



The effect of valine on the process of nickel electrocrystallization on glassy carbon electrode



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ABSTRACT

The effects of valine concentration and solution pH on nickel electrocrystallization on glassy carbon electrode were studied with linear sweep cyclic voltammetry and single potential step chronoamperometry. Chronoamperometric results show that the nucleation process of nickel followed progressive 3D nucleation mode. The change in valine concentration and solution pH significantly affect nickel nucleation kinetic process, but do not alter nickel nucleation mode. The increment of valine concentration promotes the nickel steady-state nucleation rates, while the promotion effect becomes less remarkable when solution pH changes from 4.0 to 5.0.

1. Introduction

Nickel electrodeposition has received intensive attention because of its excellent mechanical strength, corrosion resistance and heat resistance [1]. An interesting way to obtain uniform nickel electrodeposit with required quality is by adding appropriate organic compound to the bath to change and control its electrocrystallization mechanism [2–4]. Like many other organic compounds, amino acids have also been studied as additives for nickel electrodeposition owing to its ability to complex nickel ions, buffer capacity and environmental friendliness.

Among the various kinds of amino acids, glycine is the most commonly used electroplating additive for improving the quality of metal coatings. As early as in 1967, Sotskaya and Dolgikh [5] proposed to add glycine in nickel electroplating bath as a complexant. After that, glycine has been adopted as a complexing agent in the electrodeposition of Ni [5–9] and its alloys [10–11]. These researches demonstrate that glycine has a great influence in the morphology, structure and mechanical properties of these metal coatings, and it affects the electrodeposition process mainly through its complexation of nickel ions and its adsorption on the electrode.

Besides glycine, investigations have been made on the applications of other amino acids in nickel electroplating. The influences of cysteine on the electro-kinetics of Ni electrodeposition were studied by Ebadi [12]. Sotskaya and Dolgikh have investigated the kinetics of nickel electrocrystallization in electrolytes containing alanine [13] and serine [14], respectively. Moreover, amino acids have also been applied in the electrodeposition of Cu [15–18], Zn [19], Fe [20], Cr [21] and their alloys (Zn–Fe [22], Cu–Sn [23], Zn–Co [24,25]). According to these researches, the concentration of amino acid and bath pH value were the

main factors that affected the electrodeposition process on the cathode.

Valine ($C_5H_{11}NO_2$) is also an important amino acid. With the presence of valine in nickel plating solution, nickel deposit with high hardness and certain brittleness can be obtained, which is attractive as the matrix material for impregnated diamond tools. However, to our knowledge, the effect of valine on nickel electrocrystallization has not yet been studied.

The goal of present work is to examine the influence of valine concentration and solution pH on the mechanism of nickel electrocrystallization through electrochemical techniques. Solution pH was taken into consideration since the mass distribution of the complexes in the bath greatly depends on solution pH values. The nickel nucleation mechanisms were determined by using Scharifker-Hills model and Scharifker-Mostany model.

2. Experimental

The electrochemical studies were performed with a typical three-electrode cell connected to a LK2005 electrochemical workstation (Tianjin Lanlike Company). Experimental temperature was kept at $30 \pm 1^\circ C$, controlled by a thermostatic device. The working electrode is a glassy carbon electrode with a diameter of 3.0 mm. The auxiliary electrode is a platinum electrode with a size of 2.0 by 1.0 cm². A saturated calomel electrode (SCE) serves as reference electrode and all potentials reported here are expressed with respect to the SCE. Before each experiment, the working electrode was pretreated by following steps: (1) mechanical polish to a nearly mirror surface finish with 0.05 μm finer grades of alumina powders, then rinse the electrode surface thoroughly under the distilled water, and treat ultrasonically in

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Table 1
Baths composition and pH.

Solution	pH	Bath composition
S ₁	4.0	S ₀
S ₂	4.0	S ₀ + 0.01 mol/L valine
S ₃	4.0	S ₀ + 0.05 mol/L valine
S ₄	5.0	S ₀
S ₅	5.0	S ₀ + 0.01 mol/L valine
S ₆	5.0	S ₀ + 0.05 mol/L valine

sequence in absolute ethyl alcohol and nitric acid solution with a volume concentration of 50% for 3 min, finally rinse the electrode with double-distilled water; (2) to obtain a clean reproducible surface before each measurement, the GC electrode is then scanned in 0.05 mol/L H₂SO₄ solution at the potential scan rate of 50 mV s⁻¹ between $E_{s,a} \approx +0.4$ V and $E_{s,c} \approx -1.4$ V until the complete overlapped CV curve is obtained. The electrodeposition of nickel was carried out in different solutions as shown in Table 1. The composition of the basic plating solution, S₀, includes: 0.1 mol/L NiSO₄·7H₂O + 0.15 mol/L Na₂SO₄ + 0.6 mol/L H₃BO₃. All solutions were prepared with double-distilled water and analytical grade reagents purchased from Sigma-Vetec. Solution pH was adjusted by adding 10% sodium hydroxide solution or 10% sulfuric acid solution and controlled by a Rex PHS-10 pH meter (accuracy ± 0.01).

