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# Effects of Process Parameters and CrCl<sub>3</sub> Concentration on the Structure, Surface Morphology, Composition and Corrosion Resistance of Electrodeposited NiCrP Amorphous Alloy Coatings

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Abstract: Herein, NiCrP amorphous alloy coatings were prepared on copper substrates by electrodeposition. The aim of this paper is to replace Cr<sup>6+</sup> with Cr<sup>3+</sup> to prepare NiCrP amorphous alloy coating, which can reduce environmental pollution. By studying the influence of pH, temperature (T), current density  $(D_{\rm K})$ , and CrCl<sub>3</sub> concentration on the structure, surface morphology, composition, and corrosion resistance of the alloy coatings, the optimum bath formulation and process parameters were determined as follows:  $25 \text{ g} \cdot \text{L}^{-1} \text{ NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $100 \text{ g} \cdot \text{L}^{-1} \text{ CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $20 \text{ g} \cdot \text{L}^{-1} \text{ NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ , 80 g·L<sup>-1</sup> Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O (sodium citrate), 40 g·L<sup>-1</sup> H<sub>3</sub>BO<sub>3</sub>, 50 g·L<sup>-1</sup> NH<sub>4</sub>Cl, 1 g·L<sup>-1</sup> KF, 5 g·L<sup>-1</sup> C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>NS (saccharin), 0.05 g·L<sup>-1</sup> C<sub>12</sub>H<sub>25</sub>SO<sub>4</sub>Na (sodium dodecyl sulfate), and 40 mL·L<sup>-1</sup> HCOOH and T: 30 °C,  $D_{\rm K}$ : 15 A·dm<sup>-2</sup>, and pH: 3.5, respectively. NiCrP amorphous alloy coatings with high corrosion resistance were prepared under the abovementioned conditions. The crystal cells of the coating surface are uniform and fine. The corrosion resistance of the NiCrP amorphous alloy coatings was characterized by polarization curves, electrochemical impedance spectroscopy, and an immersion corrosion test and compared with that of the NiP amorphous alloy coating. The results show that Ni91.9P8.1 and Ni83.5Cr8.3P8.2 corrosion potential and corrosion current density are -0.68, -0.44 V, and 36, 7 μA·cm<sup>-2</sup> in 3.5 wt.% NaCl, respectively. With Ni91.9P8.1 and Ni83.5Cr8.3P8.2, the maximum weight loss is 61.67 and 15.42 mg  $dm^{-2}$  in a 1 mol·L<sup>-1</sup> HCl, respectively. The corrosion resistance of the NiCrP amorphous alloy coatings in 3.5 wt.% NaCl and 1 mol·L<sup>-1</sup> HCl solutions is better than that of the NiP alloy coating.

Keywords: amorphous alloy; NiCrP coatings; electrodeposition; corrosion resistance; surface morphology

#### 1. Introduction

NiP binary alloys have been widely investigated by the scientific community because of their excellent properties, such as high abrasion resistance, high corrosion resistance, high hardness, and high electrical conductivity [1]. Cr coatings have high hardness, good wear resistance, and decorative properties [2] and are widely used as decorative and functional coatings [3,4]. Initially, a  $Cr^{6+}$ -containing plating solution was used, and the resulting coating possessed excellent abrasion and corrosion resistance. However, because  $Cr^{6+}$  pollutes the environment, the Cr coating is generally obtained using a  $Cr^{3+}$ -containing plating solution [5,6]. However, the  $Cr^{3+}$ -electroplating technology shows problems such as difficulty in thickening the coating. Therefore, it can only be used to obtain decorative coatings. Contrarily, Cr as a relatively inert metal can prevent corrosion by the blocking mechanism with the substrate. However, cracks always appear on the coating surface [7]. Therefore, the co-deposition

of Cr with other elements, such as Ni and P, to obtain an electrodeposited NiCrP amorphous alloy coating on an Al substrate, has become the main research direction. An aqueous solution containing dimethylformamide and methanol was found to be favorable for achieving the NiCrP amorphous alloy coating, and the NiCrP amorphous alloy coating with a high Cr content transformed into a face-centered cubic crystal structure. After heat treatment, the hardness of the NiCrP coating reaches 1050 HV at 500 °C [8]. However, the organic-aqueous solution was not friendly to the environment. In this study, pure water was used to prepare the plating solution, which reduced the pollution of the plating solution and obtained the coating with excellent performance. An electroplated NiCr alloy coating with 1.40–26 wt.% Cr and 10–30- $\mu$ m thickness was prepared on an Al substrate [9] using a Cr<sup>3+</sup>-containing sulfate–chloride system, which effectively improved the corrosion resistance of the Al substrate.

