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Short Communication

Study on Electrochemical Behavior and Mechanical Performance of CoWP Alloy Coating Prepared on Q215A Steel by Electrodeposition

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The CoWP alloy coating is electrodeposited on the surface of Q215A steel used for mechanical arm. The effect of sodium tungstate concentrations on the corrosion resistance and mechanical performance of CoWP coated Q215A steel is studied. It is found out that CoWP coated Q215A steel is formed by co-deposition induced by tungsten and cobalt. The hypophosphate is reduced to phosphorus which can be doped into the CoW alloy to finally obtain CoWP coated Q215A steel. Tungsten atoms can enter into the cobalt lattice, which can inhibit the nucleation process of cobalt, so as to refine the grain and improve the compactness of the CoWP coated Q215A steel resulting in the decrease of roughness and increase of mechanical performance. The CoWP coated Q215A steel electrodeposited from the solution with 15 g/L sodium tungsten has the best mechanical performance and optimal corrosion resistance. However, when the concentration of sodium tungstate in the bath reaches 20 g/L, the deposition of cobalt is hindered due to the precipitation of a large number of tungsten oxides, which leads to decrease of corrosion resistance and mechanical performance.

Keywords: CoWP coated Q215A steel; Electrodeposition; Mechanical performance;

1. INTRODUCTION

Carbon steel has excellent physical and chemical performances, such as low price, excellent plasticity, better toughness and so on. Therefore, carbon steel is widely used in industry to make machine parts [1-4]. With the development of automation technology, mechanical arm is considered as a kind of common mechanical parts which is usually made of carbon steel. For example, carbon steel can be used to fabricate chains, bearings, joint of mechanical arm. Although the plasticity and toughness of carbon steel is excellent, the hardness and corrosion resistance of carbon steel is not good enough. Therefore, surface treatment technology is needed to extremely improve the corrosion resistance and mechanical performance of carbon steel to better meet the requirement of industry [5-9]. The metal cobalt has the advantages of high melting point, excellent corrosion resistance and good mechanical performances. Some cobalt-based coatings are electrodeposited on the surface of carbon steel to improve performances. For example, many scholars study the performance of CoW, CoMo, CoNi electrodeposited coatings and so on [10-14]. It is found out that the content of tungsten, molybdenum and nickel could affect the performance of electrodeposited cobalt-based alloy coatings. Moreover, according to some literatures, it is also found that doping appropriate non-metal phosphorus is beneficial to enhance the mechanical performance of electrodeposited cobalt-based alloy coatings [15-17]. However, higher content of phosphorus will decrease the toughness of metal materials. In recent years, many nano-particles such as Al_2O_3, ZrO_2, SiC, etc are used to prepare cobalt-based composite coating to improve mechanical performance [18-20]. Nonetheless, nano-particles are easily to be agglomerated which may affect the surface morphology and structure of composite coating resulting in the decrease of mechanical performance. Therefore, in this paper, the electrodeposition method is used to prepare CoWP coated Q215A steel by adding tungsten and phosphorus elements to the cobalt-based electrolyte. By regulating the content of tungsten in the CoWP alloy coating, the CoWP coated Q215A steel with excellent corrosion resistance and better mechanical property is prepared. The relationship among the composition, surface morphology, structure, roughness, thickness, corrosion resistance and mechanical performances of CoWP coated Q215A steel is described in detail.

2. EXPERIMENTAL

2.1 Materials

The Q215A steel has optimal plasticity, toughness and welding performance which is chosen as the substrate in the experiment. The chemical composition of Q215A steel is listed in Table 1.

Table 1 The chemical composition of Q215A steel

Element	**Proximate percentage (%)**
C	0.15
Mn	1.2
Si	0.35
S	0.05
Fe	Residual

The surface size of the substrate is 2 cm×3 cm which is used as the cathode during the electrodeposition. The pure platinum electrode (3 cm×4 cm) is as the anode while the saturated calomel electrode is as the reference electrode. The volume of the plating solution is 200 ml and the chemical composition of the electrolyte is listed in Table 2.

