Effect of Surfactants on the Corrosion and Wear Performance of Zinc-Epoxy Powder Composite Coatings

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Received: 9 March 2021 / Accepted: 26 April 2021 / Published: 31 May 2021

To improve the corrosion and wear resistance of the coating, zinc-epoxy powder (EP) composite coatings were prepared by alkaline zincate electrodeposition. The surfactants of sodium dodecyl sulfate (SDS), cetyl trimethyl ammonium bromide (CTAB), dodecyl dimethyl benzyl ammonium chloride (1227) and polyvinylpyrrolidone (PVP) were used to disperse the EP, respectively. SEM and EDX analysis show that EP is successfully incorporated into the zinc coating. The incorporation of EP reduces the roughness of the Zn coatings. The corrosion resistance of the composite coating prepared by using surfactant is enhanced, which may be due to the adequate wetting contact between EP and zinc and the reduction of defects. The composite coating obtained by using SDS has the lowest root mean square roughness. The grain sizes of all coatings are similar. Electrochemical impedance spectroscopy shows that the composite coating with the strongest corrosion resistance obtained by using SDS, which has the largest coating resistance and charge transfer resistance. The addition of EP reduces the friction coefficient of the Zn coatings. The composite coating obtained by using CTAB has the lowest friction coefficient and wear scar width is reduced.

Keywords: zinc; epoxy powder; corrosion resistance; wear resistance.

1. INTRODUCTION

Electrodepositing zinc on the steel surface is commonly employed in many fields, which represents a low-cost and practical surface treatment technology used to protect steel against corrosion [1]. However, due to the poor tribological and corrosion resistance associated with the conventional zinc electrodeposition, the galvanized coating is easily damaged and failed. It results in a short lifespan of the anti-corrosive coating, leading to material wastage [2, 3]. In recent years, the composite coatings have been reported in a large number of studies to exhibit ideal tribological properties and corrosion resistance [4]. Various doped reinforcing particles such as metal oxides (TiO₂ [5], SiO₂ [6], Al₂O₃ [7], Fe₂O₃ [8],
ZrO$_2$ [9], WO$_3$ [10], CeO$_3$ [11], carbides (SiC [12], WC [13], TiC$_3$ [14]), nitrides (BN [15], Si$_3$N$_4$ [16]), poly(tetrafluoroethylene) (PTFE) [17], vulcanized MoS$_2$ [18], graphene [19] and carbon nanotubes [20] as well as zinc have been deposited on the steel surface to prepare different zinc-based composite coatings. Owing to the incorporation of the reinforcing particles, the wear and corrosion resistance of the zinc-based composite coatings have been improved to varying degrees.

The reinforcing particles used in electrodeposition are mainly inorganic materials. Combining metal materials with organic materials to prepare composite materials with excellent properties of metal and organic materials is a promising research direction [21]. As an organic insulating material with excellent chemical inertness, epoxy powder (EP) has excellent wear resistance, acid and alkali resistance, and mechanical properties [22, 23]. Epoxy powder coating is also an excellent anti-corrosion coating [24].

Electrodeposition of zinc in cyanide bath, acid sulfate bath and zinc acid chloride bath are commonly employed for preparing the zinc coatings [11]. However, Cyanide electrodeposition is corrosive and highly toxic, thus, these do not meet the safety and environmental protection requirements [25]. The research related to zinc composite electrodeposition mainly focuses on the acidic system. Compared to acidic electrodeposition, zincate electrodeposition has less hydrogen evolution, and the bonding force between the coating and the substrate is stronger [26]. The basic plating solution used for zincate electrodeposition is very simple, with easy wastewater treatment and optimal zinc coating coverage. Therefore, the preparation of zinc-based composite coatings by zincate electrodeposition is also of practical significance.

In this study, epoxy powder was selected as wear and corrosion resistant reinforcing particles, and Zn-EP composite coatings were prepared by electrodeposition in alkaline zincate solution. In addition, the effect of EP on the microstructure, phase composition and surface roughness of the zinc coating was analyzed. The corrosion resistance of the composite coatings obtained by using different surfactants was analyzed by electrochemical method. The corrosion resistance of the composite coatings was compared with that of pure zinc. The wear resistance of the composite coatings was studied by tribological experiments.