By X-ray diffraction (XRD), the crystal structure of the NiCr alloy coating was determined, and the increase in the Cr content led to grain refinement and the improvement of corrosion resistance. Cr can be easily passivized, and the NiCrP amorphous alloy coating has better corrosion resistance, higher hardness, and good mechanical properties than the NiP amorphous alloy coating [10,11]. Therefore, the NiCrP amorphous alloy coating has been widely studied. However, most of the NiCrP amorphous alloy coatings are obtained by electroless plating [12] instead of electrodeposition. Therefore, herein, we mainly used the electrodeposition method to prepare the NiCrP amorphous alloy coatings with high corrosion resistance and hardness by changing the process parameters and CrCl<sub>3</sub> concentration [13]. By analyzing and characterizing the surface morphology, composition, and hardness of the alloy coatings, we obtained an ideal plating electrolyte formulation and process parameters for the electrodeposition of the NiCrP amorphous alloy coatings. Thus, the aim of this paper is to use  $Cr^{3+}$  instead of  $Cr^{6+}$  to prepare a NiCrP amorphous alloy coating to reduce environmental pollution. This can replace the existing NiP amorphous alloy coating, because NiCrP amorphous alloy coating has better corrosion resistance and wear resistance.

#### 2. Experimental Procedures and Modeling Methods

The NiCrP alloy coatings were deposited on pure copper by electrodeposition. The pure Cu substrates were machined to the dimensions of  $10 \times 10 \times 1$  mm<sup>3</sup>. The substrates were first immersed in a 15 g·L<sup>-1</sup> NaOH, 25 g·L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub>, 25 g·L<sup>-1</sup> Na<sub>3</sub>PO<sub>4</sub>, and 1 mL·L<sup>-1</sup> OP-10 mixed solution to remove cutting oils and then washed with 60–70 °C hot and cold water, respectively. Subsequently, they were immersed in a 50 g·L<sup>-1</sup> of phosphate, 20 g·L<sup>-1</sup> of nitric acid, and 30 g·L<sup>-1</sup> of acetic acid mixed solution for polishing. Then, the substrates were etched in a 160 mL·L<sup>-1</sup> of  $H_2SO_4$  and 80 mL·L<sup>-1</sup> of  $H_2O_2$ solution for 10 min and finally washed with deionized water. The following electrolytes were used: 15-30 g·L<sup>-1</sup> of NiSO<sub>4</sub>·6H<sub>2</sub>O, 80-140 g·L<sup>-1</sup> of CrCl<sub>3</sub>·6H<sub>2</sub>O, 15-30 g·L<sup>-1</sup> of NaH<sub>2</sub>PO<sub>2</sub>·H<sub>2</sub>O, 80 g·L<sup>-1</sup> of Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O, 40 g·L<sup>-1</sup> of H<sub>3</sub>BO<sub>3</sub>, 50 g·L<sup>-1</sup> of NH<sub>4</sub>Cl, 1 g·L<sup>-1</sup> KF, 5 g·L<sup>-1</sup> of C<sub>7</sub>H<sub>5</sub>NO<sub>3</sub>S (saccharin),  $0.05 \text{ g}\cdot\text{L}^{-1}$  of C<sub>12</sub>H<sub>25</sub>NaO<sub>4</sub>S (lauryl sodium sulfate), and 40 mL·L<sup>-1</sup> of HCOOH. The cathode current density ( $D_{\rm K}$ ) of 10–25 A·dm<sup>-2</sup>, pH of 3–4.5, T of 20–50 °C, and Cu (as a cathode material) were used for the NiCrP coating. Analytical reagents and deionized water were used for the plating bath, where  $5 \text{ g} \cdot \text{L}^{-1}$  of NaOH or  $5 \text{ g} \cdot \text{L}^{-1}$  of HCl was used to control the pH of the bath. The substrates were placed in a cell equipped with a numerical control double-polar pulsed electrical source (SMD300/50, Handan Dashun, Hebei, China) for electroplating. A constant temperature water bath was used to control bath temperature. The plating time was 120 min, and the thickness  $15-30 \mu m$ .

