

Electrodeposition and Characterization of Copper Coating on Stainless Steel Substrate from Alkaline Copper Solution Containing Ethylenediaminetetraacetate (EDTA)

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ABSTRACT

Copper coating was successfully deposited onto 304 stainless steel substrate from pH 8 EDTA solution containing 0.01 M Cu²⁺ ions, added as CuSO₄. The nature of 304 stainless steel electrode reactions in solutions was determined by cyclic voltammetry. Based on cyclic voltammetric analysis, -1.1 V is related to the Cu²⁺ ions reduction and the suitable applied potential for further electrodeposition process. Chronoamperometric study was done by applying a constant potential at -1.1 V at different deposition times. Morphological observation revealed that deposition time has strongly affected the surface coverage of the copper coating on the 304 stainless steel surface. Crystalline pure copper phase was determined by XRD. The coating has excellent adhesion which passed the tape test. This study showed that the copper coatings with good surface coverage and adhesion can be prepared on the 304 stainless steel substrate.

Keywords: Copper; Copper Coating; Copper Reduction; Electrodeposition; Ethylenediaminetetraacetate.

Introduction

Electrodeposition method is a much utilized copper coating process in industry for many types of applications [1] such as contacts and circuitry in the electronic industry, manufacturing printed-circuit boards, undercoating for other metals thin film coating and the protection of consumer goods. Historically, cyanide solution was successfully used as bath solution for the deposition of copper. However, in the last few years, great efforts have been made in order to replace the cyanide solution which is toxic to environment and due to the environmental protection policies [1-4]. Alternatively, non-cyanide solutions were introduced to replace the highly toxic cyanide solution such as fluoborate [5], pyrophosphate [2], citrate [5-6], lactic acid [6-7], ammonia [9], glycerol [10], glycine [4] and ethylenediaminetetraacetate (EDTA) [5, 11-15].

Since copper ions are easily oxidized and not stable in aqueous system in basic condition, the introduction of a suitable ligand and an adjustment of the pH level system are necessary to obtain a stable Cu^{2+} ions solution system and to avoid precipitation. EDTA, a strong ligand, is of preferable to use in order to maintain long-term stability of the copper ions in the solution over a wide range of pH [16]. Usually, the coatings obtained by the electrodeposition show good adherence which is a function of the substrate pre-treatment and right condition used. Surface pre-treatment and the right adjustment of deposition conditions, in general, can produce good coating quality. By effectively adjusting the parameters involved, the nature of growth and patterns of the coating films can be controlled [8, 17-22].

In this paper, we reported on electrodeposition of copper onto stainless steel substrate from EDTA-based solution. Good copper coating properties, in terms of strong adhesion between coating and substrate and uniform surface coverage, are the most important aspects to be solved in this study by choosing the right deposition potential (based on cyclic voltammetric analysis) and deposition time. This study will give knowledge on a parameter study of the electrodeposition operating conditions for copper coating onto stainless steel substrate from complexed copper solutions.

Experimental

Before electrodeposition, 304 stainless steel substrate was polished with SiC paper from P800 to P4000 grit, followed by ultrasonically cleaned in acetone, rinsed with ultrapure water and dried at room temperature. An adhesive tape was used to mask off of the stainless steel except for area 20 mm^2 on which deposition was desired. The electrodeposition of copper onto stainless steel was performed in a typical three-electrochemical cell with polished 304 stainless steel ($20 \text{ mm} \times 20 \text{ mm} \times 1 \text{ mm}$) substrate used as working electrode,

