Effects of electrolyte concentration and current density on the properties of electro-deposited NiFeW alloy coatings

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Abstract. NiWP alloy coatings were prepared by electrodeposition, and the effects of ferrous chloride (FeCl_2), sodium tungstate (Na_2WO_4) and current density (D_K) on the properties of the coatings were studied. The results show that upon increasing the concentration of FeCl_2 , initially the Fe content of the coating increased and then tended to be stable; the deposition rate and microhardness of coating decreased when the cathodic current efficiency (η) initially increased and then decreased; and for a FeCl_2 concentration of 3.6 g l^{-1} , the cathodic current efficiency reached its maximum of 74.23%. Upon increasing the concentration of Na_2WO_4 , the W content and microhardness of the coatings increased; the deposition rate and the cathode current efficiency initially increased and then decreased. The cathodic current efficiency reached the maximum value of 70.33% with a Na_2WO_4 concentration of 50 g l^{-1} , whereas the deposition rate is maximum at $8.67 \mu\text{m h}^{-1}$ with a Na_2WO_4 concentration of 40 g l^{-1} . Upon increasing the D_K , the deposition rate, microhardness, Fe and W content of the coatings increased, the cathodic current efficiency increases first increased and then decreased. When D_K was 4 A dm^{-2} , the current efficiency reached the maximum of 73.64%.

Keywords. Electrodeposition; NiFeW alloy; coatings; current efficiency; microhardness.

1. Introduction

Tungsten alloy electrodepositions, which act as deposits for chromium replacement and possess many excellent characters, such as high melting point, high hardness, excellent wear resistance and anti-attrition performance have drawn increasing attentions. Tungsten has been introduced into the NiFe alloy coatings to promote the grain refining and to improve the uniformity of organization, the surface hardness as well as the high temperature performance of the alloy coating [1–4]. NiW alloy coatings own the advantages of compact structure, high hardness and good temperature performance. Besides, they also have the merits of good wear and oxidation resistance, excellent self-lubrication and corrosion resistance performance, especially under high temperature [5–10]. Nano NiFeW alloy possesses the advantages of NiW and NiFe alloy in hardness and have good wear and corrosion resistance [11–15]. Owing to the excellent wear resistance and high mechanical strength of NiFeW ternary alloy coatings, the shortage of poor wear resistance of the NiFe alloy has been resolved and the application fields for NiFeW have been expanded [16,17]. As a result, the outstanding performances of NiFeW ternary alloy coatings have attracted increased attention [18,19]. A lot of researchers have reported the effects of the tungsten content on the microstructure and related properties

of the coatings, and citric acid ammonium salt system in the electrodeposition of NiFeW alloy was studied by cyclic voltammetry [20,21]. However, the effects of main salt concentration in the electrolyte and the current density (D_K) on the properties of plating bath and layers have not been systematically studied.

In this study, NiFeW alloy coatings were prepared by electrodeposition and their chemical components were studied. The effects of main salt concentration and D_K on deposition rate, composition, hardness and current efficiency (η) of the coatings were studied in detail and the optimized process conditions of electroplating NiFeW alloy were proposed.

2. Experimental

To ensure the surface quality of the plating substrate, we used a commercially available copper plate with a dimension of $30 \text{ mm} \times 30 \text{ mm}$ as the substrate and performed the following pre-treatments before plating: to remove the copper oxide on the surface, the substrate was first immersed in 20% sulphuric acid solution; then immersed in 5 g l^{-1} of NaOH solution, to remove cutting oils; washed by 70°C hot water and cold water, respectively; weakly etched in 5% of H_2SO_4 solution for 30 s and finally washed with deionized water.

