Influences of Saccharin on Electrochemical Behavior of Nickel Electrodeposition

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Abstract. Electrodeposition of Ni was performed in acid Watt's solutions. Saccharin concentrations were varied in order to analyze its influence on the electrochemical behaviors of Ni deposition. Investigations were conducted using CHI660D, by methods of linear potential sweep, cyclic voltammetry and A.C. Impedance. Results indicate that with the increase of saccharin concentration, the cathodic polarization, apparent activation energy and the electrochemical reaction resistance of Ni electrodeposition increase. The exchange current density decreases with the increase of saccharin concentration. The electrodeposition of Ni is a mixing process controlled by electrochemical polarization and concentration polarization. The change of saccharin concentration does not affect the electrodeposition mechanism of Ni. But there is an obvious inhibition and blocking effect of saccharin on nickel electrodeposition. When the concentration of saccharin is 4g/L, its adsorption capacity in electrode is close to saturation. The saccharin concentration should be less than 4g/L.

Introduction

Ni coating has excellent tensile strength, wear resistance, corrosion resistance, ductility and toughness. As a protective and decorative coating, it is widely used in aerospace, automotive and material engineering. The physical properties of Ni deposit are closely related to the bright agent. Due to containing polar groups C-SO$_2$- with strong polarity, saccharin molecules can be adsorbed on the surface of the cathode. It accelerates the nucleation rate and increases the number of nuclei, so that the Ni deposit is compact, uniform, bright and smooth with fine grains, and its internal stress is small. Therefore, as a good primary brightener, saccharin is widely used in the Ni plating process. There have been many reports about the effects of saccharin on electrodeposition Ni [1-13]. Most of the literature focuses on the influence of saccharin on structure and surface morphology [4-6, 9, 12], hardness [8], roughness [1], grain size [3] of Ni deposits. These reports didn’t investigate in detail the effect of saccharin on the nickel deposition process and the essential reason for saccharin improving the performance of nickel deposits. Literature on the effects of electrochemical behavior and characteristics of saccharin on nickel electrodeposition is also limited.

In this paper, influence of saccharin on the electrochemical behavior of Ni electrodeposition is investigated by cathodic polarization, cyclic voltammetry and A.C. impedance methods. Variation of kinetic parameters of the exchange current density, activation energy and electrochemical reaction resistance of Ni electrodeposition with saccharin concentration is further investigated. The aim of this paper is to provide some theoretical basis for the industrial application of nickel electroplating. The innovation in the work is to study the law of the exchange current density, activation energy and other kinetic parameters during the electrodeposition of nickel.

Experimental

The working electrode was made from a copper wire with a diameter of 1mm, its exposed surface area was 0.00785cm$^2$, while other surfaces were coated with epoxy resin. A platinum sheet with an exposed surface area of 4cm$^2$ was used as the auxiliary electrode. A saturated calomel electrode
(SCE) was used as the reference electrode. Curves of cathodic polarization, cyclic voltammetry and A.C. impedance were measured by using electrochemical workstation, CHI660D. All experiments were carried out in an H type electrolytic cell with sand core glass diaphragm. A salt bridge with Luggin capillary was used to reduce the ohmic potential drop of the solution. The Cu electrode was polished to mirror bright with fine metallographic sandpaper, then washed with alcohol and acetone, activated with dilute hydrochloric acid and then washed with distilled water. The electrolyte was prepared with analytical grade reagent and deionized water. The pH value of the electrolyte was measured with the PHS-3C type precision pH meter, and the pH value of the electrolyte was adjusted with dilute sulfuric acid solution. The linear sweep rate is 0.002V/s, and the cyclic voltammetry sweep rate is 0.05V/s.

The electrolyte was composed of 120g/L NiSO$_4$$\cdot$6H$_2$O, 45g/L NiCl$_2$$\cdot$6H$_2$O, 30g/L H$_3$BO$_3$, 1.0~5.0g/L saccharin, 0.2g/L sodium lauryl sulfate. The temperature was kept at 20~40°C, and the pH value was fixed at 2.

**Results and Discussion**

**Influences of Saccharin Concentration on Cathodic Process**

When the temperature is 27°C, the pH value is 2, influence of saccharin concentration on cathodic polarization curves of Ni electrodeposition is shown in Figure 1.

