

Electrochemical deposition of NiCu alloys in citrate solutions

Uong Van Vy*, Le Xuan Que

Institute for Tropical technology, Vietnam Academy of Science and Technology

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Abstract

This paper presents the research results on electrochemical deposition of NiCu alloy films in containing citrate solutions. Influence of the concentration of the metallic ions to the electrodeposition was studied using linear polarization method. Alloy films have been fabricated by potentiostatic and galvanostatic methods. Element composition and morphology surface of the films was analyzed using EDS and SEM methods. The polarization curves are divided into two distinct regions, the more positive potential than -0.8 V/SCE is the discharge of Cu^{2+} with the critical current density, the more negative potential than -0.8 V/SCE is the co-discharge of Cu^{2+} and Ni^{2+} to alloying of NiCu. The presence of Ni^{2+} promotes Cu^{2+} discharge with critical current density at electrode potential -0.4 V/SCE. When the cathode potential decrease causes Ni composition increased and the Cu composition decreased. Cathode current density in the range of -4 to -8 mA/cm^2 strong influence on the alloy composition, Ni composition increases with cathode current density.

Keywords. NiCu alloy films, electrodeposition, electrodes, hydrogen evolution reaction, alkaline solution.

1. INTRODUCTION

NiCu alloy plating not only has good corrosion resistance and mechanical properties, but also has catalytic activity for hydrogen evolution reaction (HER) in alkaline solutions [1-10].

In order to fabricate electrodes that have high catalytic activity for HER, hydrogen adsorption and desorption kinetics were need to be considered together, which are characterized by the hydrogen binding energy (BEH) at the surface of the catalyst. The alloying elements such as Ag, Cd, Bi, Pd, Ir, Ru, and Cu can increase the activity for HER by reducing BEH. Among them, Cu is a suitable element due to the low cost and NiCu alloys have a good corrosion resistance [4].

The NiCu alloys are fabricated on glass carbon electrode by using potentiostatic methods showed while increasing in cathode potential the Cu content in alloy increased, the particle size also increased [6]. $\text{Ni}_{51}\text{Cu}_{49}$ alloy showed the highest HER current density.

Electrodeposition of NiCu alloy on the Cu electrode was studied by galvanostatic and pulse current technique in the same component solutions [8]. As current density increases from 5 to 300 mA/cm^2 , obtained alloys have Ni composition raising from 6 to 81 mol%. Electrodes with low Ni content show high catalytic activity. Electrodes fabricated by galvanostatic have catalytic activity higher than by

pulse current. Ni content in the alloy affects to catalytic activity is stronger than affects by the morphology of electrode.

Although there have been many studies on electrochemical deposition of NiCu alloys but electrodeposition mechanism, optimization methods and particularly the catalytic mechanism for HER have not been fully discussed.

In this paper, we present the results of research on the effects of the concentration of ions Cu^{2+} , Ni^{2+} to the separate and co-electrodeposition to form NiCu film, the influence of potential electrodes and cathode current density to the composition of the alloy, which can determine the conditions suitable to precipitate alloys with desired composition.

2. EXPERIMENTAL

The chemicals used in the study $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, sodium citrate, citric acid are AR purity, Xilong chemical, China and twice distilled water.

The sulfate-plating bath containing 0.1÷0.7 M $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 0.01÷0.09 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 0.2 M $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ as a complexing and buffer agent, adjusted to pH 5 by sulfuric acid, was used in the study.

The electrochemical measurements were performed on Autolab PGSTAT 30 system. Linear sweep voltammetry measurements were performed

in the range of -0.2 to -1.2 V/SCE, the scan rate of 0.5 mV/s. Potentiostatic (PS) and galvanostatic (GS) techniques were used to fabricate alloy films.

Electrochemical cell is a system including three electrodes, the working electrode was a 1.38 cm diameter (1.5 cm² area) copper disc polished with silicon carbide (SiC)-type abrasive paper (400, 1000 and 2000 grades sequentially), Platinum (Pt) mesh and a Hg/Hg₂Cl₂ (saturated KCl) electrode (SCE) were used as the counter electrode and the reference electrode, respectively.

Surface morphology and elemental composition of the alloy was observed by SEM and analyzed by EDS on JEOL JSM LV-6510 equipment.

