoxy resin as a whole and worked as the cathode. The anode was a high-purity nickel ingot with an effective surface area of 30 mm × 20 mm and parallel to the cathode surface. The sample surfaces were ground with SiC papers to 1200-grit finish. Glass balls with diameters of 1 mm and 5 mm were equally dispersed on the cathode surface.

Figure 1. Schematic illustration of mechanically assisted electroplating set-up.
Using two types of ball at the same time can strengthen mechanical grinding on the substrate and the in-situ coating. About 1/3 surface area of each sample was coved by the glass balls. When the plating bath was vibrated, these glass balls rolled horizontally forth and back and provided mechanical ball-rolling attrition to coatings simultaneously during the plating process. The electrolyte was composed of 300 g/l NiSO₄·6H₂O, 25 g/l NiCl₂·6H₂O, 25 g/l NaCl, 10 g/l H₂PO₃, 40 g/l H₃BO₃, and 25 g/l NaH₂PO₂·H₂O. The pH value of the electroplating bath is 3. The electroplating process was carried out at 70°C for 20 min with 25 mA/cm² current density. When the set-up stopped vibration, the conventional electroplating without MA was carried out with the same plating solution composition and electrodeposition parameters as the MA assisted one.

2.2 Surface morphology and microstructure examination

The coated specimens were washed with de-ionized water and dried. Field emission scanning electron microscope (FESEM) (JSM-6700F) was used to observe the morphology of coating surface and cross-section. An X-ray diffraction instrument (MAC Science Company Ltd M21X) was used to analyze the coating structure.

2.3 Electrochemical property measurement

The corrosion resistance of the coated specimen was evaluated by polarization curves and EIS spectra, which were measured in a 35°C 3.5% NaCl electrolyte with a classical three-electrode cell system. The counter electrode and reference electrode are a platinum plate and a saturated calomel electrode, respectively. During the electrochemical test, the samples were covered by an anticorrosion tape so as to expose only the testing area of 1 cm². The PC measurements were carried out with a sweep rate of 10 mV/s. The EIS spectra were obtained over the frequency range of 10 mHz–100 kHz with an applied AC perturbation potential of 10 mV amplitude. The experimental results were interpreted on the basis of an equivalent circuit determined using a suitable fitting procedure described in Zsimpwin software.

3. Results and Discussion

3.1 Effect of MA on coating surface morphology

Figure 2 shows SEM pictures of typical surface morphologies of the conventional and MA assisted Ni-P electro coatings. It can be found from Fig. 2 that although both Ni-P coatings exhibit typical “cauliflower-like and nodule-like” surface, similar with observations by others, the size of the “cauliflower-like and nodule-like” cluster on the MA assisted Ni-P coating is much smaller than that of conventional Ni-P coating. At the same time, obvious large gaps and pores between the clusters on the conventional Ni-P coating can be easily found, as pointed out by the red arrows in Fig. 2(a). With introduction of MA during electroplating, those gaps and pores sharply reduce in size and number and no obvious cavities can be found, as shown by Fig. 2(b). The presence of these very fine nodules and great reduction of pores on the coating surface roughly gives an idea of the coating grain refinement and densification that may be achieved by MA during the electrodeposition process.

It has been reported that the microstructure in the surface layer of metals and alloys could be refined to the nanometer level by means of surface mechanical attrition treatments such as milling, grinding, shot peening. Here, as MA action applied to Ni-P electroplating, the surface coating becomes smooth and active under plastic deformation and abrasion by MA, so the current distribution on the surface of coating keeps uniform and the nucleation of Ni-P grains processes at high rate. Therefore, the condition for grains to grow large is hindered, resulting in a fine microstructure of coating. Meanwhile, the MA-assisted deposited Ni-P grains during electroplating process is peened or cold–welded together by the moving glass balls, leading to disappearance of voids between grains and compact coating.

3.2 Effect of MA on coating cross-section morphology

Figure 3 shows the cross-sectional morphologies of conventional and MA assisted Ni-P coatings. It can be seen that under MA, the coating thickness reduced to about 8 µm from about 10 µm. Ping et al. has reported that the mechanical ball-rolling makes the Ni-P coating on carbon steel thinner by about 5 µm. Our discoveries are consistent with theirs. Meanwhile, numerous tiny occluded holes can be easily found in the section of blank Ni-P electro coating without MA. Under MA, these occluded holes in the coating have been largely decreased in number and size, indicating densification of the coating and in consistent with the Fig. 2 observation. Furthermore, the interface between Ni-P coating without MA and Mg alloy substrate is linear and clear. However, the interface between Ni-P coating with MA and substrate is coarse and blurred. An obvious uneven transition layer has formed at the interface under MA. This transition layer is beneficial to enhancing the interface adhesion strength.