Table 2. The Composition of CoWP coated Q215A steel electrodeposition solution

Chemical Agent	**Concentration (gL^{-1})**
$CoSO_4·7H_2O$	28
$Na_2WO_4·2H_2O$	5, 10, 15, 20
$C_6H_8O_7$	90
H_3BO_3	35
$NaH_2PO_2 · H_2O$	10

From the table 2, it is obvious that the cobalt, tungsten and phosphorus that make up CoWP coated Q215A steel come from the cobalt sulphate, sodium tungstate and sodium hypophosphite respectively. The citric acid and boric acid are used as the complexing agent and buffering agent respectively during the plating process. The Q215A steel plate needs to be pre-treated before the electrodeposition begins. Firstly, an alkaline solution (20 g/L NaOH, 30 g/L Na_2CO_3 and 30 g/L Na_3PO_4) is used to remove grease on the surface of the substrate. And then, an acid solution (10% H_2SO_4) is used to remove rust from the surface of the substrate. Finally, pure water is used to thoroughly clean the surface of the substrate before electrodeposition. The CoWP alloy coating is electrodeposited on the surface Q215A from 200 ml plating solution for 1 hour at the condition of 2 A/dm^2 current density, pH=6 and 60 ℃.

2.2 Testing methods

Electrodeposition of CoWP is studied using the cathodic polarization curve from 0~-1.8 V at the scan rate of 10 mV/s. The cathode is the Q215A substrate with size of 1 cm×1 cm while the pure platinum electrode (2 cm×2 cm) is used as the anode. The reference electrode is the saturated calomel electrode. The thickness and roughness of CoWP coated Q215A steel are tested by probe-type surface profiler (KLA D600) with length of 3000 µm and 10 µm/s scan rate. The surface morphology and composition of CoWP coated Q215A steel is observed and tested by scanning electron microscope (Hitachi TM4000) at 10 kV voltage and energy disperse spectroscopy (EDX3000) at the condition of 40 kV working voltage and 100 µA working current. The hardness of CoWP coated Q215A steel is evaluated by Vickers hardness tester (HVS-50) at 1.96 N. Reciprocating friction and wear testing machine is used to test the wear resistance of CoWP coated Q215A steel using 10 N loading force with 5 mm wear length for 30 minutes. The potentiodynamic polarization curve is used to test the corrosion resistance of CoWP coated Q215A steel in 3.5% sodium chloride solution. The pure platinum (2 cm×2 cm) is chosen as the anode while the CoWP coated Q215A steel (1 cm×1 cm) is selected as the cathode. The reference electrode is the saturated calomel electrode. The scan voltage is from -1.4 V to -0.4 V at the scan rate of 1 mV/s.

3. RESULTS AND DISCUSSION

3.1 Electrodeposition of CoW and CoWP

The cathodic polarization curves of Q215A in different solutions are shown in Figure 1. The cathode current on Q215A surface in the pure water solution is small due to the hydrogen evolution. According to the Figure 1(a), the reduction of cobalt ions starts at the position of -0.852 V. Along with the potential moves to more negative, a reduction peak could be found at the position of -1.215 V. Krause et al. also investigates the electrodeposition of cobalt. They find that the reduction of cobalt ions begins at the potential of -0.831 V which is similar to the result in the paper. However, the reduction peak of cobalt they find is around -1.023 V which is more positive than that of in the paper due to the addition of conducting salt [21]. From the research of some literatures, the electrodeposition of cobalt is controlled by diffusion [22]. That is the mass transfer rate of cobalt ions is the lowest in the plating solution. With the negative shift of deposition potential, a large amount of cobalt ions on the cathode surface are reduced to cobalt metal. Due to the slowest mass transfer rate of cobalt in solution, the concentration of cobalt ions on the cathode surface is very low, and the cathodic current decreases greatly, thus forming a reduction peak. The deposition potential of CoW and CoWP is more negative than that of cobalt. It means that the alloy co-deposition requires a larger overpotential. Moreover, the reduction peak of CoW and CoWP electrodeposition is observed at the potential of -1.075 V and -1.022 V respectively which are both more positive than that of cobalt. The result indicates that the addition of sodium tungstate and sodium hypophosphite to the bath is beneficial to increase the mass transfer rate and accelerate the electrochemical reaction, which makes the metal ion concentration on the cathode surface decrease rapidly and the reduction peak shift positively at the initial stage of electrodeposition. The effect of metal ions on electrodeposition of cobalt is researched in some papers [23-25].