2. EXPERIMENTAL

2.1. Preparation of Pure Zn and Zn-EP coatings

As shown in Fig. 1, pure Zn coating and Zn-epoxy powder composite coatings were obtained by electrodeposition in three electrode system using DC power supply. The Zn plate with size of 30×10 mm$^2$ was used as anode, and the low carbon steel plate with size of 20×15 mm$^2$ was used as cathode. The surfactants of Surfactant sodium dodecyl sulfate (SDS), cetyl trimethyl ammonium bromide (CTAB), dodecyl dimethyl benzyl ammonium chloride (1227) and polyvinylpyrrolidone (PVP) were used to disperse EP, respectively. In order to disperse EP, the electroplating solution was mechanically stirred for 24 hours at a stirring speed of 1200 rpm. Table 1 shows the operating parameters and the composition of the electrodeposition solution used for electrodeposition.
To determine the composition of the epoxy powder (EP) in the experiment, the epoxy powder was analyzed by SEM, FT-IR and XRD. The SEM image of the epoxy powder has been presented in Fig. 2. As can be observed, the epoxy powder exhibits irregular block structures of varying sizes. The enlarged surface of the blocks demonstrates the typical smooth surface of the organic matter, which can be suggested as the main component of the epoxy powder.
Figure 2. SEM image of epoxy powder (EP).

Figure 3. FTIR spectrum of epoxy powder (EP).
Figure 4. XRD pattern of epoxy powder (EP) and standard XRD pattern of BaSO$_4$, CaCO$_3$, TiO$_2$, SiO$_2$ and CaF$_2$.

The FT-IR spectrum of the epoxy powder has been provided in Fig. 3. The absorption peaks at 1608, 1582, 1510 and 830 cm$^{-1}$ are assigned to the epoxy benzene ring. The absorption peaks at 1297, 1245, 1180 and 1036 cm$^{-1}$ are attributed to the C-O-C asymmetric pulling. The absorption peaks at 2915, 2870 and 1460 cm$^{-1}$ are due to the symmetrical and asymmetric stretching of CH$_2$ groups. On the other hand, the absorption peaks at 2950 and 1384 cm$^{-1}$ appear due to the asymmetric and symmetrical stretching of CH$_3$ groups. The absorption peaks in the range 3400-3500 cm$^{-1}$ are attributed to the -OH stretching vibrations [27,28,29]. The observed peaks confirm the structure of the bisphenol A epoxy resin. The XRD pattern (Fig. 4) of the epoxy powder revealed the presence of BaSO$_4$, CaCO$_3$ and SiO$_2$ useful for improving the wear resistance, along with the pigments TiO$_2$ and CaF$_2$.

2.2. Characterization

The CuK ray source was used to obtain the X-ray diffractograms (XRD) of the coatings using Bruker D8-Advance X-ray diffractometer. The Fourier transform infrared spectrum (FTIR) of epoxy powder was acquired by using FTIR-850. Hitachi S4800 scanning electron microscope (SEM) was employed to study the surface morphology and microstructure of the deposited coatings. Agilent 5500AFM/SPM atomic force microscope (AFM) was used to observe the coating surface at room
temperature and to obtain the corresponding 3D images. Further, the element composition of the coatings was determined by energy dispersive spectroscopy (EDS).

Conventional three-electrode system was used for the electrochemical analysis of the coatings. Saturated calomel electrode (SCE) was used as the reference electrode, platinum foil was used as the auxiliary electrode and the electrodeposited coatings with an exposed area of 1 cm² was used as the working electrode. 3.5% NaCl solution was used as the electroactive medium, and the electrochemical tests were performed on the samples at room temperature. Prior to each EIS measurement, the sample was immersed in the NaCl solution for 1 h to obtain a stable open circuit potential. Subsequently, EIS was measured at the OCP value in the frequency range of 100 KHz to 0.01 Hz, and the sinusoidal signal amplitude is 10 mV. ZsimpWin software was used to fit the electrochemical impedance data.