The phase composition of the alloy coatings was characterized by an X-ray diffractometer (XRD, D/MAX2500HB+/PC, Rigaku, Akishima, Tokyo, Japan) using Cu K $\alpha$  radiation ( $\lambda$  = 0.154178 nm) and a monochromator at 40 kV and 200 mA with a scanning rate of 2°/min and scanning step of 0.02°. The alloy coatings were cut into 10 × 10 mm<sup>2</sup> square pieces using a wire-cutting machine for XRD measurements. Before using jade software to analyze the phase composition of the sample, the angle and instrument broadening were calibrated with standard Si.

The HS-4800 field emission electron microscope (Hitachi, Tokyo, Japan) attached with the INC 250 spectrometer (EDS) (Chelmsford, MA, USA) was used to analyze the microstructure and composition of the alloy coatings.

A CHI660A electrochemical workstation was used to obtain the polarization curves to derive the corrosion resistance of the alloy coatings in 3.5 wt.% NaCl and 1 mol·L<sup>-1</sup> of HCl solutions. A three-electrode cell, comprising the NiCrP alloy coating, a platinum piece, and a saturated calomel electrode as the working, counter, and reference electrodes, was used. The polarization curves were acquired at the initial potential of -1.0 V and final potential of 1.0 V at the scan rate of 5 mV/s, which were placed for 60 min before polarization.

#### 3. Results and Discussion

The pH has a relatively obvious impact on the electrodeposition of the NiCrP alloy coatings. At a *T* of 30 °C,  $D_{\rm K}$  of 15 A·dm<sup>-2</sup>, 100 g·L<sup>-1</sup> of CrCl<sub>3</sub>·6H<sub>2</sub>O, and keep the other components of the bath, the influence of the pH of bath on the morphology and composition of the alloy coatings was investigated.

Figure 1 shows the surface morphology of the coating at different pH values. As observed, when pH is 3, the coating has an uneven grain size and the surface smoothness is poor because a small pH leads to a high hydrogen-ion concentration in the plating solution. When pH is 3.5, the OH<sup>-</sup> concentration is high in the bath, and consequently, the hydrogen evolution reaction is restrained. Thus, the grains become uniform. However, when pH increases to 4.0, the coating deposition rate becomes faster and the coating surface becomes rough. When pH increases to 4.5, the grain size of the coating becomes larger, the grain boundary is clear, the surface is dim, and cracks appear. Therefore, when the pH of the plating solution is very high, Cr(OH)<sub>3</sub> accounts for the main part of the plating solution. This leads to the adsorption of a large number of Cr(OH)<sub>3</sub> molecules on the cathode surface, resulting in a poor coating quality or even defects.



**Figure 1.** Scanning electron microscopy (SEM) images of the NiCrP alloy coatings at T = 30 °C,  $D_{\rm K} = 15$  A/dm<sup>2</sup> and 100 g/L of CrCl<sub>3</sub>·6H<sub>2</sub>O with different pH values: (**a**) 3.0, (**b**) 3.5, (**c**) 4.0, and (**d**) 4.5.

Figure 2 shows the effect of pH on the composition of the alloy coating. As noticed, with the increasing pH, the Cr content in the alloy coating first increases and then decreases, i.e., it reaches the maximum value when pH is 3.5. The P content in the alloy coating exhibits an increasing trend with the increasing pH. This is because when pH is low, the coordination ability of the coordination agent complex is poor,  $Cr^{3+}$  exists in the bath as  $[Cr(H_2O)_6]^{3+}$ , and the stability of the complexes is extremely high, which can hardly separately deposit from the solution. This affects the  $Cr^{3+}$  cathode discharge and makes the Cr content in the alloy coating low. When pH > 3.5, the OH<sup>-</sup> concentration increases,  $Cr(OH)_3$  easily forms in the plating solution, and a large number of  $Cr(OH)_3$  molecules adsorb on the cathode surface. This hinders the electrodeposition of  $Cr^{3+}$ , and the Cr content in the alloy coating will

be reduced. In the abovementioned pH range, the P content is always greater than 8 wt.% and the coating is amorphous. Based on the abovementioned analysis, the bath pH should be selected as 3.5.