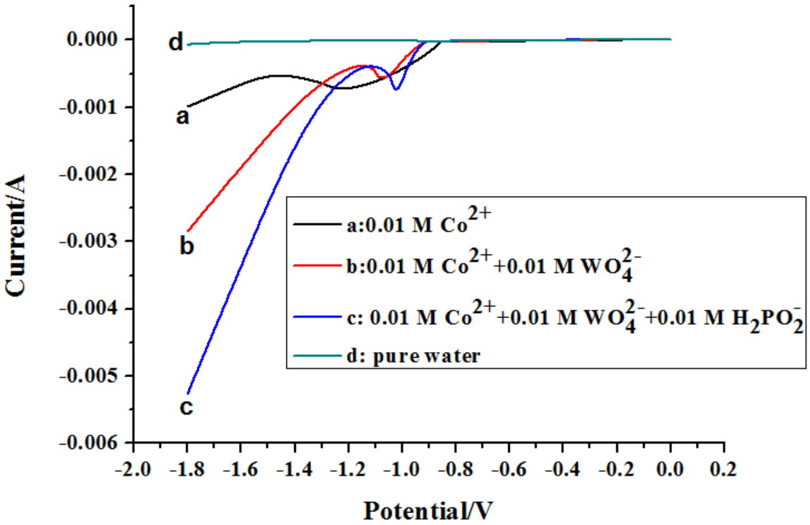


Figure 1. The cathodic polarization curve of Q215A substrate in different solutions: a. 0.01 mol/L $CoSO_4$; b. 0.01 mol/L $CoSO_4$ and 0.01 mol/L Na_2WO_4; c. 0.01 mol/L $CoSO_4$, 0.01 mol/L Na_2WO_4 and 0.01 mol/L NaH_2PO_2; d. pure water;

The co-deposition mechanism of CoWP can be explained by the equations below. The tungsten is very hard to be electrodeposited from the aqueous solution. However, in the presence of cobalt ions in the bath, tungsten and cobalt can form induced co-deposition to obtain CoW. Moreover, the hypophosphate can get electrons and be reduced to phosphorus which can be doped into the CoW alloy to form CoWP [26-27].

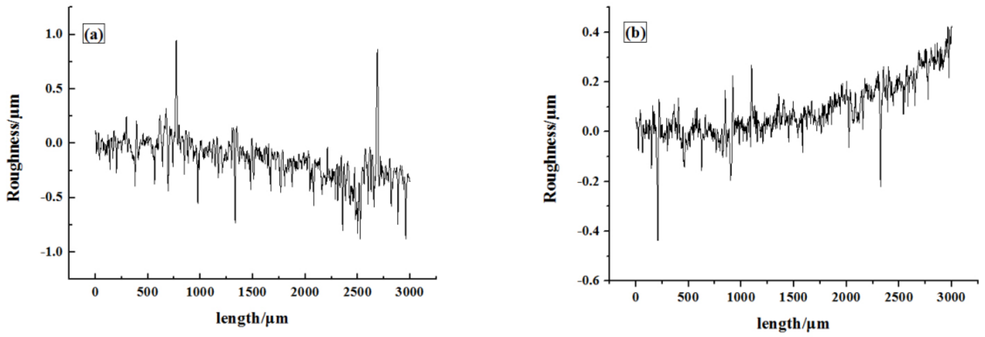
$$WO_4^{2-} + 4H_2O + 2e^- \rightarrow WO_2(2H_2O) + 4OH^- \tag{1}$$

$$WO_2(2H_2O) + 4H(Co) \rightarrow Co(W) + 2H_2O \tag{2}$$

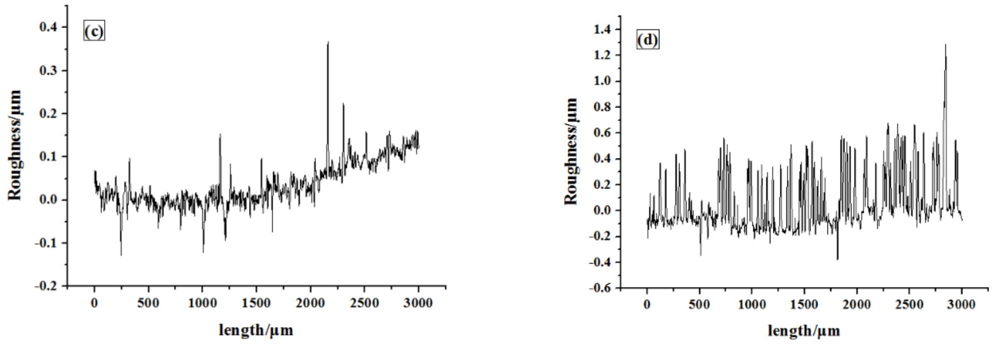
$$H_2PO_2^- + e^- \rightarrow P + 2OH^- \tag{3}$$

3.2 Roughness and surface morphology of CoWP coated Q215A steel

According to the CoWP electrodeposition, the tungsten is hard to be deposited directly from aqueous solution, but in the presence of cobalt ions in the bath, tungsten and cobalt can be deposited together to obtain CoWP. The tungsten has high melt point and better hardness. Doping tungsten in the CoWP will effectively affect its mechanical performance. Moreover, the influence of tungsten on the mechanical performance of materials has been verified by some scholars [28-30].



