Influence of duty cycle on behaviors: wear, corrosion and tribocorrosion resistance of Ni-P coatings

Li Chen*, Mingxia Zhang
Lanzhou University of Technology, Lanzhou, China
*Chenli1981@163.com

Abstract. Ni-P coatings were prepared on carbon steel in ammonia-citrate bath by pulse electrodeposition. The effect of pulse duty cycle on the microstructure, wear, corrosion and tribocorrosion resistance of Ni-P coatings were investigated systematically. The results showed that pulse duty cycle has less effect on the microstructure of the Ni-P coatings. However, the Ni-P coating prepared under 50% duty cycle exhibited superior wear, corrosion and tribocorrosion resistance. In addition, the corrosion plays a leading role in tribocorrosion process.

1. Introduction
The wear and corrosion of metal surface occurs in various fields, such as aerospace, chemical and other industries. However, wear and abrasion do not occur alone. The subject of tricorrosion started in the late 1980s and has now developed an active research area since experimental techniques have been growled[1]. There are many research’s about the tricorrosion behavior of various materials, moreover, they put forward the tri-corrosion mechanism[2-7]. S. Mischief [8] has pointed out the interactions of tri-corrosion damages is not simply the sum of mechanical wear measured in separate experiments. Yong Sun [9] found the total tribocorrosion material loss increases with increasing applied potential at experiment as corrosion pits inside the wear track can promote crack initiation and propagation to result in accelerated wear. M.T. Mathew [10] putted forward the wear mechanisms in major factor that the wear and corrosion and their synergistic effect on the tribocorrosion process with Taxco thin films. As far, there are few reports about the tribocorrosion properties of nickel-based alloys.

Ni-based alloys or composites materials are characterized by their anti-corrosion properties and strong wear-resistance that are very useful in automobiles, aviation, printing, chemical industrial machine and other fields [11-15]. Among these, Ni–P material possess magnetic property [16], high hardness, high strength and other superior mechanical properties, it also exhibits wear and corrosion resistance that makes it valuable in the development on the each field [17-19]. Pulse current (PC) plating is an established method of electrodepositing metals and alloys, and it significantly affects the mechanism of metal crystallization. The pulse parameters (such as peak current density, duty cycle and frequency) influence the adsorption or desorption of a species in the electrolyte and surface diffusion in several more ways than in DC plating [20].

Ni-P composite coatings were prepared on carbon steel in ammonia-citrate bath. This work was aimed at the impact of duty cycle on wear, corrosion and tribocorrosion resistance of Ni-P coatings by using the PC electrode position technique. Furthermore, discussing the relationship between tribocorrosion resistance and wear, corrosion resistance.
2. Experimental
Ni-P coating were deposited from an ammonia-citrate bath. The 45# steel (18×16×2 mm³) was used as the cathode, which were previously polished to a 0.08~0.12 μm surface finish. Then, they were dipped in 5% HCl for 1 min and finally cleaned with distilled water followed by drying with nitrogen gas. Pure graphite sheet (99.9%) was used as the anode, which size is 60×100×3 mm³. Details of the solution and deposition conditions used are given in Table 1. All the chemical reagents used in this experiment were in analytical grade (AR).

| Composition            | Conditions             |
|-----------------------|------------------------|
| Nickel sulphate       | 240 g/L                |
| Nickel chloride       | 20 g/L                 |
| Disodium citrate      | 36 g/L                 |
| Phosphoric acid       | 30 g/L                 |
| Orthoboric acid       | 30 g/L                 |
| Sodium dodecyl sulfate| 0.1 g/L                |
| Sodium saccharine     | 0.15 g/L               |

The crystalline structure of the Ni-P coatings were determined by X-ray diffraction (XRD, Philips-X’pert PRO, Netherlands) using a Cu Kα radiation source. The diffraction angle ranged from 20° to 100°. The friction and wear tests were carried out on a rotational wear test machine using a ball (Si3N4, φ 3 mm) on disk pair. The amplitude and frequency are 5 mm and 0.5 Hz. Each test was repeated three times under the same conditions. The wear rate was calculated using Eq. 1:

\[ k = \frac{V}{S \cdot F} \]  

Where V is the wear volume, S is the total friction distance, and F is the load.

The wear volume and morphology were examined by non-contact optical profiler (MicroXAM-800, KLA-Tencor, America). The corrosion behavior of the coatings in 3.5 wt. % NaCl solution was investigated electrochemically (CS300, China). High purity graphite was used as the counter electrode, while the sample was used as the working electrode. The potential range and scanning rate were ±300 mV and 0.5 mV/s, respectively.

The tribocorrosion behaviors of the coatings were tested by a ball-on-disk tribometer (MFT-R4000, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, China) in linear reciprocating sliding mode in a 3.5 wt. % NaCl solution. High purity graphite was used as the counter electrode, the samples as the working electrode and a saturated calomel electrode (SCE) is as the reference electrode. The load of 5 N is applied on the sample through a Si3N4 ball (φ3 mm).