According to the electrochemical theory, overpotential is the drive of reaction from metal ion to metal atom and is formed by the polarization. There are two important polarizations at the interface of cathode and boundary layer, namely, electrochemical polarization and concentration polarization. There exists a limited current density, i_L, which is determined by concentration polarization. When the external plating current density is below i_L, the electroplating process is controlled by electrochemical polarization. In this study, the galvanostatic plating was conducted with and without MA. Current efficiency generally depends on the electrode.
potential. In the case of Ni deposition, the main side reaction which lowers the current efficiency seems H₂ evolution. The H₂ evolution reaction is generally controlled by electrochemical polarization and the external plating current density is usually below iₕ. At the same time, there is no obvious change in the cell electrolysis voltage for convention plating and MA-enhanced one, indicating the current efficiencies for both kinds of plating are the same. On the other hand, Mechanical ball-rolling in-situ mechanically polished the surface, worn out any protruding summits, remove hydrogen bubbles occluded in the coating, slow down the growth of Ni-P grains, dislodge some loose Ni-P grains from the coating surface, peen and weld the grains. As a result, a thin but densified coating is obtained for MA-enhanced plating, in comparison with the conventional one.

At the initial stage of MA assisted electroplating, plastic deformation occurs on the surface of Mg alloy, owing to the soft nature of Mg and mechanical attrition. Much active channels for atom diffusion such as vacancy and dislocation are produced in the deformed part. Ni and P atoms deposit onto the deformed surface atom by atom, and diffuse into the deformed layer of Mg alloy, resulting in a blurred interface and forming a transition layer at the Ni-P coating/Mg alloy interface.

3.3 Effect of MA on coating structure

Figure 4 shows XRD patterns of conventional and MA assisted Ni-P coatings. In Fig. 4, an interesting observation is that the phase structure of the Ni-P coating was changed by MA. For the conventional Ni-P coating, it is noticed that for 2θ = 40 to 55°, a broad peak occurs and no other peaks can be found, indicating that the conventionally electroplated Ni-P coating is a mixture of amorphous and microcrystalline. For the MA assisted Ni-P coating, the above broad peak becomes sharp, corresponding to crystalline Ni (111). Meanwhile, two new peaks for Ni (200) and Ni₃P (141) also occur. This result reveals that crystallization and phase transformation in Ni-P plating can be prompted by MA.

The crystallization and phase transformation behavior of Ni-P coating during thermal processing has been the subject of investigations, in which the driving force for crystallization comes from thermal energy. In the present case, the energy for crystallization comes from mechanical attrition. We assume that the impact of glass balls on the Ni-P coating can enhance the mobility of atoms, promoting the diffusion of Ni and P atoms in the coating to form crystallized Ni-P phase. However, the energy from MA is not enough strong for fully crystallization. Only two new weak peaks for Ni (200) and Ni₃P (141) occur after MA assisted electroplating and indicated formation of partly crystallized structure. EDS analysis further indicates that the P content is about 8.3 wt% in the conventional blank Ni-P electro coating without MA and about 9.0 wt% in the MA assisted one. MA can increase the P content in the Ni-P coating, consistent with others’ report. The reason for the P content increase in the Ni-P coating via MA is still not clear. When the P content is higher than 8%, Ni-P coatings are usually amorphous. Therefore, as expected, the conventional blank Ni-P electro coating without heat treatment was amorphous and has been partly transformed into crystalline one with MA, as evidenced by the Fig. 4 XRD patterns.

3.4 Effect of MA on coating corrosion resistance

Figure 5 gives the polarization curves of Mg alloy substrate, traditional and MA assisted Ni-P coatings in 3.5% NaCl solution at room temperature. The Mg alloy substrate has the most negative corrosion potential (Ecorr) of −1.52 V and the most positive corrosion current (Icorr) of 24.05 mA/cm². Once the substrate was coated by the conventional blank Ni-P coating without MA, the Ecorr and Icorr were shifted to about −1.37 V, 12.36 mA/cm², respectively. The MA assisted Ni-P coating exhibits the most positive Ecorr and the most negative Icorr about −0.28 V and 7.12 mA/cm², respectively. Here, −0.28 V is also slightly higher than Ecorr value, −0.35 V reported by Guo, et al., in the same solution for Ni-P electroless coating on Mg substrate. Usually, the Ecorr and Icorr are related to the corrosion susceptibility and corrosion rate of the coating and substrate, respectively. High Ecorr and low Icorr mean good corrosion resistance. Therefore, the MA assisted coating can provide better anti-corrosion protection to magnesium alloy substrate than that of traditional one.
frequency range in this investigation. To account for the corrosion time-constant capacitance behavior is predominant over the substrate, traditional Ni-P coating and UI assisted one. A single coating.