The following chemicals were used: ferrous chloride (FeCl_2) $\cdot$ $4\text{H}_2\text{O}$ (1.5 – 4.5 g l^{-1}), $\text{Ni}(\text{NH}_2\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$ (290 – 310 g l^{-1}), sodium tungstate (Na_2WO_4) $\cdot$ $2\text{H}_2\text{O}$ (20 – 60 g l^{-1}), H_3BO_3 (40 g l^{-1}), $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ (40 g l^{-1}), ascorbic acid (Vc, as stabilizer, 3 g l^{-1}), saccharin (as stress removal agent and brighteners, 5 g l^{-1}), sodium lauryl sulphate (as wetting agent, 0.1 g l^{-1}). Analytical reagents and deionized water were used to prepare the plating bath, where 5 g l^{-1} NaOH or 5 g l^{-1} H_2SO_4 was used to control the pH value, which was adjusted to 3.8 – 4.2 . A copper sheet was used as cathode for plating. The plating temperature was 55 – 65°C and the D_K was in the range of 3 – 5 A dm^{-2} .

A HS-4800 field emission electron microscope (Hitachi, East coast port city, Honshu Island), attached to a INC250 spectrometer (EDS), was used to analyse the content of Ni, Fe and W in the NiFeW alloy coatings. A FM-ARS9000 hardness tester was used to measure the hardness of the alloy coatings. The applied force and time were 50 g and 15 s , respectively. The hardness value was the average of hardness from five measurements.

The deposition rate is characterized by the coating thickness difference method. The thicknesses of the samples before and after electrodeposition were measured by using a micrometer, respectively. Before every thickness measurement the samples were cleaned by ethanol and completely dried. The coating deposition rate was obtained by dividing the thickness difference by the electrodeposition time. The deposition rate was obtained by taking the average value of five measurements.

The computing method of η shown in the below equation (1) is based on the analysis of the components of ternary alloy membrane [22].

$$\eta = \frac{\sum_{i=1}^n G \times a_i \times k_i}{Q_{\text{total}}} \times 100\% \quad (1)$$

where n is the number of components ($n = 3$), G is the total weight of coatings (g), a_i is i percentage of components in the alloy and K_i is i electrochemical equivalent value of components ($\text{A} \cdot \text{h g}^{-1}$).

3. Results and discussion

3.1 Influence of FeCl_2 concentration on the properties of NiFeW alloys

The Fe element of coatings was provided by ferrous ion (Fe^{2+}) reduced in the plating solution, hence, the iron content in coatings was affected directly by the concentration of Fe^{2+} in the plating solution. In this study, NiFeW alloy coatings were prepared according to the optimal solution formula with changing only the content of FeCl_2 in the solution. The process parameters were temperature of 60°C , D_K of 4 A dm^{-2} and pH value of 4.0 . Later, the coating performance was tested and

the influence of FeCl_2 concentration on NiFeW alloy coating was investigated.

The relation curve of FeCl_2 concentration and Fe content in coatings is shown in figure 1a. It can be found easily that the Fe content in coatings increases with the increasing of FeCl_2 concentration in the solution. The Fe content increases from 4.37 to 8.1% with the increasing of FeCl_2 concentration in the range of 1.5 – 3.6 g l^{-1} and it tends to increase very slowly with higher FeCl_2 concentration. In the process of electrodeposition, the ionic strength of Fe^{2+} increases with the increasing of FeCl_2 concentration in the solution, and the Fe^{2+} concentration in cathode increases accordingly with the increasing of Fe^{2+} in the solution, which could promote the deposition of Fe^{2+} , thus the Fe content in coatings will increase. However, when the Fe^{2+} concentration in the solution reaches a certain value and the deposition of Fe^{2+} in cathode is saturated, and as a result the Fe content in coatings shows a slight change with the increasing concentration of FeCl_2 .