(a) 5 g/L Na_2WO_4, Ra=0.385 µm (b) 10 g/L Na_2WO_4, Ra=0.234 µm



(c) 15 g/L Na_2WO_4, Ra=0.128 µm (d) 20 g/L Na_2WO_4, , Ra=0.416 µm

Figure 2. The effect of sodium tungstate concentration on the surface roughness of CoWP coated Q215A steel: a. 5 g/L Na_2WO_4; b. 10 g/L Na_2WO_4; c. 15 g/L Na_2WO_4; d. 20 g/L Na_2WO_4; The scan length is 3000 µm at the scan rate of 10 µm/s with 2 mg applied force.

Figure 2 shows the effect of sodium tungstate concentration on the surface roughness of CoWP coated Q215A steel. It can be seen that, along with the increase of sodium tungstate concentration in the plating solution, the surface roughness of CoWP coated Q215A steel is ranged from 0.128 μm to 0.416 μm. The CoWP coated Q215A steel electrodeposited at the condition of 15 g/L Na_2WO_4 has the smallest surface roughness 0.128 μm. The main reason is that in the co-deposition process of cobalt and tungsten, tungsten atoms enter the cobalt lattice, which can inhibit the nucleation process of cobalt, so as to refine the grain and improve the compactness of the CoWP coated Q215A steel resulting in the reduce of surface roughness. The co-deposition and structure of CoW electrodeposited coating is reported in some literature [31-33]. Excessive sodium tungstate in the bath is easy to generate a large amount of tungsten oxide on the surface of the alloy, which greatly increases the surface roughness of CoWP coated Q215A steel. The CoWP coated Q215A steel prepared from the plating solution with 20 g/L Na_2WO_4 possesses the largest surface roughness which is about four times larger than that of electrodeposited from 15 g/L Na_2WO_4.

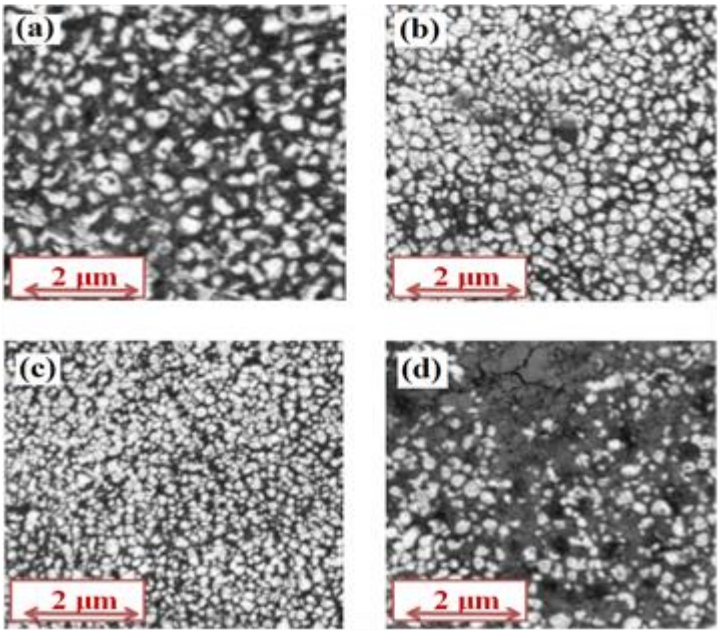


Figure 3. The effect of sodium tungstate concentration on the surface morphology of CoWP coated Q215A steel: a. 5 g/L Na_2WO_4; b. 10 g/L Na_2WO_4; c. 15 g/L Na_2WO_4; d. 20 g/L Na_2WO_4; The accelerating voltage is 10 kV with 5 mm working distance.

The surface morphology of CoWP coated Q215A steel electrodeposited from plating solutions containing different concentrations of sodium tungstate is shown in Figure 3. The electrodeposited CoWP coated Q215A steel shows different surface morphology composed of spherical particles which are also reported in some papers [34-35]. The surface particle of CoWP coated Q215A steel prepared at 5 g/L sodium tungstate is not uniform and compact enough. The main reason is that when the concentration of sodium tungstate in the bath is low, a large number of hexagonal and tetragonal cobalt metals will be generated, which makes the uniformity and compactness decrease. With the increase of sodium tungstate from 5 g/L to 15 g/L, the particle size of the CoWP coated Q215A steel decreases gradually and the compactness increases dramatically. Tungsten entering into the crystal lattice and grain boundary of cobalt is beneficial to inhibit nucleation and refine grains, so as to obtain compact coating with smaller particle size. However, the surface morphology of CoWP coated Q215A steel electrodeposited at 20 g/L sodium tungstate is loose with some cracks due to many oxide of tungsten deposited on the surface.