3. Result and discussion
3.1. Microstructure and phase analysis
Figure 1 shows the XRD patterns of the Ni-P coatings under various duty cycles. There is no obvious difference between these coatings. When phosphorous is incorporated into the structure, most of the peaks become winder and less intense. The incorporation of phosphorous in the structure has not affected the peak positions. There is a single broad peak around 2θ=44°that is characteristic of Ni (111) peak, indicating an amorphous structure [21].
3.2. Anti-wear properties of Ni-P coatings

Figure 2 shows the relationships between duty cycles and friction coefficient, wear rate at a load of 5N. The friction coefficient and wear rate decreases with the increasing duty cycle. When the duty cycle exceeded 50%, the friction coefficient and wear rate increased. The coating have the lowest friction coefficient and wear rate under the duty cycle of 50%, which due to the smooth surface relative to the other coatings (Figure 3).

Figure 3 shows the 3D optical morphology of the wear groove generated after dry friction experiments at 5N. The coating has a smooth surface with the condition of 50% duty cycle, relatively. The surface morphology within the wear tracks showed plastic deformation for the coatings showed Fig.3 (a, b, c). However, the coating (Fig.4, c) has narrow wear track width and neat edge grinding crack. The damaged form of the coating is scratch. The reason is that the appropriate duty cycle eliminates the concentration of polarization, so that metal ions neatly stacked on the substrate.
3.3. Electrochemical properties of Ni-P coatings

Figure 4 shows the potentiodynamic polarization curves of the Ni-P coatings. The electrochemical parameters calculated from the Teal plots using the CS-330 system are listed in Table 2. Corrosion current density (I_{corr}) and self-corrosion potential (E_{corr}) are used to evaluate the protective property of coatings. It can be seen from Table 2 that the E_{corr} of coatings increases with increasing the duty cycle, and the I_{corr} of coatings decreases with increasing the duty cycle.

Table 2. Electrochemical parameters calculated from the Teal plots

| Samples            | E_{corr}(V) | I_{corr}(\mu A/cm^{-2}) |
|--------------------|-------------|--------------------------|
| 30% Ni-P coating   | -0.5794     | 1.1656                   |
| 40% Ni-P coating   | -0.3684     | 0.1380                   |
| 50% Ni-P coating   | -0.3523     | 0.3863                   |
| 60% Ni-P coating   | -0.3013     | 0.0890                   |
3.4. Tribocorrosion properties of Ni-P coatings

Figure 5 shows the wear rate of Ni-P coatings with different duty cycle in 3.5 wt. % Nalco solution. For all the coatings, the change rules of wear rate in Nalco solution is same to that under the dry friction. Compare with the dry friction condition, all the Ni-P coatings in Nalco solution have lower wear rate, which due to the lubricity of solution. From Table 2, we can see that the coating prepared under the duty cycle of 30% has the highest corrosion current density; as a result, the tribocorrosion property of the coating is very poor.

![Wear rate of Ni-P coatings with different duty cycle in 3.5 wt. % Nalco solution.](image)

Figure 5. Wear rate of Ni-P coatings with different duty cycle in 3.5 wt. % Nalco solution.

Figure 6 shows the 3D image of wear track of Ni-P coatings with 50% duty cycle after tribocorrosion. Pitting corrosion occurred on the surface of the coating. The maximum wear track depth is up to 0.784 mm with the action of wear and corrosion. The cracks provide channels and thereby accelerate the diffusion of Nalco solution. It has been reported that chloride ion plays a major role in inducing the pitting corrosion of materials [22, 23].

A typical tribocorrosion curve shows the OCP of the Ni-P coating with 50% duty cycle in 3.5 wt. % Nalco solution, as shown in Figure 7. The coating exhibits a stable friction coefficient of 0.056 during the whole tribocorrosion period, indicating a better tribocorrosion resistance [24]. It can be seen that the coating exhibits a relatively stable OCP value of -0.388 V during the soaking. In the loading and unloading moment, the coating appears passivation phenomenon that resulted in OCP rising. During the tribocorrosion, wear leads the surface of the alloy exposed to the electrolyte and the repassivation results in an OCP peak [25]. The OCP value decreases to 0.0156 V during tribocorrosion and increases gradually to -0.399 V during passivation. Moreover, the slight decline in OCP value and stable friction coefficient, indicating that corrosion plays a leading role at wear-corrosion effect.
Figure 6. 3D image of wear track of Ni-P coatings with 50% duty cycle after tribocorrosion.

Figure 7. Tribocorrosion curve with OCP of Ni-P coating with 50% duty cycle in 3.5 wt. % Nalco solution.

4. Conclusions
The tribological behaviors, electrochemical behaviors and tribocorrosion behaviors of Ni-P coatings with different duty cycle was investigated in this work. The results indicated that the duty cycle has less effect on the microstructure of the Ni-P coatings, but it could affect the flatness of the coating surface. The Ni-P coating prepared under 50% pulse duty cycle has lowest friction coefficient and wear rate. The Ecor of Ni-P coatings increased with the increasing duty cycle, and the Iscor of coatings decreased with the increasing duty cycle. In addition, Ni-P coatings show a lower wear resistance in 3.5 wt. % Nalco solution than that in air. The slight decline in OCP value and stable friction coefficient, indicating that corrosion plays a leading role at wear-corrosion effect.

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