The effect of FeCl_2 concentration on the hardness of the alloy coatings is shown in figure 1b. It reveals that the microhardness of alloy coatings decreases from 598.60 to 429.83 HV with the increase of FeCl_2 concentration in the plating bath. The microhardness decreases rapidly when the concentration of FeCl_2 is very low. The ionic strength of Fe^{2+} increases with the increasing of FeCl_2 concentration in the solution, and the concentration of Fe^{2+} in the cathode increases, meanwhile the increase of Fe^{3+} concentration in the bath results in the increase of hydroxides of iron. The hydroxides of iron in the alloy coatings will make coatings more brittle, thus reducing the microhardness of the coatings. Moreover, the hydroxides of iron and hydrogen in the cathode at the same time will increase the porosity of the coatings, thereby lowering the microhardness of the coatings.

Figure 1. (a) Fe content, (b) microhardness and (c) deposition rate of the coatings vs. FeCl_2 concentration of the plating bath. Depositions were done in a solution containing different concentrations of FeCl_2 , and at D_K of 4 A cm^{-2} , pH value of 4.0 and temperature of 60°C .

Figure 2. Current efficiency vs. FeCl_2 concentration of plating baths. Depositions were done in a solution containing different concentrations of FeCl_2 , and at a D_K of 4 A cm^{-2} , pH value of 4.0 and temperature of 60°C .

Figure 1c shows the influence of FeCl_2 concentration on the deposition rate (v). It can be seen that when the FeCl_2 concentration increases, the deposition rate decreases gradually from 11.33 to $6.33 \mu\text{m h}^{-1}$. Therefore, FeCl_2 concentration shows a great influence in the deposition rate. The reason should be related to the formation of coordination compounds of Fe^{2+} in the bath solution, sodium citrate and consumption of plating a liquid part of the complexing agent. In the solution, the ionic strength of Fe^{2+} increases with the increase in FeCl_2 concentration. In addition, around the substrate there is an abundance of Fe^{2+} and its coordination compounds, the relative Ni^{2+} and its coordination compound is difficult to reduce, therefore, the deposition rate exhibits a decrease [23]. Moreover, when there are too many Fe^{2+} ions in the electrolyte, there will be increased precipitation hydroxide of iron, which will hinder the deposition of metal ions in the cathode, thus lowering the rate of deposition.

Figure 2 shows the effect of FeCl_2 concentration on η . It reveals that the concentration of FeCl_2 shows a great influence on both the total and partial η of nickel. The ionic strength of Fe^{2+} increases with the increasing of FeCl_2 concentration in the solution. In addition, the total η and each partial η increases with the increasing of FeCl_2 concentration. Moreover, the partial current of nickel increases rapidly, thus leading to the rapid increase of the total η ; whereas the partial current efficiencies of both tungsten and iron increase slowly. When the concentration of FeCl_2 reaches 3.6 g l^{-1} , the total η at the cathode reaches its maximum value of 74.23% . However, the partial η of nickel declines, when the concentration is larger than 3.6 g l^{-1} . At the same time, the partial current efficiencies of tungsten and iron decreased gently, and hence the total η is in a downward trend. The ionic strength of Fe^{2+} increases with the increasing of FeCl_2 concentration in the solution, when the

concentration of FeCl_2 is relatively low. The increase of Fe^{2+} accelerates the co-deposition of other metal ions, each partial η can be increased, thus promoting the addition of the total η . When the concentration of Fe^{2+} is excessive, although the ionic strength of Fe^{2+} increases with the increasing of FeCl_2 concentration in the solution, Fe^{2+} will intensify the reduction of H^+ as well as the hydrogen evolution. This process will consume much electric energy, and the hydroxyl generated in this reaction will transform into precipitation of metal hydroxide, consequently hindering the deposition of metal ions and reducing the η .

3.2 Influence of Na_2WO_4 concentration on the properties of NiFeW alloys

The addition of tungsten can improve the wear resistance and the properties of the coatings. In the coatings, the element tungsten was mainly from the WO_4^{2-} in the bath solution. NiFeW alloy coatings were prepared by changing the content of Na_2WO_4 in the bath solution. The processing parameters were as below: temperature of 60°C , D_K of 4 A dm^{-2} and pH value of 4.0. The properties of the prepared coatings were tested, and the effect of Na_2WO_4 concentration in the bath solution on NiFeW alloy coatings was analysed.