3.3 Thickness and composition of CoWP coated Q215A steel

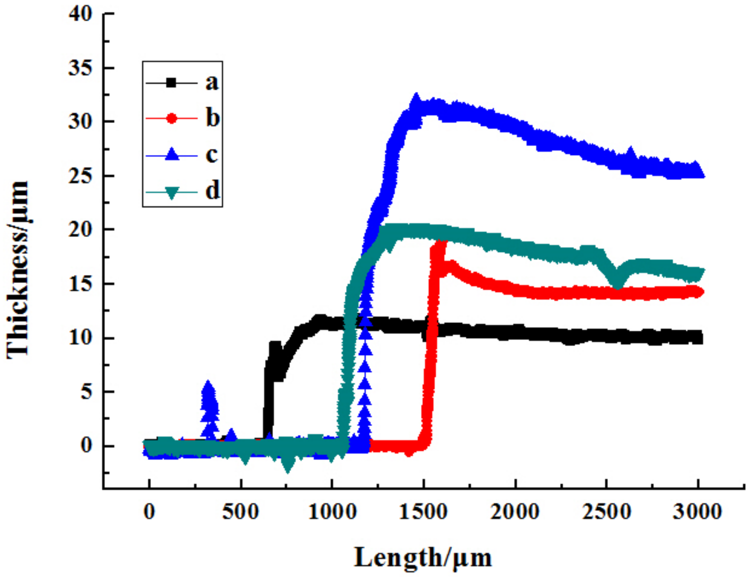


Figure 4. The effect of sodium tungstate concentration on the thickness of CoWP coated Q215A steel: a. 5 g/L Na_2WO_4; b. 10 g/L Na_2WO_4; c. 15 g/L Na_2WO_4; d. 20 g/L Na_2WO_4; The scan length is 3000 μm at the scan rate of 10 μm/s with 2 mg applied force.

Table 3. Thickness of CoWP coated Q215A steel electrodeposited from solutions containing different concentrations of sodium tungstate

Sodium tungstate (g/L)	Maximum Thickness (μm)	Minimum Thickness (μm)	Average Thickness (μm)
5	11.52	9.98	11.37
10	16.45	14.14	15.92
15	31.39	25.38	28.23
20	19.83	15.54	17.39

The thickness of CoWP coated Q215A steel is show in Figure 4 and listed in Table 2. It can be seen that, with the increase of sodium tungstate concentration in the plating solution, the thickness of CoWP coated Q215A steel increases gradually and then decreases. Tungstate ions in the bath are beneficial to improve the mass transfer rate of cobalt ions and increase the cathode current, resulting in the improvement the electrodeposition rate and the thickness of CoWP coated Q215A steel. However, when there is excessive sodium tungstate in the bath, a large amount of tungsten oxide is easily precipitated on the surface of CoWP coated Q215A steel, which hinders the electrodeposition of cobalt to a certain extent, resulting in a decrease in deposition rate and thickness. Thickness can affect the mechanical performance of metal alloys. The relationship between thickness and mechanical performance of materials is reported in some published papers [36-37].