Figure 2. Relationship between the pH and composition of the alloy coatings.

*T* affects the solubility of each component of the electroplating solution, the mass transfer rate of the liquid phase, the viscosity of the electroplating solution, and the adsorption of surface-active substances on the electrode surface. Subsequently, it affects the surface morphology and composition of the alloy coatings. Therefore, it is particularly important to study the effect of *T* on electrodeposition by changing the bath T and keeping other conditions unchanged. At a pH of 3.5,  $D_{\rm K}$  of 15 A·dm<sup>-2</sup>, 100 g·L<sup>-1</sup> of CrCl<sub>3</sub>·6H<sub>2</sub>O, and maintaining the other components of the bath, the influence of the bath *T* on the morphology and composition of the alloy coatings was investigated.

Figure 3 shows the surface morphology of the alloy coatings at different *T*. As observed from Figure 3, when the *T* is 20 °C, the grain size is small, but there are folds. When the *T* reaches 30 °C, a fine and bright alloy coating is obtained. When the *T* reaches 40 °C, the coating surface is rough and gray without metallic luster. The coating shows cracks when the bath *T* reaches 50 °C. This seriously affects the application of the coating. The experimental results show that the increasing *T* can increase the activity of ions, reduce concentration polarization, which is conducive to the  $Cr^{3+}$  deposition, and increase the diffusion migration rate [14]. That is, the simultaneous increase in the number of ions arriving near the cathode promotes the deposition rate and can effectively relieve the internal stress. However, when the *T* is too high, the deposition potential of hydrogen will be reduced, the hydrogen evolution reaction will be enhanced, and the pH near the cathode will be increased. The increase in *T* will accelerate the supplement rate of metal ions and make the surface grains of the coatings coarse [15].

Figure 4 shows the composition of the alloy coatings at different *T*. As the *T* increases, the Cr content in the alloy coatings decreases, whereas the P content in the alloy coatings increases. Because the increase in the bath *T* is advantageous to ion diffusion and migration, it simultaneously changes the polarization potential of the metal-ion cathode and enhances the reaction rate. However, each ion is differently affected by *T*. For example, with the increasing *T*, the polarization of  $Cr^{3+}$  with the hydroxyl group is enhanced, whereas the polarization of Cr is reduced. Therefore, the Cr content in the coating decreases. When the *T* increases, the thickness of the diffusion layer decreases. This increases the deposition rate of P. Thus, the P content in the alloy coating increases. Based on the abovementioned analysis, the optimal *T* for the coating is 30 °C.



**Figure 3.** SEM images of the NiCrP alloy coatings at pH = 3.5,  $D_K = 15 \text{ A/dm}^2$  and 100 g/L of  $CrCl_3 \cdot 6H_2O$  with different temperatures: (a) 20 °C, (b) 30 °C, (c) 40 °C, and (d) 50 °C.



Figure 4. Relationship between the temperature and composition of the alloy coatings.

At a pH of 3.5, *T* of 30 °C, 100 g·L<sup>-1</sup> of CrCl<sub>3</sub>·6H<sub>2</sub>O, and maintaining the other components of the bath, the influence of the *D*<sub>K</sub> on the morphology and composition of the alloy coatings was investigated.

Figure 5 shows the surface morphology of the alloy coatings at different  $D_{\rm K}$ . As shown in Figure 5, the surface morphology of the coating changes from a flat crystal cell to a raised ball with the increasing  $D_{\rm K}$ . When the  $D_{\rm K}$  is 15 A·dm<sup>-2</sup>, the crystal cell becomes most uniform and detailed. When the  $D_{\rm K}$  increases, the coating starts to crack, and the surface becomes rough. With the increasing  $D_{\rm K}$ , cathodic polarization is improved and the reaction power is increased. The decrease in activation energy (Cr<sup>3+</sup> $\rightarrow$ Cr) [16,17] promotes the rapid reduction of Cr<sup>3+</sup> to Cr, which is favorable for Cr deposition and increases the deposition rate. It also promotes the nucleation rate of the crystal and causes grain refinement. Thus, the crystal cell is uniform and small.