Insulated, accounting for improvement in the corrosion resistance of possible galvanic cell between Ni-P coating and steel substrate were improved by MA. The Ni and Ni₃P precipitated in the amorphous density of the coatings. Meanwhile, Under MA action, plastic matrix by nanosize could diminish the interspaces and improve the hardness, resistance against abrasion, etc. At such high temperature, microcracks and micro open holes can propagate in the coating, due to mechanical constraints of substrate and volume contraction in the transition of coating from an amorphous state to a crystalline one, as well as evaporation of H₂ pinned in occluded holes. On the other hand, it was well known that nickel was a kind of cathodic coating on the anodic magnesium alloys substrate, and their potential difference was quite remarkable. Once microcracks and microholes penetrating the coatings reached the magnesium alloys substrate, severe galvanic corrosion would happen and the substrate materials could suffer catastrophic damage. One open pore suffices for arising of the serious electrochemical corrosion of the Mg substrate. From this point, we think that it is more important to densify the coating than to eliminate its grain boundary for corrosion resistance.

In this research, the crystallinity of N-P coating is in-situ improved by MA. The Ni and Ni₃P precipitated in the amorphous matrix by nanosize could diminish the interspaces and improve the density of the coatings. Meanwhile, Under MA action, plastic deformation takes place continuously on the surface of Ni-P coating and the coating becomes fine and compact as shown by Fig. 2 and Fig. 3. The pores and cracks in coating were eliminated and the possible galvanic cell between Ni-P coating and steel substrate were insulated, accounting for improvement in the corrosion resistance of coating.

Figure 5 shows the Nyquist plots obtained for Mg alloy substrate, Ni-P coatings without and with MA in 3.5% NaCl solution.

Table 1. Equivalent circuit parameters of the EIS and results of polarization curves.

| Samples              | $R_{ct}$ ($\Omega \cdot cm^2$) | $Q_{dl}$ ($\mu S \cdot cm^{-2} \cdot s^{-n}$) | $n$ | $i_{corr}$ (mA cm$^{-2}$) | $E_{corr}$ (mV, vs SCE) |
|----------------------|-------------------------------|---------------------------------------------|-----|--------------------------|-------------------------|
| substrate            | 1728                          | 0.6138                                      | 0.9747 | 20.05                     | -1520                   |
| Traditional coating  | 4673                          | 0.4756                                      | 0.9515 | 12.37                     | -1370                   |
| MA-assisted coating  | 7810                          | 0.2913                                      | 0.9329 | 7.12                      | -280                    |

It is generally agreed that amorphous alloys exhibit better corrosion resistance than equivalent polycrystalline materials, because of the absence of grain or phase boundaries and because of the glassy films which form on the surface to make it passive. But for N-P coating, in most cases, the transformation of amorphous state to polycrystalline one is usually realized by heat treatment above 400°C in order to increase its mechanical properties such as hardness, resistance against abrasion, etc. At such high temperature, microcracks and micro open holes can propagate in the coating, due to mechanical constraints of substrate and volume contraction in the transition of coating from an amorphous state to a crystalline one, as well as evaporation of H₂ pinned in occluded holes. On the other hand, it was well known that nickel was a kind of cathodic coating on the anodic magnesium alloys substrate, and their potential difference was quite remarkable. Once microcracks and microholes penetrating the coatings reached the magnesium alloys substrate, severe galvanic corrosion would happen and the substrate materials could suffer catastrophic damage. One open pore suffices for arising of the serious electrochemical corrosion of the Mg substrate. From this point, we think that it is more important to densify the coating than to eliminate its grain boundary for corrosion resistance.

In this research, the crystallinity of N-P coating is in-situ improved by MA. The Ni and Ni₃P precipitated in the amorphous matrix by nanosize could diminish the interspaces and improve the density of the coatings. Meanwhile, Under MA action, plastic deformation takes place continuously on the surface of Ni-P coating and the coating becomes fine and compact as shown by Fig. 2 and Fig. 3. The pores and cracks in coating were eliminated and the possible galvanic cell between Ni-P coating and steel substrate were insulated, accounting for improvement in the corrosion resistance of coating.

Figure 6 shows the Nyquist plots obtained for Mg alloy substrate, Ni-P coatings without and with MA in 3.5% NaCl solution.

Table 1, which also gives the values of $E_{corr}$ and $i_{corr}$ for different samples. In Table 1, factor $n$ represents the $Q_{dl}$ power, which is usually between 0.5 and 1. When $n = 1$, a $Q_{dl}$ is equivalent to an ideal capacitor. The higher value of $R_{ct}$, obtained for the MA assisted Ni-P coating, imply a better corrosion protective ability than the conventional one, in consistent with Fig. 5 observation.