Figure 3a shows the curve of Na_2WO_4 concentration in the bath and W content of coating. The change of Na_2WO_4 concentration in the plating solution is the same as that of the W, and increases at the same time. When the plating solution concentration of Na_2WO_4 is low, W content of the coating increases rapidly. When the solution concentration of Na_2WO_4 is above 40 g l^{-1} , the W contents, in the coating, gradually increase. When Na_2WO_4 is low, the presence of Ni^{2+} and Fe^{2+} promotes the fast co-deposition of W with increase of Na_2WO_4 . Although the Na_2WO_4 concentration increases to be in excess, the Ni^{2+} concentration keeps

Figure 3. (a) W content, (b) microhardness and (c) deposition rate of the coatings vs. Na_2WO_4 concentration of the plating baths. Depositions were done in a solution containing different concentrations of Na_2WO_4 , and at D_K of 4 A cm^{-2} , pH value of 4.0 and temperature of 60°C .

constant. In this case, Na_2WO_4 is ready to form a precipitate, which will prevent the metal ion co-deposition, thus affecting the content of W in the coating.

Figure 3b shows the relationship between Na_2WO_4 concentration and microhardness of the alloy coatings. It can be seen that when the Na_2WO_4 concentration increases from 20 to 60 g l^{-1} , the microhardness of the alloy coatings increases from 463.66 to 581.98 HV. When the Na_2WO_4 concentration is relatively low, the microhardness of the alloy coatings gradually increases. As the Na_2WO_4 concentration reaches 40 g l^{-1} , the microhardness of the alloy coatings increases rapidly with the increase in Na_2WO_4 concentration.

The reason is that the content of tungsten increases with the increase of Na_2WO_4 concentration, and tungsten could be used for hardening because of its high level of hardness; therefore, tungsten could improve the hardness of coatings. In addition, the atomic radius of tungsten has a great difference from those of both nickel and iron. When the concentration of tungsten in the coatings is increased, the lattice deformation would be intensified to induce an increase in the dislocation motion resistance and the slippage is difficult to proceed, resulting in the improvement of hardness of the coatings. The effects of solution strengthening are related to the atomic radii difference and the content of the elements. When the concentration of Na_2WO_4 is relatively low, the effect of solution strengthening is not that obvious, there is no considerable change in the hardness of coatings. However, with the increase of the concentration of Na_2WO_4 , the effect of solution strengthening is improved, and the hardness of alloy coatings increases rapidly [24].

Figure 3c shows the relationship between Na_2WO_4 concentration in the bath solution and the deposition rate. It can be clearly seen that with the increase of Na_2WO_4 concentration, the deposition rate initially increases and then decreases. When Na_2WO_4 concentration is 40 g l^{-1} , the deposition rate reaches its maximum value of $8.67 \mu\text{m h}^{-1}$. As the concentration of Na_2WO_4 is higher than 40 g l^{-1} , the deposition rate decreases from 8.67 to $6.67 \mu\text{m h}^{-1}$. In the process of deposition, W could not deposit independently of the bath solution, but it was possible to deposit with iron and nickel by the induction effect. As the concentration of Na_2WO_4 in the solution increases, the concentration of WO_4^{2-} in the cathode simultaneously increases. In addition, a higher amount of WO_4^{2-} , Fe^{2+} and Ni^{2+} will accelerate deposition to improve its rate. However, when the concentration of Na_2WO_4 reaches a specific value, the excessive consumption will lower the concentration of nickel ions. In addition, the Fe^{2+} concentration is originally low, and thus the concentration balance among every component will be broken. It could influence induced deposition and reduce the deposition rate. At the same time, the concentration of Na_2WO_4 increases and the bath solution becomes acidic. Na_2WO_4 would transform tungstate precipitation, and its formation could affect the stability of the bath solution and reduce the deposition rate.