The CERT UMT-2 multifunctional friction tester was used to carry out the reciprocating sliding experiment to measure the tribological properties of the coatings at room temperature. The displacement amplitude is 2 mm, the load is 5 N, the sliding speed is 5 mm/s, and the sliding time is 20 minutes. The size of the wear specimen is 20×15 mm². After the test, the wear width was measured by VHX-2000C microscope.

3. RESULTS AND DISCUSSION

3.1. Morphology, composition and phase of the coatings

![Figure 5. SEM of pure Zn, Zn-EP (SDS), Zn-EP (CTAB), Zn-EP (1227), and Zn-EP (PVP) coatings.](image-url)
Figure 6. The EDS element surface distribution map shows the distribution of Zn, C and O in the coatings.

Fig. 5 shows the SEM images of pure Zn, Zn-EP (SDS), Zn-EP (CTAB), Zn-EP (1227), and Zn-EP (PVP) coatings at 10000X magnification. All coatings show no microcracks and the surface structure is smooth and compact. By using surfactants SDS and CTAB, the presence of EP can be observed in the coatings. The Zn-epoxy powder composite coatings was successfully prepared. The content of EP in Zn EP (CTAB) coating is more. By using surfactants 1227 and PVP, the surface morphology of the coatings is basically similar, and EP is not found in the coatings. Fig. 6 shows the element surface distribution diagrams of pure Zn, Zn EP (SDS), Zn EP (CTAB), Zn EP (1227) and Zn EP (PVP) coatings. In the Zn-EP (SDS), Zn-EP (CTAB) and Zn-EP (1227) coatings, the aggregated state of C and O elements are observed. C and O only exist in epoxy powder, which further indicates the successful preparation of Zn-EP composite coatings. In the Zn-EP (PVP) coating, no aggregation of C and O elements is found, which indicates that the Zn-EP composite coating cannot be formed by using PVP.

Fig. 7 shows the surface microstructure of pure Zn, Zn-EP (SDS), Zn-EP (CTAB), Zn-EP (1227) and Zn-EP (PVP) coatings. The roughness (RMS) of the pure Zn, Zn-EP (SDS), Zn-EP (CTAB), Zn-EP (1227), and Zn-EP (PVP) coatings are 825.96 Å, 281.99 Å, 719.93 Å, 502.08 Å, and 675.43 Å,
respectively. The addition of EP enhances the uniformity of Zn coatings and reduces the roughness of the Zn coating. It can be found from Fig. 7 that the Zn-EP (SDS) coating has a flat and smooth surface. The surface uniformity of the Zn-EP (CTAB) coating is poor, and there are some recessed areas. Adding an appropriate amount of EP to the zinc coating can improve the structure of the coating. Excessive EP will lead to the destruction of the coating structure and create more defects in the coating.

Figure 7. AFM images of pure Zn, Zn-EP (SDS), Zn-EP (CTAB), Zn-EP (1227) and Zn-EP (PVP) coatings.

Figure 8. X-ray diffraction pattern (a) of the coating and texture coefficient (b) of zinc crystallites.
Fig. 8 (a) shows the XRD curves of pure Zn, Zn-EP (SDS), Zn-EP (CTAB), Zn-EP (1227) and Zn-EP (PVP) coatings. Zn and Fe phases are found in the XRD peak in Fig. 8(a), in which Zn is from the coating and Fe is from the steel substrate. The grain size of the coating was calculated by Scherrer formula [30,31] and FWHM of three main diffraction peaks in XRD curve. The average grain sizes of pure Zn, Zn-EP (SDS), Zn-EP (CTAB), Zn-EP (1227) and Zn-EP (PVP) coatings are 22.7, 24.8 nm, 25.9 nm, 25.7 nm, 23.1 nm, respectively. All coatings have similar grain size. The XRD peak intensity of Zn phase is used to calculate the texture coefficient ($T_c$) values of pure Zn and Zn EP using equation (1) [32,33], as shown in Fig. 8 (b). Where the $I_{hkl}$ value represents the (hkl) peak intensity of the coatings, and the $I_{0hkl}$ value represents the (hkl) peak intensity of the standard reference pattern. Due to the difference of surface energy, the grains with low surface free energy grow preferentially, and different grain orientations are formed during the deposition process. It is reported that the change of texture orientation in the coatings will affect the corrosion [34] and wear resistance [35] of the zinc coating.