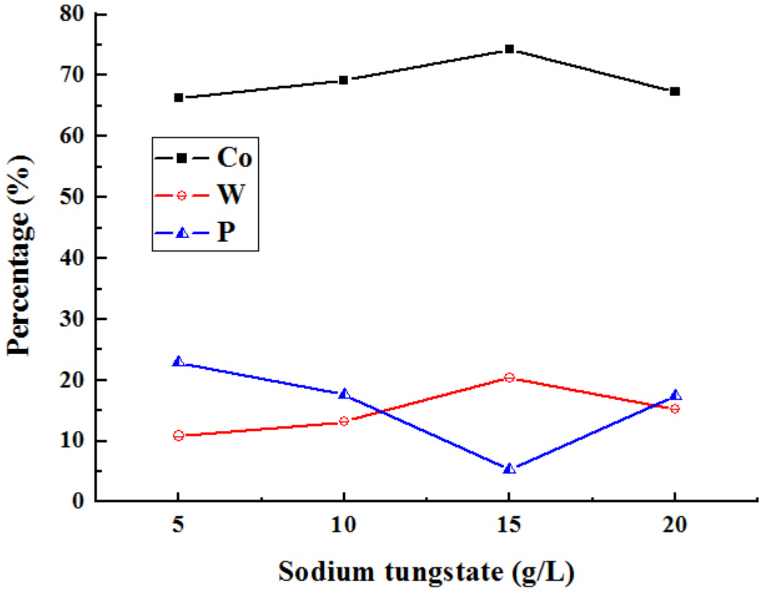


Figure 5. The effect of sodium tungstate concentration on the composition of CoWP coated Q215A steel: a. 5 g/L Na_2WO_4; b. 10 g/L Na_2WO_4; c. 15 g/L Na_2WO_4; d. 20 g/L Na_2WO_4; The working voltage of EDX3000 is 40 kV while the working current is 100 μA.

Table 4. Composition of CoWP coated Q215A steel electrodeposited from solutions containing different concentrations of sodium tungstate

Sodium tungstate (g/L)	**Cobalt (%)**	**Tungsten (%)**	**Phosphorus (%)**
5	66.3	10.8	22.9
10	69.2	13.2	17.6
15	74.3	20.4	5.3
20	67.3	15.3	17.4

The effect of sodium tungstate concentration on the composition of CoWP coated Q215A steel can be seen in Figure 5 and Table 3. With the increase of sodium tungstate concentration from 5 g/L to 15 g/L, the content of cobalt and tungsten in the CoWP coated Q215A steel increases gradually, while the content of phosphorus decreases gradually. It can be found that cobalt and tungsten have a synergistic effect, increasing the amount of tungstate ions in the bath is beneficial to accelerate the mass transfer rate of cobalt ions and improve the cathode current that contribute to the increase of cobalt and tungsten content in the CoWP coated Q215A steel. However, when the concentration of sodium tungstate in the bath reaches 20 g/L, due to the high concentration of tungstate ions in the bath, a large number of tungsten oxides are precipitated on the surface of the CoWP coated Q215A steel, which inhibits the deposition of cobalt ions, so that the content of cobalt and tungsten in the alloy coating decreases at the same time.

3.4 Mechanical performance and electrochemical corrosion of CoWP coated Q215A steel

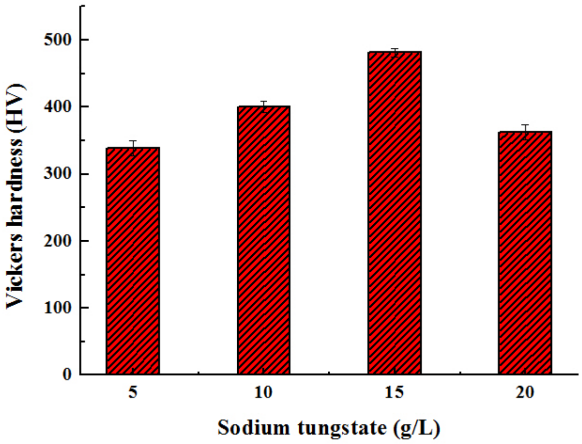
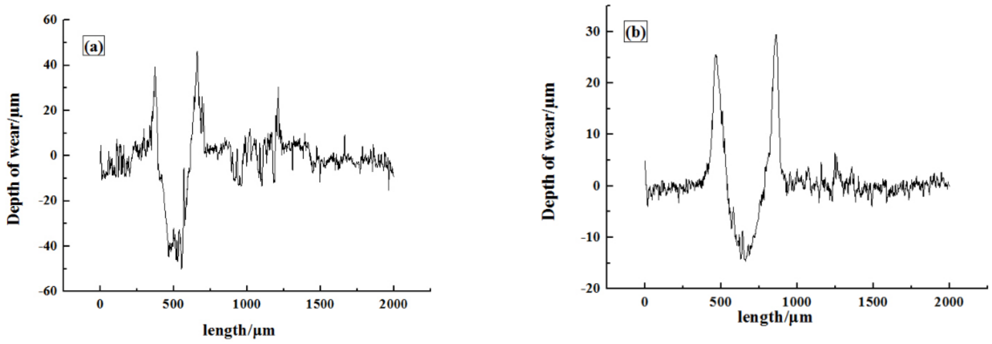
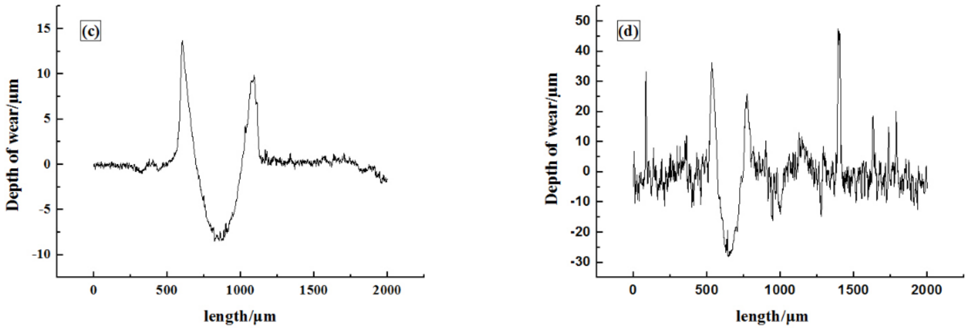