3. RESULTS AND DISCUSSION

3.1. The individual discharge of Ni²⁺ and Cu²⁺

Polarization curves in solutions with NiSO₄ concentrations varied from 0.1 to 0.7 M and sodium citrate 0.2 M are shown in figure 1.

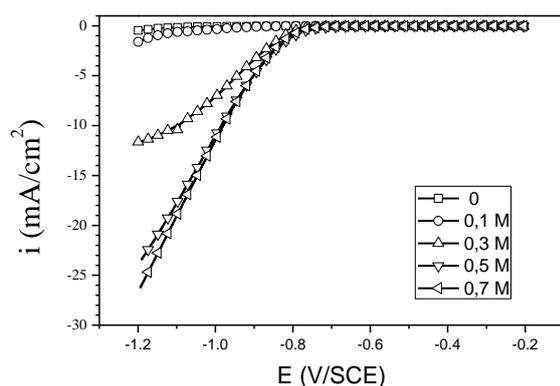


Figure 1: Polarization curves in containing 0÷0.7 M NiSO₄ and 0.2 M sodium citrate solutions

Observe polarization curves can see Ni²⁺ ions starting discharge at electrode potential from -0.8 V/SCE, the electrode potential more negative then cathode current density higher. The slope of the polarization curve increases with increasing of Ni²⁺ ion concentration, polarization curves in solution Ni²⁺ 0.3 M began appearing critical current when electrode potential more negative than -1.1 V/SCE, while not observing critical current in higher concentrations.

Polarization curves in different concentrations of Cu²⁺ solutions are shown in figure 2. We can see Cu²⁺ ions starting discharge at electrode potential more negative than -0.6 V/SCE, when Cu²⁺ concentration increases the cathode current also increases almost linearly, appeared critical current density at the electrode potential -0.8 V/SCE for

samples have Cu²⁺ concentrations 0.5 and 0.7 M, the sample with 0.9 M only reached critical current density after -1.0 V/SCE, however, cathode current density of all the samples are relatively small.

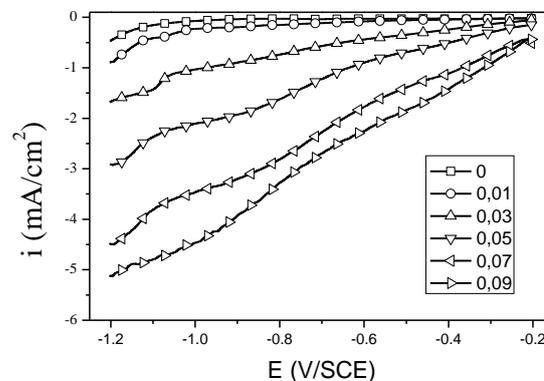


Figure 2: Polarization curves in containing 0÷0.09 M CuSO₄ and 0.2 M sodium citrate solutions

3.2. The co-discharge of Ni²⁺ and Cu²⁺

The influence of the concentration of Ni²⁺ and Cu²⁺ on co-deposition polarization curves is shown in figure 3. It can be noticed that the polarization curves are divided into two distinct regions, more positive electrode potential than -0.8 V/SCE is only Cu²⁺ discharge at saturation current density, Cu²⁺ concentrations is greater the saturation current density is higher, rating variation is almost linear. The presence of Ni²⁺ ions affects the discharge of ions Cu²⁺, reaching the limit current density at the electrode potential -0.4 V/SCE.

Ni²⁺ ion starts discharge from electrode potential negative than -0.8 V/SCE, the higher in Ni²⁺ concentration the greater slope in polarization curves, cathode current density increases while reducing electrode potential. Thus in order to obtain the required NiCu alloy need to apply electrode potential more negative than -0.8 V/SCE. Cu²⁺ ions discharge with limit current density during alloying potential range.

By changing the ratio of the concentration of metal ions, changing the applied electrode potential or changing the cathode current density we can fabricated composition desired alloys.

3.3. Effect of fabrication methods on obtained alloy components

The solution with 0.5 M NiSO₄, 0.05 M CuSO₄ and 0.2 M Na₃C₆H₅O₇ was selected to study on effects of electrode potential and cathode current density on alloy composition.