Figure 6 shows the effect of  $D_{\rm K}$  on the composition of the alloy coatings. With the increasing  $D_{\rm K}$ , the Cr content in the alloy coatings gradually increases, while the P content in the alloy coatings decreases. As the  $D_{\rm K}$  increases, the negative shift in the cathode potential can increase the reaction power and accelerate the Cr and Ni deposition, which is conducive to grain refinement and improving the surface quality of the coatings. However, P precipitates out during the chemical reduction reaction regardless of the  $D_{\rm K}$ , and the deposition rate remains unchanged. Thus, the P content in the alloy coating relatively decreases, which is the same as reported in previous studies [18–20]. However, when the  $D_{\rm K}$  is too high, the hydrogen evolution reaction intensifies and the coating surface develops cracks. Based on the abovementioned analysis, the optimal value of  $D_{\rm K}$  is 15 A·dm<sup>-2</sup>.



**Figure 5.** SEM images of the NiCrP alloy coatings at T = 30 °C, pH = 3.5, and 100 g/L of CrCl<sub>3</sub>·6H<sub>2</sub>O with different  $D_{\rm K}$ : (**a**) 10, (**b**) 15, (**c**) 20, and (**d**) 25.



**Figure 6.** Relationship between the  $D_{\rm K}$  and composition of the alloy coatings.

As the CrCl<sub>3</sub> concentration in the bath was different, the ion concentration of the bath and the ion diffusion rate of the electrodeposition were different, which directly affected the composition and the surface morphology of the alloy coatings. At a pH of 3.5, *T* of 30 °C, and  $D_{\rm K}$  of 15 A·dm<sup>-2</sup>, the influence of CrCl<sub>3</sub> concentration on the surface morphology and composition of the coatings was studied by keeping the other components of the bath constant and only changing the CrCl<sub>3</sub> concentration.

Figure 7 shows the surface morphology of the coatings at different  $CrCl_3$  concentrations. As noticed, when the  $CrCl_3$  concentration is 80 g·L<sup>-1</sup>, the coating surface is more delicate. Moreover, when the  $CrCl_3$  concentration is changed from 80 to 100 g·L<sup>-1</sup>, the grains become more uniform, compact, bright, and delicate. As the  $CrCl_3$  concentration increases, both the ion concentration of the bath and the electrodeposition rate increase, the  $Cr^{3+}$  polarization behavior intensifies,  $Cr^{3+}$  becomes more prone to deposit, and the hydrogen evolution reaction is inhibited. Consequently, the surface becomes more uniform and denser. With a further increase in the  $CrCl_3$  concentration in the bath to 120 g·L<sup>-1</sup>, the alloy coating begins to crack, leading to a low-quality coating. Although the  $Cr^{3+}$  concentration increased, the concentration of the other components in the bath remained unchanged. The hydroxyl bridge reaction in the plating solution was intensified, creating a large number of  $Cr(OH)_3$  precipitates on the coating surface. This resulted in electrodeposition defects such as cracks and pores.



**Figure 7.** SEM images of the NiCrP alloy coatings at T = 30 °C,  $D_{\text{K}} = 15 \text{ A/dm}^2$  and pH = 3.5 with different CrCl<sub>3</sub> concentrations: (**a**) 80 g·L<sup>-1</sup>, (**b**) 100 g·L<sup>-1</sup>, (**c**) 120 g·L<sup>-1</sup>, and (**d**) 140 g·L<sup>-1</sup>.

Figure 8 shows the effect of the CrCl<sub>3</sub> concentration on the composition of the alloy coatings. When the CrCl<sub>3</sub> concentration is 80 g·L<sup>-1</sup>, the maximum Cr and P contents are 10.20% and 8.44% in the alloy coatings, respectively. With the increasing CrCl<sub>3</sub> concentration in the bath, the Cr content in the alloy coatings increases. This is because, when the CrCl<sub>3</sub> concentration is low, the Cr<sup>3+</sup> concentration on the cathode surface is low, the number of precipitated Cr atoms is less, and therefore the Cr content in the alloy coating is also low. With the increasing CrCl<sub>3</sub> concentration, the electrical activity of Cr<sup>3+</sup> is enhanced. Thus, the Cr content in the alloy coatings continues to increase. However, the P content in the coating does not change mainly because during electrodeposition, P is significantly influenced by the ion concentration and temperature [21,22]. The continuous increase in the Cr<sup>3+</sup> content of the bath will also cause the hydroxyl bridge reaction, which will lead to a decline in the coating quality and cracks. According to the abovementioned analysis, the concentration of the CrCl<sub>3</sub> plating solution should be 100 g·L<sup>-1</sup>.