3. Results and discussion

3.1. Cyclic voltammetry curves

Figs. 1 and 2 show the cyclic voltammograms recorded for the GC electrode in plating solution with different concentration of valine at pH = 4.0 and pH = 5.0 respectively, at a scan rate $\nu = 0.02$ V/s between $E_{s,a} = 0.3$ V and $E_{s,c} = -1.3$ V. It is found that all voltammograms exhibit similar characteristic trend to the results published by Ewa Rudnik [26]. On the scan to negative potentials, tiny cathode current is not detected until the potential arrived at around -0.9 V. The nickel deposits appear at more negative potential, where current increases gradually with the increasing negative potential before a

certain point and a high value of slope “ $d i / d E$ ” occurs after the point as shown as the point A in the inset of Fig. 1 for the solution S₃. The corresponding potential of point A is defined as the initial deposition potential (E_0) of nickel on the GC electrode. A high value of slope “ $d i / d E$ ” means the presence of cathodic depolarization which caused by the reduction of nickel ions [27]. Subsequently, there is a well-formed cathodic peak occurring at the cathodic peak potential (E_{cp}).

On the return scan, there are intersections occurring on the cathode branches in the forward and reverse potential range. It can be seen that the first cross-over potential is quite clear but the second cross-over potential is poorly defined. This is the ‘complex, irreversible’ type identified by Fltcher and Halliday [28]. Thus, the corresponding potential of the second intersection cannot be unambiguously regarded as the equilibrium thermodynamical potential E_e of Ni/Ni²⁺ electrode.

As the scanning potential continues to move forward, a positive current occurs due to the oxidation of freshly electrodeposited nickel which is a mixture of its interstitial hydrogen alloys α -Ni and β -Ni [29]. The values of E_0 and E_{cp} are listed in Table 2.

According to the data in Table 2, the initial deposition potential (E_0) and the cathodic peak potential (E_{cp}) are negatively shifted with the increase in the concentration of valine at the same pH value. The shift in E_0 and E_{cp} indicates primarily the formation of nickel complexes with valine, and could also be related to the adsorption of valine molecules on the GC electrode.

In addition, in solutions without valine, E_0 and E_{cp} shift negatively with increase in the pH value. This result is in agreement with the conclusions proposed by Boubatra [30]. However, the changes in E_0 and E_{cp} with the increment of valine concentration diminish in the solutions at pH 5.0, comparing with those in the solutions at pH 4.0; that is, the inhibition of valine to nickel electrodeposition decreases with the increase in solution pH. The less negative shifts of E_0 and E_{cp} are probably associated with certain active nickel-valine complex specie formed at high solution pH.

3.2. The chronoamperometry curves

To further investigate the influence of valine on nickel deposition kinetics on the GC electrode, chronoamperometry technique was applied to get the potentiostatic current transients for the 6 plating

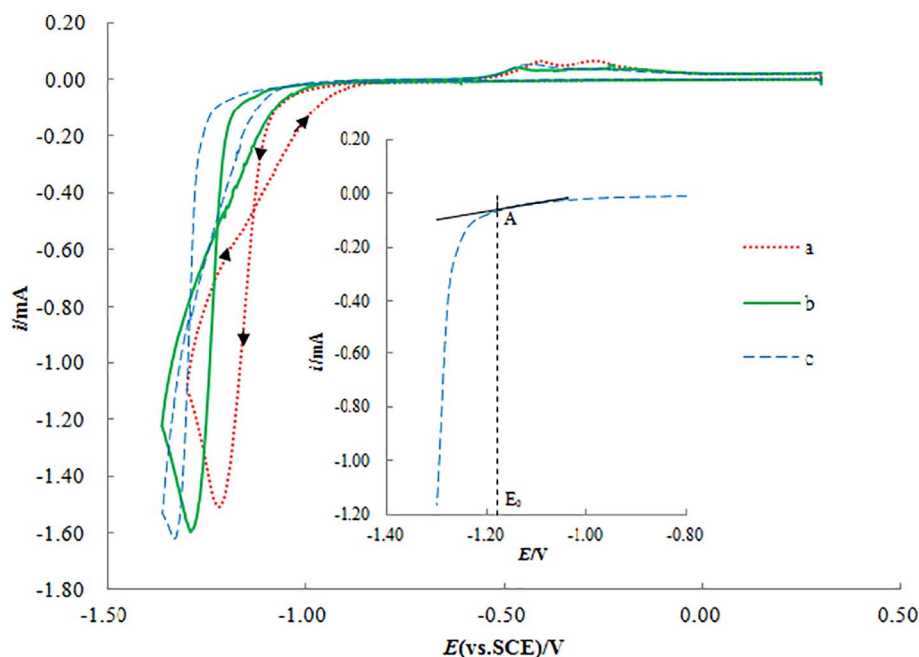


Fig. 1. Cyclic voltammograms recorded for the GC electrode in plating solution with different concentration of valine at the pH = 4.0 and 30 °C. (a) S₀, (b) S₀ + 0.01 mol/L valine, (c) S₀ + 0.05 mol/L valine.

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