platinum rod as a counter electrode and Ag/AgCl as a reference electrode. The electrodeposition process was done by cyclic voltammetry (CV) and chronoamperometry (CA) techniques controlled using an Autolab Potentiostat (Aut302 FRA2), interface with a PC running NOVA software. Two different pH 8 solutions were used: 0.3 M NaOH + EDTA solution with and without 0.01 M Cu^{2+} ions, added as CuSO_4 . All experiments were performed under room temperature. CV experiments were carried out using polished 304 stainless steel electrode in EDTA solution with or without Cu^{2+} ions. The first experiment was done in the EDTA solution without Cu^{2+} ions. The objective was to verify whether EDTA suffers electrochemical processes in the range of potential bounded by the reduction of copper. Then, CV was conducted using again polished 304 stainless steel electrode in the EDTA solution containing 0.01 M Cu^{2+} ions. In this case, the objective was to identify the cathodic and the anodic peaks related to the Cu^{2+} ions reduction and Cu oxidation, respectively. For CA experiments, the effect of deposition time was carried out in the EDTA solution containing 0.01 M Cu^{2+} ions by applying constant applied potential of -1.1 V for different deposition times (i.e.: 60 s, 120 s, 180 s, 300 s, 600 s and 900 s). The surface morphology of the prepared coatings was examined by Field Emission Scanning Electron Microscope (FESEM, Carl Zeiss SMT Supra 40VP). The crystallography and structure of the prepared coatings were analyzed by a diffractometer (X'pert pro-MPD, PANalytical) with thin film X-ray diffraction (TF-XRD) capability. The adhesion test of the prepared coatings to the stainless steel surface was tested by Tape test using Scotch[®] Tape.

Results and Discussion

Figure 1 presents overlay of the comparison among cyclic voltammograms of 304 stainless steel in EDTA solution with and without Cu^{2+} ions. The curves were scanned from $+0.5$ V to -2.0 V and reversed returning to $+0.5$ V with 10 mV/s scanning rate. There is no peak produced unless increment in cathodic current due to the hydrogen evolution reaction (HER) during the scanning of the 304 stainless steel substrate in EDTA solution without Cu^{2+} ions. This was confirmed clearly through visual observation with the formation of hydrogen bubbles on the 304 stainless steel electrode surface during cathodic sweeping. It means that EDTA is an electrochemically inactive component over wide range of potential.

Whilst, in solution containing Cu^{2+} ions, several cathodic and anodic peaks appeared: three cathodic peaks (C1, C2 (zoom view) and C3) during cathodic scan and two anodic peaks (A1 and A2) during anodic scan. In order to study the mechanism of the copper deposition, some tests were made to identify the peaks related to the reduction of copper on the cathodic scan.

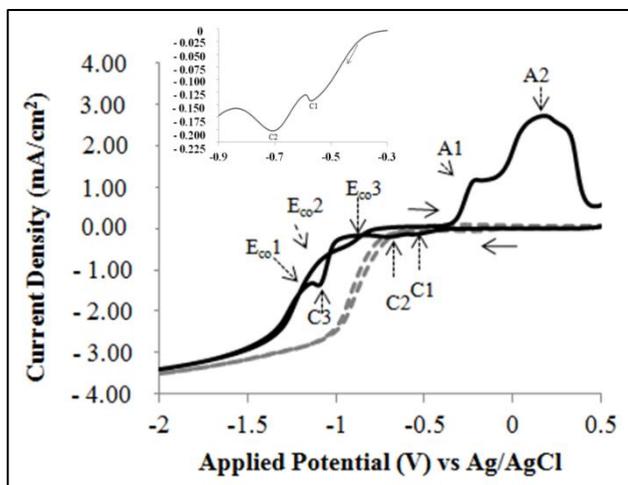


Figure 1: Cyclic voltammograms of 304 stainless steel substrate in pH 8 solution containing EDTA without (dashed line) and with Cu^{2+} ions (solid line) and at 25 °C. Scan rate: 10 mV/s. (Inset: zoom view of the C1 and C2 peaks).

Thus, the surface of 304 stainless steel was observed after the cathodic peaks of C1 and C2 (inset): no deposition was observed on the stainless steel surface even after maintaining the stainless steel electrode at -0.5 V (C1) or -0.7 V (C2) for 900 s using chronoamperometry. So, it was concluded that the C1 and C2 peaks are not related to the copper reduction. At -1.1 V (C3), a copper coating was seen formed on the 304 stainless steel surface, which referred to the reduction of Cu^{2+} ions. The large overpotential for Cu^{2+} ions reduction onto 304 stainless steel electrode in EDTA solution is due to a large current required to break the complexation binding between Cu-EDTA before Cu^{2+} ions can be reduced on the stainless steel. It can be suggested that the Cu-EDTA complex in the bulk solution will firstly diffuse to the inter-surface of anode, then decomposed into Cu^{2+} and EDTA^{4-} (reaction 1) at the anode surface. Afterwards, the Cu^{2+} was released into the bulk solution before moving towards stainless steel cathode electrode via diffusion and finally reduced and deposited at the stainless steel surface (reaction 2).