The alloy samples were fabricated by PS

technique, electrode potential varied from -0.85 V/SCE to -1.05 V/SCE, electrodeposition time was applied so that the alloy film thickness in the range of 10 to

12 μm . EDS pattern of the alloy sample, Figure 4, do not appear other metallic elements except for Ni and Cu.

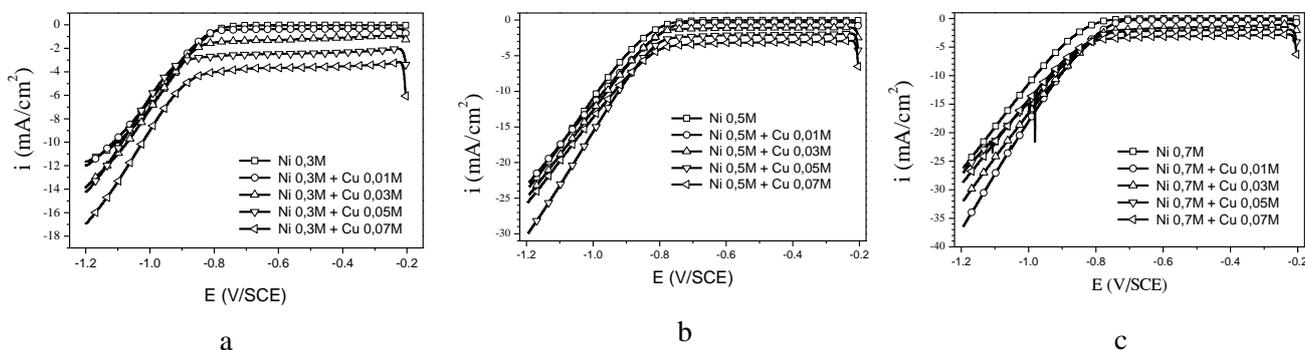


Figure 3: Polarization curves in containing CuSO_4 0÷0.07 M, Ni^{2+} 0.3 M (a); 0.5 M (b), 0.7 M (c) and sodium citrate 0.2 M solutions

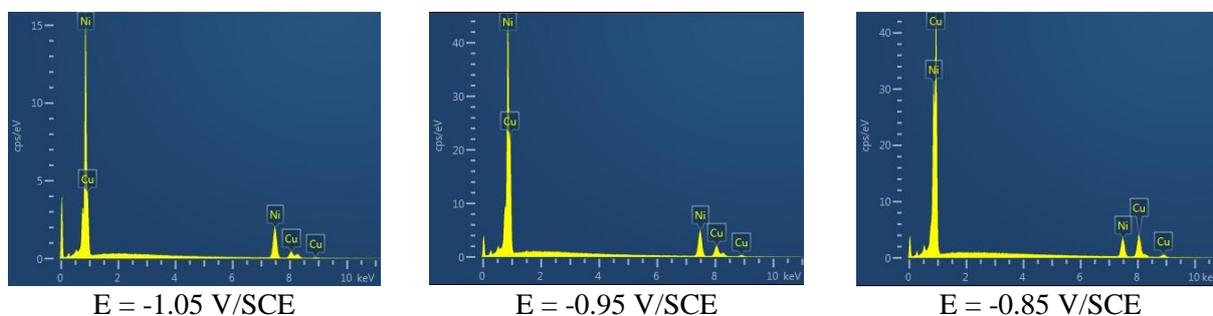


Figure 4: EDS patterns of the alloy films were fabricated by PS technique

Influence of electrode potential on the alloy composition is shown in figure 5. The results show that when the electrode potential decreases, Ni content increases and Cu content decreases, similar results [8]. This is also suitable with the results by polarization curves, Cu^{2+} discharge at limited current density when electrode potential is more negative than -0.80 V/SCE while the discharge rate of Ni^{2+} is controlled by thermodynamics, the potential electrode is more negative the cathode current density is higher.