Figure 8. Relationship between the CrCl<sub>3</sub> concentration and composition of the alloy coatings.

The corrosion resistance of the alloy coatings affects their quality and service life. The alloy coatings with different Cr and P contents were prepared based on the optimum process parameters and formulation. Simultaneously, XRD, EDS, and scanning electron microscopy (SEM) were used to analyze the changes in the microstructure, composition, and surface morphology of the alloy coatings during immersion and study the corrosion resistance of the alloy coatings. Herein, the alloy coatings with different element contents were prepared and wrapped with cold inserts. The contact area between the coating surface and the solution was  $1 \times 1 \text{ cm}^2$ . The corrosion resistances of different alloy coatings

were analyzed based on the changes in the surface morphology, structural characteristics, and anode polarization curves and compared with that of the NiP alloy coatings.

Under the optimized formulation and process conditions, the NiCrP amorphous alloy coatings with different compositions were prepared. The composition of the amorphous alloy coatings is presented in Table 1.

Alloy Coatings	Ni (wt.%)	Cr (wt.%)	P (wt.%)
NiP	$91.9 \pm 0.2$	0	$8.14 \pm 0.2$
NiCrP	$84.3\pm0.2$	$8.3 \pm 0.2$	$7.4 \pm 0.2$

 Table 1. Composition (wt.%) of the NiCrP amorphous alloy coatings.

Figure 9 shows the surface morphology of the NiP and NiCrP amorphous alloy coatings. Figure 9a presents an SEM image of the NiP alloy coating, and the surface of the alloy coating is flat and cellular. Figure 9b show the SEM images of the NiCrP alloy coatings, and the cell shape of the coating is small. The higher the Cr content in the coating, the smaller the cell shape. The cellular structures are basically uniform spherical particles. The addition of Cr can promote the grain refinement and improve the uniformity of the coating.



Figure 9. SEM images of the (a) NiP, and (b) NiCrP alloy coatings.

Figure 10 shows the XRD patterns of the alloy coatings. As observed in Figure 10, the alloy coating shows a scattered "steamed bread peak" near  $2\theta = 45^{\circ}$ , indicating that the internal structure of the atoms of alloy coatings is in a disordered state, that is, the structure of the coating is amorphous. For the NiP alloy coating, the P content should be more than 8 wt.% to reach an amorphous structure, whereas for the NiCrP alloy coating, the P content of only 7.34 wt.% is required to reach the amorphous structure. Thus, the addition of Cr can promote the formation of an amorphous structure in the NiCrP alloy coatings.



Figure 10. XRD patterns of the (a) NiP, and (b) NiCrP<sub>4</sub> alloy coatings.

Figure 11 shows the polarization curves of the NiP and NiCrP amorphous alloy coatings in a 3.5 wt.% NaCl solution at room temperature. The scanning potential is -1 V, and the scanning speed is 5 mV/s. The corrosion potential and corrosion current of the alloy coatings can be obtained from the polarization curves shown in Figure 11. The corrosion current and corrosion rate are positively correlated, and the corrosion potential represents the degree of difficulty in corrosion, as presented in Table 2. As noticed in Figure 11, the polarization curves of the alloy coatings have similar trends. Based on the corrosion current density, the corrosion resistance order is NiCrP > NiP, indicating that the NiCrP alloy coating has the smaller corrosion rate in the NaCl solution and better corrosion resistance. The addition of Cr to the alloy coating can not only promote the transformation of the crystal structure to the amorphous structure, but also improve the corrosion resistance of the coating.



**Figure 11.** Anodic polarization curves of the alloy coatings in a 3.5 wt.% NaCl solution at room temperature.

Table 2. Corrosion potential and corrosion current density of the alloy coatings in 3.5 wt.% NaCl solution.