It can be seen the multiple crossover points (e.g. E_{co1} , E_{co2} and E_{co3}) in between forward and reverse scan in cathodic branch as in Fig. 1. It may indicate the nucleation mechanisms involving complex reactions. The anodic peaks (A1 and A2) appeared could be related to the dissolution of copper deposit. Since the focus of this study is the electrodeposition of copper, anodic peaks will not be discussed in detail.

It is well-known that EDTA as well as other complexing agents used have similar effects in the electrodeposition of metals onto metallic substrates [5]. The inhibition effect of the Cu^{2+} ions reduction could be associated with the complex species formation with Cu^{2+} ions.

Likewise to the curve obtained from the solution without Cu^{2+} ions, at potentials more negative than -1.2 V refers to the HER occurred dominantly during sweeping. The HER occurred at more negative potentials in solution containing Cu^{2+} ions compared to in solution without Cu^{2+} ions due to the strong complexation bonding between Cu^{2+} and $EDTA^{4-}$. Figure 2 shows the suggested schematic presentation of reaction mechanisms regarding water and Cu-EDTA reduction during scanning at negative potentials.

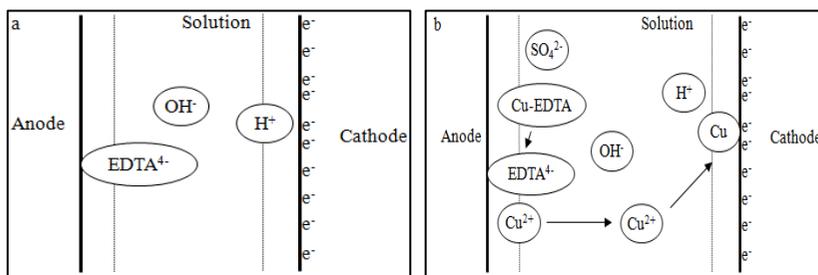


Figure 2: Schematic presentation of electrochemical reactions mechanism for solution containing EDTA (a) without and (b) with Cu^{2+} ions.

If the applied potential chosen for the deposition of Cu in the region of HER (i.e.: $E > -1.5$ V), it will result in porous and coarse structure of the coating. Some cracks might be formed due to the formation of stress because hydrogen gases may grow as nucleation and growth mechanism simultaneously with copper deposition. Finally, when escape by their own accord, it can create porosity and the adhesion between the coating and substrate is poor. Therefore, for further chronoamperometric study, -1.1 V was chosen and applied for further deposition process.

The kinetics of nucleation and growth of the copper coating were studied by analyzing current transient during chronoamperometry. Figure 3 shows chronoamperometric curve for copper deposition from EDTA solution containing 0.01 M Cu^{2+} ions on stainless steel electrode at -1.1 V for 900 s.

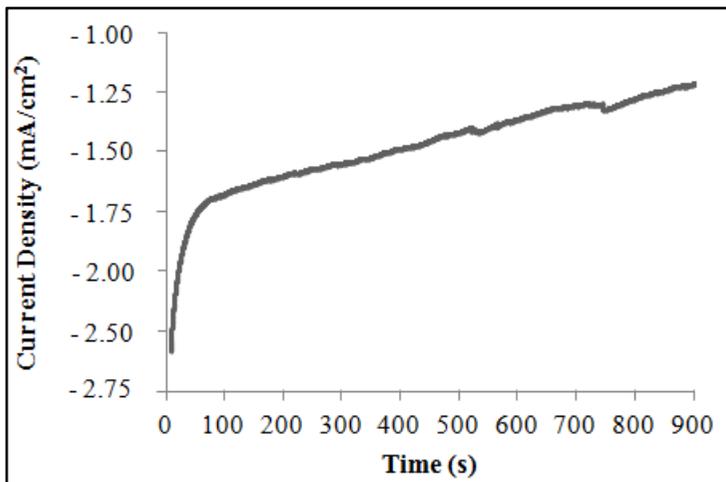


Figure 3: Chronoamperometric curves for copper deposition on 304 stainless steel in pH 8 solution containing 0.01 M Cu^{2+} ions at -1.1 V for 900 s.