$$T_c(hkl) = \frac{I_{hkl}}{\Sigma I_{hkl}} \times \frac{\Sigma I_{0hkl}}{I_{0hkl}}$$ (1)

3.2 Corrosion resistance

Figure 9. (a) Nyquist, (b) Impedance modulus and (c) Phase angle plots of pure Zn, Zn EP (SDS), Zn EP (CTAB), Zn EP (1227) and Zn EP (PVP) coatings after immersion in 3.5% NaCl solution for 1 hour.
Figure 10. Equivalent circuit for fitting EIS data.

As shown in Fig. 9, impedance data are represented by Nyquist and Porter diagrams for all coatings. The Nyquist impedance curve results from the fitting of the measured EIS data. It can be seen from Fig. 9(a) that there are two capacitive reactance arcs in the Nyquist impedance curve, which corresponds to the phase angle diagram in Fig. 9(c). The Zn-EP (SDS) coating has the largest capacitive arc radius. The impedance modulus (|Z|₀.₀１Hz) at the lowest frequency (Zf=10mHz) in the Bode diagram can be used as a semi-quantitative index for evaluating corrosion resistance [36]. It can be seen from Fig. 9(b) that the impedance modulus of Zn-EP (SDS) is much higher than that of other coatings. The Zn-EP (SDS) composite coating obtained by using SDS has the strongest corrosion resistance. The impedance modulus of the pure Zn, Zn-EP (SDS), Zn-EP (CTAB), Zn-EP (1227) and Zn-EP (PVP) coatings are 923.76 Ω cm², 3443.28 Ω cm², 1147.89 Ω cm², 852.07 Ω cm² and 1524.92 Ω cm², respectively. To obtain the impedance parameters, the EIS data obtained from the experiment was fitted with the equivalent circuit model in Fig. 10 using zsimpwin software [37]. In Fig. 10, Rₛ is the solution resistance between the surface of the reference electrode and the working electrode. The high-frequency elements corresponding to R_coat and Q_coat are the coating resistance and coating capacitance, respectively, the low frequency elements can be attributed to the coupling of the double layer capacitance C_dl and the charge transfer resistance R_ct at the coating electrolyte interface [19, 38, 39].

The impedance spectral parameters of pure Zn, Zn-EP (SDS), Zn-EP (CTAB), Zn-EP (1227) and Zn-EP (PVP) coatings are listed in Table 2. The Zn-EP (SDS) coatings has the largest R_coat. The incorporation of EP enhances the uniformity of the electrodeposited Zn coating and reduces the defects between the Zn particles, which are active sites for corrosion. EP is an impermeable material, and EP dispersed in the coating can hinder the penetration of corrosive medium. The R_ct value of Zn-EP (SDS) composite coating is the largest. This indicates that the surface activity at the interface is reduced, and the active surface area in contact with the corrosive medium decreases. The insulating EP can act as a corrosive ion barrier. This makes the ion mass transfer process more difficult. EP is an inert material. In the composite coatings composed of EP and Zn, the active contact area between Zn and corrosive media is reduced. The R_coat and R_ct values of the composite coatings prepared by using surfactants become larger, which may be due to the sufficient wetting contact between EP and zinc and the reduction of defects.
Table 2. Fitting results of EIS data obtained from the coating in 3.5% NaCl solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>R_s (Ω cm^2)</th>
<th>Q_{coat} (S^nΩ/cm^2)</th>
<th>n</th>
<th>R_{coat} (Ω cm^2)</th>
<th>C_{dl} (µF/cm^2)</th>
<th>R_{ct} (Ω cm^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Zn</td>
<td>6.939</td>
<td>4.761×10^{-5}</td>
<td>0.84</td>
<td>570.9</td>
<td>5.3×10^{-3}</td>
<td>312.7</td>
</tr>
<tr>
<td>Zn-EP(SDS)</td>
<td>8.145</td>
<td>5.762×10^{-5}</td>
<td>0.79</td>
<td>1479</td>
<td>2.2×10^{-3}</td>
<td>1671</td>
</tr>
<tr>
<td>Zn-EP(CTAB)</td>
<td>9.593</td>
<td>3.277×10^{-5}</td>
<td>0.85</td>
<td>802.7</td>
<td>1.9×10^{-3}</td>
<td>337.1</td>
</tr>
<tr>
<td>Zn-EP(1227)</td>
<td>10.000</td>
<td>5.275×10^{-5}</td>
<td>0.81</td>
<td>447.0</td>
<td>2.0×10^{-3}</td>
<td>421.2</td>
</tr>
<tr>
<td>Zn-EP(PVP)</td>
<td>5.171</td>
<td>3.857×10^{-5}</td>
<td>0.86</td>
<td>996.4</td>
<td>4.1×10^{-3}</td>
<td>530.2</td>
</tr>
</tbody>
</table>