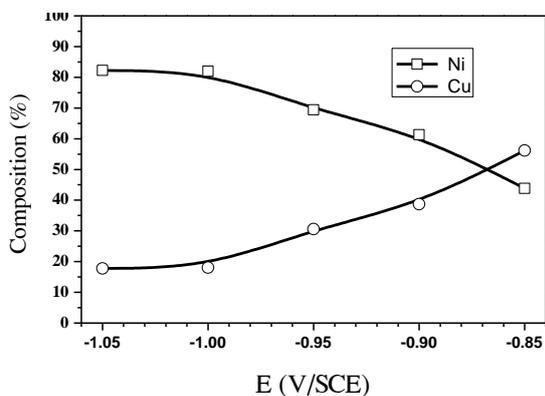


Figure 5: Influence of electrode potential on alloy compositions

Effects of cathode current density to alloy components were performed by GS technique, the current density in the range of -4 mA/cm^2 to 20 mA/cm^2 , results are shown in figure 6.

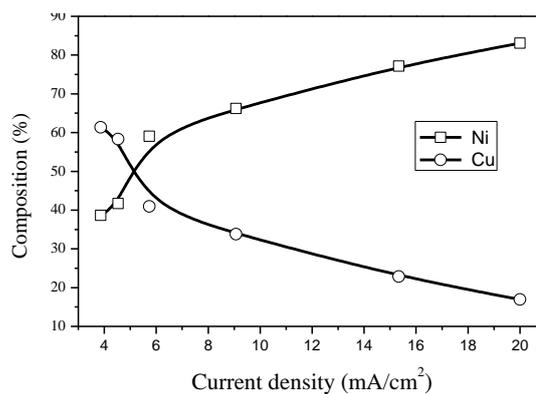


Figure 6: Influence of cathode current density of alloy compositions

Cathode current density in the range of -4 to -8 mA/cm^2 strongly influences the alloy composition, when cathode current density increases the copper content decreases, whereas Ni content increases, then the influence is weaker. When

increasing cathode current density, the Ni content in the alloy also increases, this result is due to Cu^{2+} in line tipping discharge, particular current density of Cu^{2+} was constant throughout the current density range examined, cathode current density increase is due to the contributions of the particular current density of Ni^{2+} .

SEM picture in figure 7 shows the electrode surface covered, uniformity, no cracks; the more negative electrode potential the surface is smoother.

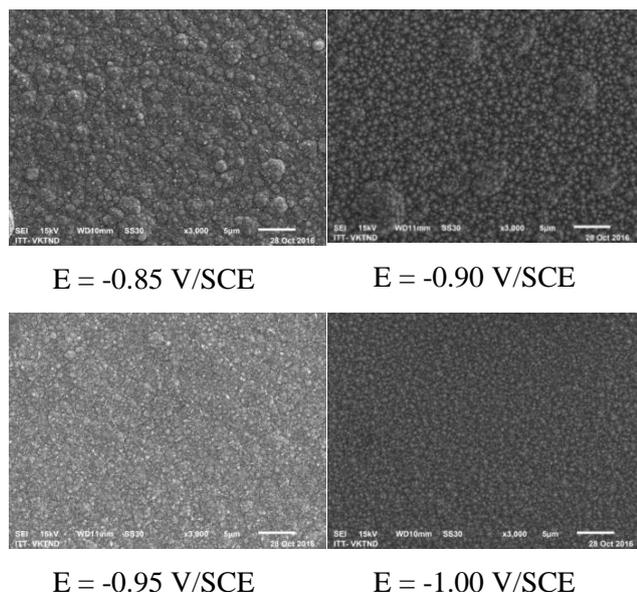


Figure 7: SEM picture of NiCu film electrodeposit by PS in Ni^{2+} 0.5 M, Cu^{2+} 0.05 M, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ 0.2 M

4. CONCLUSIONS

Study on the discharge of Cu^{2+} , Ni^{2+} ions by linear sweep voltammetry measurements showed that in potential positive than -0.8 V/SCE only Cu^{2+} ion discharge at limited current densities, in potential negative than -0.8 V/SCE Cu^{2+} and Ni^{2+} ions co-discharge to form NiCu alloys.

Potential and current density cathode strongly influence the obtained alloy composition, especially in the region potential from -0.95 to -0.85 V/SCE

Corresponding author: **Uong Van Vy**

Institute for Tropical technology
Vietnam Academy of Science and Technology
No. 18, Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam
E-mail: uongvanvy@itt.vast.vn.

and cathode current density lower than 10 mA/cm^2 .

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