The current density-time transients exhibited an expected behavior with the start of double layer, followed by nucleation and growth of the copper onto electrode, as have been reported previously [5, 23-24]. The transients were characterized by an initial and abrupt decrease in cathodic current density for short times due to double layer charging (non-faradaic current) that occurred at the beginning of the process. At this time, the structure of the interface may change and there is no involvement of electrodeposition process. After that, a continuous decrease in cathodic current density is due to the formation of oxide or hydroxide during the nucleation and growth of copper onto stainless steel. The decrease of cathodic current density with increasing time might due to the distribution of oxide or hydroxide during the copper deposition process since the deposition is carried out in alkaline solution. Oxide layers developed simultaneously in solution containing ligands which belongs to process that is often attended during the electroreduction of Cu^{2+} ions and may affect the copper deposition [24-25].

The time dependence of the appearance of copper coating was observed visually before imaged by FESEM. Fig. 4 shows visual observation of the copper coatings prepared on the 304 stainless steel surface at different deposition times. It can be obviously seen that the entire exposed stainless steel surface (20 mm^2 in solution during electrodeposition process) was covered with smooth and uniform red-brown coatings. The increase of

deposition time allows more copper deposited on the stainless steel surface and results in more concentrated red-brown color coating.

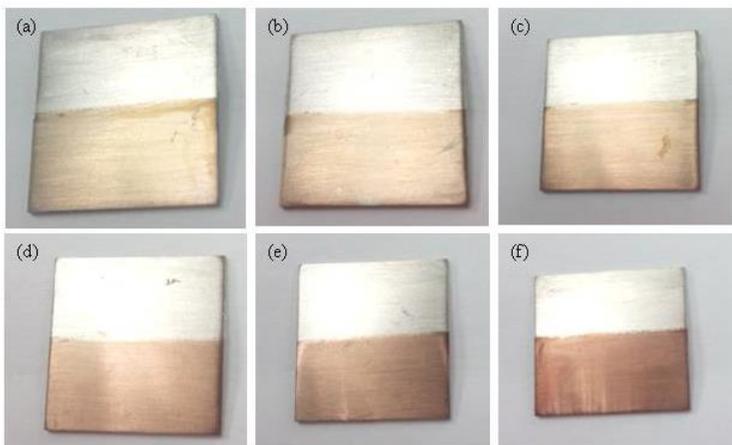


Figure 4: Visual observation of copper coatings prepared on 304 stainless steel substrate from pH 8 solution containing 0.01 M Cu^{2+} ions at -1.1 V for (a) 60 s, (b) 120 s, (c) 180 s, (d) 300 s, (e) 600 s and (f) 900 s. (Note: The sample can be divided into two partitions with the top part is uncoated stainless steel whilst the bottom part indicates copper coating produced on the stainless steel surface).

Figure 5 shows surface morphologies of the copper coatings prepared on the stainless steel surface at various deposition times as imaged by FESEM. It was found that the deposition time has strongly affected the density of copper and surface coverage. From visual observations (Fig. 4), it can be seen that the red-brown color coating covered the entire surface of the exposed stainless steel. Nevertheless, the image taken by FESEM shows that the copper coating prepared at <300 s did not fully cover the stainless steel surface in which nucleation and growth of the copper occurred only at favorable sites on the stainless steel surface. Subsequently, the growth of copper coating has been continuously deposited over time and overlapping over the whole stainless steel surface. By extending the time to >300 s, the stainless steel surface was fully covered with copper. The longer the deposition time makes continuation deposition of copper on the deposited copper layer. More compact and dense copper particles with size in the range of about 38-66 nm (measured based on FESEM image) were produced when the time was extended to 600 s and 900 s. It is noteworthy to mention that the porous-free nature of the copper coating is due to small grain size of copper

deposited on the stainless steel surface when deposition potential before HER was applied.