![Figure 1. Influence of saccharin concentration on cathodic polarization curves at 2mV/s.](image1)

![Figure 2. Tafel curves at different saccharin concentration at 27°C, pH 2.](image2)

It is known from the electrodeposition kinetic equation $W = K \exp\left(-\frac{b}{\eta}\right)$ that nucleation rate increases with increase of over potential $\eta$. Figure 1 shows that with increase of saccharin concentration, cathodic polarization curves shift to more negative potential direction, and cathodic polarization increases, indicating that the addition of saccharin helps to refine grains of Ni deposit and improve the brightness. When the saccharin concentration increased from 3g/L to 4g/L, the polarization curve significantly shifted to negative potential. But when the saccharin concentration increased from 4g/L to 5g/L, distance between two polarization curves and the polarization degree were gradually reduced. This indicates when saccharin concentration is increased to 4g/L, the adsorption of saccharin molecules on the cathode surface gradually saturates. When the saccharin concentration is further increased, the effect of cathodic polarization is not obvious, at the same time, the content of organic impurities in the deposit increases, which is not conducive to the improvement of the quality of Ni coating.

The abscissa of each polarization curves in Figure 1 is subtracted from the respective open circuit potential, then multiplied by -1, and the abscissa is transformed to the over potential. On the basis of the above, the ordinate of each curve is divided by the electrode area, and their logarithms taken. The resulting curves are Tafel curves. Figure 2 shows cathodic Tafel curves for electrodeposition Ni at 3 different concentrations of saccharin. By linear fitting of Tafel curves, the slope $B$ of the curve
1, 2 and 3 is obtained at 0.21505, 0.14295, 0.1354, and the intercept A is 1.28782, 1.1535, 1.16214, respectively.

According to Tafel formula \( \eta = -\frac{2.303RT}{\alpha ZF} \lg i_0 + \frac{2.303RT}{\alpha ZF} \lg i = A + B \lg i \), the formula \( \lg i_0 = -\frac{A}{B} \) can be deducted. It can be shown that at saccharin concentrations of 2g/L, 4g/L and 5g/L, the exchange current density \( i_0 \) of Ni electrodeposition is 1.027×10^{-6} A/cm², 8.526×10^{-9} A/cm², and 2.612×10^{-9} A/cm², respectively. Thus, the exchange current density decreases with the increase of saccharin concentration. But when the saccharin concentration is increased to 4g/L, exchange current density \( i_0 \) is drastically reduced. The exchange current density value at 4g/L of saccharin is only 0.83% of the exchange current density at 2g/L of saccharin. Thus, when saccharin concentration is increased to 4g/L, the resistance of reduction reaction of Ni²⁺ taking place on the cathode is very large. The saccharin concentration should be lower than 4g/L.

**Influences of Saccharin Concentration on the Cyclic Voltammetry**

When the temperature is 27°C, the pH value is 2, influence of saccharin concentration on cyclic voltammetry curves is shown in Figure 3.

**Figure 3.** Influence of saccharin on cyclic voltammetry curves at 5mV/s.

**Figure 4.** Relationship between \( \ln i_p \) and \( (\varphi_p - \varphi^0) \) at 27°C, pH 2.

It is known from Figure 3 that cathodic process was strongly influenced by the concentration of saccharin in solution. However, the shapes of the cyclic voltammetry curves at various concentrations of saccharin are similar. There is a wide cathodic reduction peak near -1.43V, the voltammetry curves showed no characteristic oxidation peaks, which indicates that electrodeposition of Ni is an irreversible process. Figure 3 shows cathodic peak potentials appeared
at -1.453V for 1.0g/L, at -1.448V for 2.0g/L, at -1.433V for 3.0g/L, at -1.43V and -1.419V for 4.0g/L and 5.0g/L saccharin in solution. Therefore, when the concentration of saccharin is increased, the peak potential is only slightly shifted toward the positive potential. The number of the cathodic peak did not change with the increase of saccharin, which indicates that the influence of saccharin on the mechanism of Ni electrodeposition is not obvious. The reduction peak current decreases with increase of saccharin concentration, showing that saccharin makes the reduction rate of Ni electrodeposition slow down. Too high of a saccharin concentration is unfavourable for the electrodeposition of Ni.

The characteristic equation of irreversible electrode reaction is shown as:

\[ \ln i_p = \ln(0.227nFAC_0^0K_S) - \frac{\alpha nF}{RT}(\varphi_p - \varphi^0) \]  

where \( i_p \) is the cathodic peak current, F is the Faraday constant, A is the electrode area, \( C_0^0 \) is the bulk ionic concentration, \( \varphi_p \) is the cathodic peak potential, \( \varphi^0 \) is standard electrode potential, \( K_S \) is the standard reaction rate constant, \( \alpha \) is electron exchange coefficient and \( n \) is the number of electron.

According to the above equation, there is a linear correlation between \( \ln i_p \) and \( (\varphi_p - \varphi^0) \). \( \alpha \) and \( K_S \) can be obtained from the linear slope and intercept. The relationship between \( \ln i_p \) and \( (\varphi_p - \varphi^0) \) is shown in Figure 4. The slope and intercept of the fitting straight line were -19.15459, -29.71855, respectively. Therefore, it can be concluded that \( \alpha \) is 0.2577 and \( K_S \) is 1.2399×10^{-11} \text{ cm/s}.