	NiP	NiCrP
Corrosion potential (V)	-0.68	-0.44
corrosion current density ( $\mu A \cdot cm^{-2}$ )	36	7.0

The NiCrP and NiP amorphous alloy coatings were etched in a 1 mol·L<sup>-1</sup> HCl solution. After being separately soaked in the 1 mol·L<sup>-1</sup> HCl solution for 12, 24, 48, and 72 h, the alloy coatings were rinsed with deionized water. The corrosion products on the surface were removed with a brush after drying. We weighed the samples before and after immersion, and the corrosion weightlessness and time

curve were obtained, as shown in Figure 12. The corrosion rate of the NiP alloy coating continuously increases in the first 48 h, leading to the maximum weight loss of  $61.67 \text{ mg} \cdot \text{dm}^{-2}$ , and then due to the formation of oxides (hydroxides) on the surface of the coating, further reaction between the coating and the solution is prevented. In the first 24 h, the corrosion rate of the NiCrP alloy coating increases with time, and the maximum weight loss of  $15.42 \text{ mg} \cdot \text{dm}^{-2}$  is achieved at 24 h. Between 24 and 72 h, the corrosion rate decreases with the minimum weight loss of  $4.44 \text{ mg} \cdot \text{dm}^{-2}$ . The corrosion weight of the NiCrP amorphous alloy coating is lower than that of the NiP amorphous alloy coating. The high corrosion resistance of the NiCrP amorphous alloy coating is due to the presence of Cr.



**Figure 12.** Relationship between the time and corrosion weight loss of the alloy coatings in a 1 mol· $L^{-1}$  HCl solution.

Figure 13 shows the SEM and EDS images of the NiP amorphous alloy coatings after immersion in the 1 mol·L<sup>-1</sup> HCl solution for 12, 24, and 72 h. As shown in Figure 13, after 12-h immersion, the NiP alloy coating surface has metallic luster and is partially corroded and black. After 24-h immersion, deep grooves begin to appear in the center of the coating surface, the cracks continue to expand, and some pitting corrosion occurs. With the increasing corrosion time, Cl<sup>-</sup> would enter the coating through these grooves, thereby increasing the corrosion rate. After 72-h immersion, serious cracks appear on the coating surface, which lead to more deep grooves, and then, the cellular structure no longer exists. Subsequently, the cracks become even larger and denser, and a grid is formed. Figure 13e,f shows the EDS distribution of P in the plating state and after 72-h immersion, respectively. As observed, after the 72-h immersion, the P content in the alloy coating significantly increased, reaching 21.06%. The figures show that the distribution of P is uneven and there are few cracks, which may be because of the high energy and instability of the investigated area. During immersion, Cl<sup>-</sup> enters the coating and produces a large internal stress, which will further widen and deepen the cracks.



**Figure 13.** SEM and EDS images of the NiP alloy coatings before and after immersion: (**a**) as-deposited coating, coatings immersed for (**b**) 12, (**c**) 24, (**d**) and 72 h, (**e**,**g**) P and O surface distribution in the as-deposited coating, and (**f**,**h**) P and O surface distribution after 72-h immersion.

Furthermore, a large number of oxygen atoms are observed in the EDS images, because during immersion Ni can react with oxygen to form oxide that prevents the contact between the internal coating and the HCl solution to prevent corrosion. However, with the increasing immersion time, the Cl<sup>-</sup> ions have a strong penetrating power and gradually react with Ni.

Figure 14 shows the SEM and EDS images of the NiCrP amorphous alloy coatings after immersion in the 1 mol·L<sup>-1</sup> HCl solution for 0, 12, 24, and 72 h. After 24 h of immersion, the coating surface still had metallic luster, and black spots appeared only at the edge.



**Figure 14.** SEM and EDS images of the NiCrP alloy coatings before and after corrosion: (**a**) as-deposited coating, coatings immersed for (**b**) 12, (**c**) 24, and (**d**) 72 h, (**e**–**g**) P, Cr and O surface distribution in the as-deposited coating, and (**h**–**j**) P, Cr and O surface distribution after 72-h immersion.

After a 72-h immersion, the coating surface was covered with a layer of black powder corrosion products, which no longer had the metallic luster. After a 12-h immersion, some areas of the coating surface collapsed due to the corrosion of Cl<sup>-</sup> that easily entered the coating from the hole. After a 24-h immersion, although most of the coating surface still retained the cellular structure, some grain structures started to fall off or crack under the corrosion of HCl. As shown in Figure 14d, after a 72-h immersion, the cellular structure transformed into a layer of block structure, holes disappeared, and the cracks were connected. This may be because the upper layer of the coating falls off due to corrosion, leaving an internal layer of coating. Figure 14e–j show the EDS distribution of P, Cr and O in the plating state and after 72-h immersion, respectively. The EDS revealed that after a 72-h immersion, the distribution of Cr and O was more uniform than that of P in the as-deposited coating. The peak of oxygen was present in the energy spectrum because Ni and Cr formed oxides to prevent corrosion during immersion.