Figure 4 shows the relationship curve between Na_2WO_4 concentration in the bath and the η . It reveals that

Figure 4. Current efficiency vs. Na_2WO_4 concentration of the plating baths. Depositions were done in a solution containing different concentrations of Na_2WO_4 , and at D_K of 4 A cm^{-2} , pH value of 4.0 and temperature of 60°C .

the concentration of Na_2WO_4 has a great effect on the total η and the sub-current efficiency of Ni^{2+} . When the Na_2WO_4 concentration is low, the current efficiencies of Ni increases rapidly, while that of Fe decreases a little, leading to an increase of the total η . When Na_2WO_4 concentration reaches 50 g l^{-1} , the total efficiency exhibits its maximum value of 70.33%. With further increase of Na_2WO_4 concentration, the total η and sub-current efficiencies begin to decrease. The sub-current efficiency of Ni decreases rapidly, whereas those of W and Fe decrease inconspicuously. When the Na_2WO_4 concentration is higher than 50 g l^{-1} , the polarization in cathode will be intensified, leading to evolution of hydrogen and excessive consumption of electric energy. Furthermore, the increase of pH value in cathode makes the formation of hydroxide precipitate easier, hindering the deposition of metal ions and thus decreasing the η .

3.3 Effect of D_K on the properties of NiFeW alloys

Current density is defined as the current in a certain area, which is equal to the current divided by the unit area where the current flowed. It is an important parameter in electro-deposition experiments, having a great effect on the crystal grain size in the coating. Low D_K will result in thicker crystal grains leading to low hardness of the coating, whereas high D_K will lead to a bad coating quality and it may even produce a 'burning' phenomenon. The optimal preparation can be obtained by modifying the NiFeW alloy coating and changing D_K at a temperature of 60°C and pH value of 4.0. The effects of current densities on the performance of the obtained NiFeW alloy coatings were studied.

Figure 5a and d shows the dependence of D_K on W, Fe content of the coatings, respectively. Figure 5a shows that the

Figure 5. (a) W composition, (b) microhardness, (c) deposition rate and (d) Fe composition of the coatings vs. the D_K . Depositions were done in a solution containing different D_K , at pH value of 4.0 and temperature of 60°C.

W contents gradually increased from 12.3 to 14.45% with increase of D_K . At the same time, the Fe contents increased rapidly from 5.2 to 7.8% (figure 5d). When the D_K was above 3 A dm⁻², the Fe contents remained almost constant. The current densities have greater effects on contents of Fe than that of W. When D_K increases, the excess ferrous ions are reduced in the cathode, and Fe content in the coating increases correspondingly.

However, when D_K is too large, the cathodic polarization intensifies the ion reduction; while the diffusion rate of ions in the solution is constant, the ion concentration at the cathode will be reduced. This behaviour will inhibit the further increase of the element content in the coatings, in this case Fe content in the coatings only exhibit a slight change or even decrease.

Figure 5b is the curve of D_K vs. hardness. With the increase of D_K , microhardness of coatings increased from 382.11 to 592.78 HV. When the D_K is above 4 A dm⁻², the hardness of the coating gradually increases. At low D_K range, the increase of D_K improves cathodic polarization, refines the grain size and increases the precipitation amount of the cathodic hydrogen, leading to an increase of the hydrogen content in the coatings and improving the microhardness of the coatings. On the other hand, when D_K increases to 4 A dm⁻², the growth of the hardness of the coating becomes very slow. As the cathodic D_K is large, the deposition rate is accelerated. The atoms deposited in the coatings cannot be diffused at the right time, so this heightens defects in the coating, thereby increasingly affecting the hardness of the coatings. In addition, cathodic hydrogen evolution reaction will produce a hydrogen aggregation, consequently inducing the hydrogen embrittlement of the coating. The concurrent formation of ferric hydroxide will make the evaluated hydrogen easier absorbed on the cathode to generate pores and defects, which further affects the coating quality and leads to a decrease of the coating hardness.