Figure 6. The effect of sodium tungstate concentration on the hardness of CoWP coated Q215A steel: a. 5 g/L Na_2WO_4; b. 10 g/L Na_2WO_4; c. 15 g/L Na_2WO_4; d. 20 g/L Na_2WO_4; The applied force is 1.96 N for 15 s holding time.

The Vickers hardness of CoWP coated Q215A steel prepared from plating solution with different amounts of sodium tungstate is presented in Figure 6. As can be seen from Figure 6, with the increase of sodium tungstate concentration in the bath, the prepared CoWP coated Q215A steel shows a trend of increasing first and then decreasing. The hardness of CoWP coated Q215A steel prepared at 5 g/L sodium tungstate is 338.4HV. As the concentration of sodium tungstate increases from 5g/L to 15g/L, the hardness of CoWP coated Q215A steel increases gradually. The CoWP coated Q215A steel prepared under the condition of 15 g/L sodium tungstate has the largest tungsten content with the largest hardness, about 481.6 HV. According to the literature reports, the electrodeposited CoWP mainly shows Co_3W tetrahedral structure [38-39]. Phosphorus is mainly doped at the grain boundary of the CoWP. Under the action of tungsten and phosphorus, the hardness of CoWP alloy coating is greatly improved. The influence of phosphorus on the mechanical performance of materials is also verified by many researchers [40-41]. However, when the concentration of sodium tungstate in the bath reaches 20 g/L, the deposition of cobalt is hindered due to the precipitation of a large number of tungsten oxides, which leads to the decrease of tungsten content and the increase of phosphorus content in the CoWP coated Q215A steel, resulting in the obvious decrease of hardness.



(a) 5 g/L Na_2WO_4 (b) 10 g/L Na_2WO_4



(c) 15 g/L Na_2WO_4 (d) 20 g/L Na_2WO_4

Figure 7. The effect of sodium tungstate concentration on the wear resistance performance of CoWP coated Q215A steel: a. 5 g/L Na_2WO_4; b. 10 g/L Na_2WO_4; c. 15 g/L Na_2WO_4; d. 20 g/L Na_2WO_4; The loading force is 10 N with 5 mm wear length for 30 minutes.

Table 5. The size of scratch on the CoWP coated Q215A steel electrodeposited from solutions containing different concentrations of sodium tungstate

Sodium tungstate (g/L)	Depth of scratch (μm)	Sectional area of scratch (μm^2)	Volume of scratch (μm^3)
5	89.25	15850.43	79.25×10^6
10	42.09	10962.75	54.81×10^6
15	20.44	6939.2	34.70×10^6
20	59.42	9207.6	46.04×10^6

The reciprocating friction and wear testing machine is used to make a scratch on CoWP coated Q215A steel using 10 N loading force with 5 mm scratch length for 30 minutes. The size of scratch is calculated to evaluate the wear resistance performance of CoWP coated Q215A steel shown in Figure 7 and Table 3. The scratch volume of CoWP coated Q215A steel elecctrodeposited from plating solution with 5 g/L sodium tungstate is the largest, indicating poor wear resistance performance due to looser surface morphology and lower content of tungsten. Along with the increase of sodium tungstate concentration from 5 g/L to 15 g/L, the wear resistance performance of CoWP coated Q215A steel increases extremely. The wear volume of CoWP coated Q215A steel electrodeposited from plating solution containing 15 g/L sodium tungstate is the smallest indicating the best wear resistance performance. That is because that tungsten entering into the crystal lattice and grain boundary of cobalt is beneficial to inhibit nucleation and refine grains, so as to obtain compact coating with smaller particle size. However, when the sodium tungstate is 20 g/L, larger amounts of tungsten oxides precipitated on the surface of CoWP coated Q215A steel will lead to the decrease of surface compactness and wear resistance performance.