Figure 15 shows the XRD patterns of the alloy coatings before and after immersion in the 1 mol·L<sup>-1</sup> HCl solution. As shown in Figure 15a, the NiCrP amorphous alloy coating corroded in 48 h, the XRD pattern shows no significant difference between the coating obtained after 48-h immersion and the original coating, and only slight changes in the peak spacing and height were observed. However, after 72-h immersion, the diffraction peak significantly changed, and the diffraction peak of Cu appeared, which originated from the base Cu, indicating that a part of the coating corroded after 72 h of immersion. Furthermore, the coating became thinner such that the Cu phase could be detected. As observed from Figure 15b, the NiP amorphous alloy coating was corroded in 24 h and the diffraction peak of Cu appeared. Moreover, with the extension of immersion time, the coating became thinner and the corrosion deepened. By comparing the diffraction spectra of the two amorphous alloy coatings, it can be observed that the addition of Cr improves the corrosion resistance and decreases the corrosion rate.



**Figure 15.** XRD patterns of the (**a**) NiCrP and (**b**) NiP alloy coatings before and after immersion in the  $1 \text{ mol} \cdot L^{-1}$  HCl solution.

### 4. Conclusions

Herein, an optimum formulation and plating parameters of a NiCrP amorphous alloy coating were determined as follows:  $25 \text{ g}\cdot\text{L}^{-1} \text{ NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $20 \text{ g}\cdot\text{L}^{-1} \text{ NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ ,  $100 \text{ g}\cdot\text{L}^{-1} \text{ CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $40 \text{ g}\cdot\text{L}^{-1} \text{ H}_3\text{BO}_3$ ,  $50 \text{ g}\cdot\text{L}^{-1} \text{ NH}_4\text{Cl}$ ,  $80 \text{ g}\cdot\text{L}^{-1} \text{ Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ,  $0.05 \text{ g}\cdot\text{L}^{-1} \text{ C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ ,  $5 \text{ g}\cdot\text{L}^{-1} \text{ C}_7\text{H}_5\text{O}_3\text{NS}$ , and  $1 \text{ g}\cdot\text{L}^{-1} \text{ KF}$  and pH: 3.5,  $D_{\text{K}}$ :  $15 \text{ A}\cdot\text{dm}^{-2}$ , and T: 30 °C, respectively. Under the abovementioned conditions, the NiCrP amorphous alloy coating surface is uniform and compact without obvious defects, which improves the corrosion resistance of the Cu substrate.

Cr added to the NiP alloy coating can effectively refine the grains and promote the uniformity of the coating. The crystal lattice distortion caused by the Cr and Ni solid solution is beneficial to the formation of an amorphous structure. The self-corrosion potential and current density of nip and nicrp amorphous alloy coatings are -0.68 and -0.44 V, 36 and  $7.0 \mu$ A/cm<sup>2</sup>, respectively, in the 3.5 wt.% NaCl

solution. The corrosion resistance of the NiCrP amorphous alloy coating is better than that of the NiP amorphous alloy coating in the 3.5 wt.% NaCl solution.

The NiCrP and NiP amorphous alloy coatings were immersed in the 1 mol·L<sup>-1</sup> HCl solution. The corrosion rate of the NiP alloy coating continuously increases in the first 48 h, leading to the maximum weight loss of 61.67 mg·dm<sup>-2</sup>. In the first 24 h, the corrosion rate of the NiCrP alloy coating increases with time, and the maximum weight loss of 15.42 mg·dm<sup>-2</sup> is achieved at 24 h. Between 24 and 72 h, the corrosion rate decreases with the minimum weight loss of 4.44 mg·dm<sup>-2</sup>. The NiP amorphous alloy coating surface gradually flattened during immersion, and corrosion holes and large cracks appeared in local areas, resulting in intensified corrosion. With the increasing corrosion time, the original cellular structure of the NiCrP amorphous alloy coating was corroded. However, there were no cracks. The NiCrP amorphous alloy coating is flatter and filled in the gaps between the former cellular structures after immersion, blocking the contact between the solution and the internal alloy coating and thus improving the corrosion resistance.

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