3.3 wear resistance

Fig. 11 shows the friction coefficient of pure Zn, Zn-EP (SDS), Zn-EP (CTAB) and Zn-EP (PVP) coatings as a function of sliding time at room temperature. It can be found that the friction coefficients of all coatings are reduced compared to pure Zn coatings.

Figure 11. The friction coefficient curve of pure Zn, Zn-EP (SDS), Zn-EP (CTAB) and Zn-EP (PVP) coatings

After 20 minutes of wear, there is no significant increase in the coefficient of friction, indicating that the coating can withstand friction for a long time. The friction coefficient reflects the wear resistance to a certain extent, which indicates that the wear resistance of the coating is enhanced after EP
incorporation. The addition of EP reduces the surface roughness of the coating. The smoother surface has lower friction coefficient and higher wear resistance [40, 41]. The solid lubricating film in the coating can reduce the friction coefficient of the coating [42]. EP has low friction coefficient. EP in the composite coating can act as a lubricant and reduce the coefficient of friction. Zn-EP (CTAB) coating has the smallest coefficient of friction. This is due to the fact that Zn-EP (CTAB) coating has the highest content of EP with lubricating effect.

The coating wear scar width is an important parameter to characterize the coating performance. A smaller wear mark width indicates a lower wear loss [43]. The wear scar widths of pure Zn, Zn-EP (SDS), Zn-EP (CTAB) and Zn-EP (PVP) coatings are 877μm, 806μm, 809μm and 906μm, respectively. Using surfactants SDS and CTAB, the wear loss of the prepared composite coating is reduced, and the wear resistance is enhanced. The composite coating with the lowest wear loss can be obtained by using SDS. EP enhances the wear resistance of the coating in two ways. First, the friction coefficient of the composite coating is reduced after EP is incorporated into the coating. The friction coefficient directly affects the friction performance of the coating. Second, the EP incorporated in the coating can be used as the reinforcing particle and the dispersion strengthening effect of EP hinders the movement of dislocations during the friction process.

4. CONCLUSION

The Zn-epoxy powder (EP) composite coatings were successfully prepared on steel substrates by adding epoxy powder to zincate electroplating solution and dispersing it by using different surfactants. The coating resistance and charge transfer resistance values of the composite coatings prepared by using surfactants become larger, which may be due to the adequate wetting contact between EP and zinc and the reduction of defects. All the coatings have a smooth and compact surface structure without microcracks. The incorporation of EP enhances the uniformity of the Zn-EP composite coatings, and the roughness of the coatings decreases, but the grain size of the coatings changes less. The coating obtained in the presence of SDS has the minimum surface roughness. The composite coating obtained by using SDS has the largest low frequency impedance modulus, the biggest value of coating resistance and the charge transfer resistance, and it has the strongest corrosion resistance. Compared with pure Zn coatings, the friction coefficients of composite coatings obtained by using different surfactants are all reduced. The friction coefficient of the coating obtained by using CTAB is the smallest. The composite coating obtained by using SDS has the smallest wear scar width and enhanced wear resistance.

ACKNOWLEDGMENTS
This work was supported by National Natural Science Foundation of China (No.51871164, No.51671144, No. U1960204), Tianjin Science and Technology Project (No.20YDTPJC01780, No.18YFZCGX00050), and Shandong Taisha-n Industry Leading Talents Project (No. SF1503302301).
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