Figure 6. Current efficiency vs. the D_K . Depositions were done in a solution containing different D_K , at pH value of 4.0 and temperature of 60°C.

Figure 5c describes the process used in D_K and coating deposition rate graphs. The deposition rate exhibits a remarkable increase in D_K from 3.67 to 15.33 $\mu\text{m h}^{-1}$, with the increase of D_K . During the experiment, the increase can generate a much pronounced cathodic polarization, promoting the deposition of metal ions; therefore, the observed deposition rate shows a notable increase.

Figure 6 shows the relationship between D_K and η . When D_K is relatively low, with increasing D_K the total current efficiency shows an increase, similar tendency has been observed for the partial current efficiencies of nickel, iron and tungsten. However, when the D_K is larger than 1.5 A dm⁻², both the total and partial current efficiencies decrease. When the D_K is 4 A dm⁻², the total η is 73.64%. This is due to low D_K , low cathodic polarization and slower deposition rate of metal ions. Hydrogen evolution reaction accounted for a larger proportion, so the η is not high. With the increase of D_K , the deposition rate of metal ions in the solution increased, and therefore the η also increased [25]. Once the D_K is too large, the cathode hydrogen ion increases, resulting in excessive hydrogen, affecting the deposition of metal ions, but also consumes a lot of electric energy, resulting in decreased η .

4. Conclusions

1. Preparation of the optimized formulation of the ternary alloy NiFeW: Ni(NH₂SO₃)₂ · 4H₂O 300 g l⁻¹, Na₂WO₄ · 2H₂O 40 g l⁻¹, FeCl₂ · 4H₂O 3.6 g l⁻¹, Na₃C₆H₅O₇ · 2H₂O 40 g l⁻¹, H₃BO₃ 40 g l⁻¹, sodium dodecyl sulphate 0.1 g l⁻¹, saccharin 5 g l⁻¹, Vc 3 g l⁻¹. Plating parameters: pH value of 4.0, D_K of 4 A dm⁻² and temperature at 60°C. Under the optimized formulation and technological conditions, the surface coating is uniform and compact without

obvious defects and the coating possesses the crystalline NiFeW phase, which improves the performance of the copper substrate.

2. The Fe content in the coating increases with the increase of the FeCl_2 concentration in the plating bath. When the FeCl_2 concentration is above 3.6 g l^{-1} , the Fe content in the coating changes little with further increase of the FeCl_2 concentration. The microhardness and deposition rate of the coating decreases with the increase of FeCl_2 concentration, and the cathodic η first increased and then decreased. The η of cathodic current is 74.23% when the FeCl_2 concentration is 3.6 g l^{-1} .
3. The W content in the coating and micro-hardness of the coating increases with the increase of Na_2WO_4 concentration below 40 g l^{-1} . The content of Na_2WO_4 is more than 40 g l^{-1} , the W content of coating is basically unchanged, but the hardness is increased rapidly. The cathodic η and the coating deposition rate increased first and then decreased with the increase of Na_2WO_4 concentration. When the Na_2WO_4 concentration is 50 g l^{-1} , the cathodic η reaches the maximum value of 70.33%. The maximum coating deposition rate is $8.67 \mu\text{m h}^{-1}$ when the concentration of Na_2WO_4 is 40 g l^{-1} .
4. With the increase in D_K , the deposition rate increases, and simultaneously the Fe and W content in the coating also increases. When the D_K is above 3 A dm^{-2} , the Fe content of the coating remains stable. Initially, the microhardness of coating increases rapidly with the increase of D_K , and it remains stable when D_K is above 4 A dm^{-2} . The cathodic η increases first and then decreases, and reaches the maximum value of 73.64% with a D_K of 4 A dm^{-2} .

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