Finally, though the effect of mechanical attrition on electroplating Ni-P coating on magnesium alloy is studied in this paper, the mechanism of mechanical attrition enhanced electroplating Ni-P coating are still in need further explored. The parameters such glass ball diameters and filling volume in the electrolyte, vibrating frequency, etc. of in-situ mechanical attrition should also be optimized in the ongoing work to further improve the performance of electroplated Ni-P coating. However, it is reasonable to postulate that the experimental results of this work provide promising opportunities for fabrication of advanced Ni-P coating on magnesium alloy substrate for industrial application such as in anti-corrosion cases.

4. Conclusions

A new process of mechanical attrition-enhanced electroplating Ni-P coating on magnesium alloy substrate was developed and the main conclusions can be obtained as below.

1. The imposition of mechanical attrition action during electroplating can refine, density and compact the coating, and promote transforming the coating from amorphous state to crystallized one.
2. The corrosion resistance of Ni-P electroplated coating on magnesium alloy can be improved greatly by in-situ mechanical attrition. This can be ascribed mainly to the reduction in the pores and cracks in the coating and insulating the potential bimetallic cell between substrate and plating layer.

3. In-situ mechanical attrition during electroplating Ni-P coating on Mg magnesium alloy can help to form a transition layer at the coating-substrate interface, beneficial to enhancing the coating adhesion strength.

Acknowledgments

The work is financially supported by the Natural Science Foundation of Shandong Province, China (Grant No. ZR2017MEM019), Technology and Culture Innovation Fund for Student of Liaocheng University (Grant No. 26312171923) and Innovative Entrepreneurship training Program for College students of Liaocheng University (Grant No. 201710447009).

References

1. Y. W. Song, D. Y. Shan, R. S. Chen, and E. H. Han, Surf. Eng., 23, 334 (2007).
2. M. Mohedano, R. Arrabal, B. Mingo, A. Pardo, and E. Matykina, Surf. Coat. Tech., 334, 328 (2018).
3. S. Nezamidoust, D. Seifzadeh, and Z. Rajabalizadeh, Surf. Coat. Tech., 335, 228 (2018).
4. A. A. Zuleta, E. Correa, J. G. Castaño, F. Echeverria, A. Baron-Wiechec, P. Skeldon, and G. E. Thompson, Surf. Coat. Tech., 321, 309 (2017).
5. L. P. Wu, Z. D. Yang, and G. W. Qin, J. Alloys Compd., 694, 1133 (2017).
6. J. A. Calderón, J. P. Jiménez, and A. A. Zuleta, Surf. Coat. Tech., 304, 167 (2016).
7. F. Touyeras, J. Y. Hihn, X. Bourgoin, B. Jacques, L. Halicz, and V. Branger, Ultrason. Sonochem., 12, 13 (2005).
8. F. Touyeras, J. Y. Hihn, M. L. Doche, and X. Roisard, Ultrason. Sonochem., 8, 285 (2001).
9. T. N. Tran, G. Yu, B. N. Hu, Z. H. Xie, R. Tang, and X. Y. Zhang, T. J. Met. Finish., 90, 209 (2012).
10. Y. D. He, H. F. Fu, X. G. Li, and W. Gao, Scr. Mater., 58, 504 (2008).
11. X. W. Zhou and Y. F. Shen, Appl. Surf. Sci., 324, 677 (2015).
12. L. P. Wu, J. J. Zhao, Y. F. Xie, and Z. D. Yang, T. Nonferr. Metal. Soc., 20, 630 (2010).
13. Z. X. Ping, Y. D. He, C. D. Gu, and T. Y. Zhang, Surf. Coat. Tech., 202, 6023 (2008).
14. Y. W. Song, D. Y. Shan, R. S. Chen, and E. H. Han, T. Nonferr. Metal. Soc., 18, s339 (2008).
15. H. H. Zhou, Z. W. Liao, C. X. Fang, H. X. Li, B. Feng, S. Xu, G. F. Cao, and Y. F. Kuang, T. Nonferr. Metal. Soc., 28, 88 (2018).
16. S. Bagherifard, D. J. Hickey, S. Fintová, F. Pastorek, I. Fernandez-Pariente, M. Bandini, T. J. Webster, and M. Guagliano, Acta Biomater., 66, 93 (2018).
17. Q. T. Yao, J. Sun, G. L. Zhang, W. P. Tong, and H. Zhang, Vacuum, 142, 45 (2017).
18. D. Guo, Z. G. Fan, and Z. D. Yang, Rare Met. Mater. Eng., 37, 1475 (2008).