The potentiodynamic polarization curve is used to test the electrochemical corrosion of CoWP coated Q215A steel in 3.5% sodium chloride solution. The result is shown in Figure 8 and Table 6.

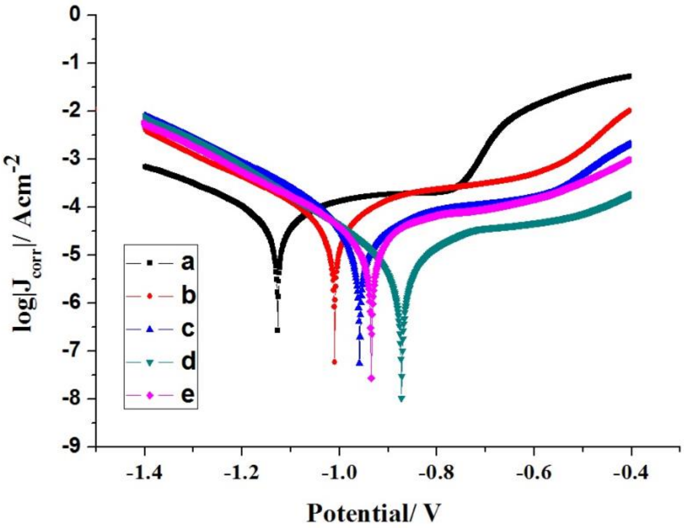


Figure 8. Potentiodynamic polarization curves of CoWP coated Q215A steel in 3.5% sodium chloride solution (a. Q215A; CoWP coated Q215A prepared in b. 5 g/L Na_2WO_4; c. 10 g/L Na_2WO_4; d. 15 g/L Na_2WO_4; e. 20 g/L Na_2WO_4)

Table 6. Corrosion current density and corrosion potential of CoWP coated Q215A steel in 3.5% sodium chloride solution (a. Q215A; CoWP coated Q215A prepared in b. 5 g/L Na_2WO_4; c. 10 g/L Na_2WO_4; d. 15 g/L Na_2WO_4; e. 20 g/L Na_2WO_4)

Samples	**Sodium tungstate/ gL^{-1}**	**J_{corr}/ µAcm^{-2}**	**E_{corr}/ V**
a	-	63.82	-1.12
b	5	52.71	-1.01
c	10	28.18	-0.96
d	15	10.96	-0.87
e	20	24.82	-0.93

The corrosion current density and corrosion potential of the substrate Q215A steel is 63.82 µAcm^{-2} and -1.12 V respectively. The CoWP coated Q215A steel shows different corrosion resistance performance. With the increase of sodium tungstate concentration from 5 g/L to 20 g/L, the corrosion current density of CoWP coated Q215A steel increase gradually and then decrease. The CoWP coated Q215A steel electrodeposited from solution containing 15 g/L sodium tungstate has the lowest corrosion current density and the most positive corrosion potential indicating the best corrosion resistance. Appropriate amount of tungsten entering into the crystal lattice and grain boundary of cobalt is beneficial to inhibit nucleation and refine grains, so as to obtain compact coating with smaller particle size leading to better corrosion resistance. However, when the sodium tungstate is 20 g/L, larger amounts of tungsten oxides precipitated on the surface of CoWP coated Q215A steel contributes directly to poor corrosion resistance.

4. CONCLUSION

In order to improve the corrosion resistance and mechanical performance of Q215A steel, the CoWP coated Q215A steel is prepared by electrodeposition. The influence of sodium tungstate concentration on surface morphology, thickness, roughness, hardness, corrosion resistance and wear resistance performance of CoWP coated Q215A steel is investigated.

(1) In the presence of cobalt ions in the bath, tungsten and cobalt can form induced co-deposition to obtain CoW. Moreover, the hypophosphate can get electrons and be reduced to phosphorus which can be doped into the CoW to form CoWP. The tungsten atoms enter the cobalt lattice, which can inhibit the nucleation process of cobalt, so as to refine the grain and improve the compactness of the CoWP coated Q215A steel resulting in the decrease of roughness and increase of mechanical performance.

(2) The CoWP coated Q215A steel electrodeposited from the solution with 15 g/L sodium tungsten possesses compact surface morphology with the largest thickness and smallest surface roughness. Moreover, at the condition of 15 g/L sodium tungsten, the electrodeposited CoWP coated Q215A steel has the best mechanical performance and corrosion resistance. However, when the concentration of sodium tungstate in the bath reaches 20 g/L, the deposition of cobalt is hindered due to the precipitation of a large number of tungsten oxides, which leads to decrease of mechanical performance and corrosion resistance performance.

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