**Influences of Saccharin Concentration on Activation Energy**

From the Arrhenius formula \( i = B \exp\left(-\frac{E_i}{RT}\right) \), the formula: \( \lg i = A - \frac{E_i}{2.303RT} \) can be derived, which indicates the reciprocal of temperature (1/T) is linear with the logarithm of the current density (lgi), the apparent activation energy \( E_i(\eta) \) of Ni electrodeposition at a certain overpotential \( \eta \) is obtained from the slope of the straight line. When the pH value is 2, saccharin concentration is 1g/L, the cathodic polarization curves of Ni electrodeposition at different temperature is shown in Figure 5.

Figure 5 shows that with the increase of temperature, the cathodic polarization curves shift to the positive potential direction, and the reduction reaction rate of Ni electrodeposition is accelerated. After converting the curves in Figure 5 to Tafel curves, the relationship curves between 1/T and lgi at various overpotential can be obtained. Figure 6 indicates the relationship between 1/T and lgi for the Ni electrodeposition at the overpotential of 0.65V. By linear fitting, the apparent activation energy of Ni electrodeposition is 59.897 kJ/mol, which is calculated from the linear slope.
Figure 7 shows the influences of saccharin concentration on the apparent activation energy of Ni electrodeposition. Among them, the overpotential $\eta$ corresponding to the curves of 1, 2, 3, 4 and 5 were 0.65V, 0.70V, 0.75V, 0.80V and 0.85V, respectively.

Figure 7 shows that the curves show a similar upward trend. Namely at a certain overpotential, the apparent activation energy of Ni electrodeposition increases with the increase of saccharin concentration, indicating that the increase of concentration of saccharin plays a role in inhibiting the deposition of Ni, and makes the deposition rate of Ni slow down. When the saccharin concentration is 1~4g/L, the apparent activation energy increases rapidly with the increase of saccharin concentration. When the saccharin is greater than 4g/L, the increase of the apparent activation energy is relatively small in range. Thus, when the saccharin concentration is less than 4g/L, the activation energy is smaller. At the same time, it can be found that when saccharin concentration is constant, the apparent activation energy decreases with the increase of overpotential. Larger overpotential is favorable for the electrodeposition of Ni.

**Influence of Saccharin Concentration on A.C. Impedance**

When the temperature is 27°C, pH value is 2, the amplitude of the sine wave is 5mv, the frequency is 100kHz~0.1Hz and the electrode potential is -0.331V, influence of saccharin concentration on the A.C. impedance complex plane of electrodeposition of Ni is shown in Figure 8. Figure 8 shows that the shape of the A. C. impedance spectroscopy of electrodeposition of Ni doesn’t change significantly with changes in saccharin concentration. All A. C. impedance spectroscopy are composed of a semicircular arc and a straight line at an angle of about 45° to the horizontal, which has the characteristics of electrochemical polarization and concentration polarization. This illustrates that the electrodeposition of Ni is a mixing process controlled by electrochemical polarization and concentration polarization. The change of saccharin concentration does not affect the electrodeposition mechanism of Ni. This is different from the report in the literature[10],there is a flattened semi-circular arc in high frequency region, and there are 2 small capacitive arcs at the low frequency region. It can be seen in Figure 8 that the solution resistance is small, and with the increasing of saccharin concentration, solution resistance remained almost unchanged. However, the diameter of the semicircle arc increased with increase of saccharin concentrations, indicating that the electrochemical reaction resistance $R_r$ for Ni electrodeposition increases with increase of saccharin concentrations. According to the formula $C_d = \frac{1}{\omega_b R_r}$, it is known that double layer differential capacity $C_d$ decreases gradually with the increase of saccharin concentration, indicating that the adsorption quantity of saccharin on the cathode increases with increasing concentration. It is also known from formula $R_e = \frac{RT}{i_0 n F}$ that the exchange current density $i_0$ decreases with increasing the concentration of saccharin, which is consistent with the results obtained in the previous
calculation. It can be found that when the saccharin concentration increased from 1g/L to 4g/L, the diameter of the semicircle increased greatly. When the saccharin concentration is increased from 4g/L to 5g/L, the diameter of the semicircle increases to a lesser extent, indicating that when the concentration is 4g/L, the adsorption capacity of saccharin on the electrode is close to saturation. According to the above analysis, the more appropriate saccharin concentration should be less than 4g/L.

**Conclusion**

(1) In the process of electrodeposition of Ni, the cathodic polarization, the apparent activation energy and the electrochemical reaction resistance increased with increasing concentration of saccharin.

(2) Electrodeposition of Ni is a mixing process controlled by electrochemical polarization and concentration polarization. The change of saccharin concentration does not affect the electrodeposition mechanism of Ni.

(3) The concentration of saccharin should be less than 4g/L.

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**References**