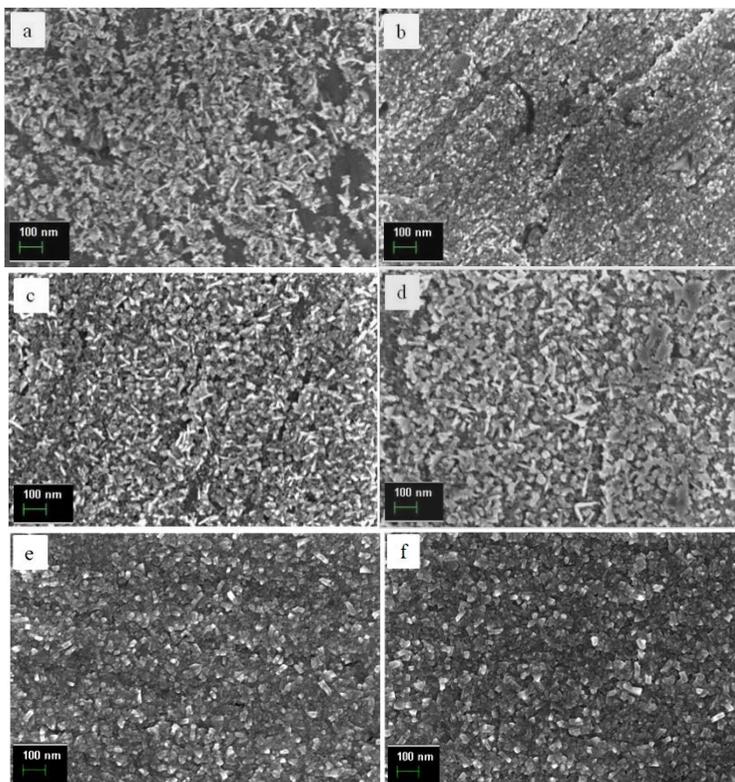


Figure 5: FESEM images of copper coatings prepared on stainless steel substrate from pH 8 solution containing 0.01 M Cu^{2+} ions at -1.1 V for (a) 60 s, (b) 120 s, (c) 180 s, (d) 300 s, (e) 600 s and (f) 900 s. (Magnification: 25000x)

Figure 6 shows XRD patterns of copper coatings prepared on 304 stainless steel surface at different deposition times. Three peaks at 2θ values of 43° , 51° and 73° corresponding to (111), (200) and (220) planes of copper were observed and compared with the standard from database reference pattern copper 03-065-9743. A diffraction peak of copper at 43° appeared as shoulder to diffraction peak of austenite phase of 304 stainless steel (44.8°). This is due to the reflection between copper and 304 stainless steel which is

very close. Taking no account of the stainless steel peaks, the patterns show that copper coatings prepared at all deposition times are crystalline.

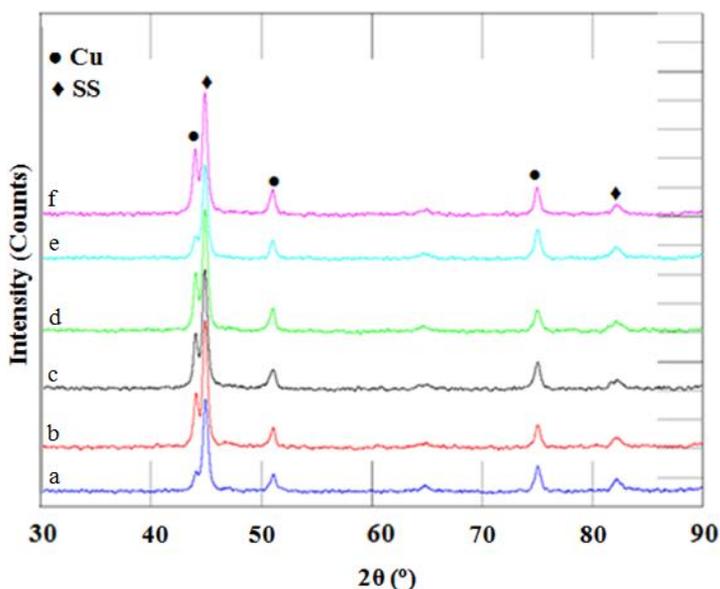


Figure 6: XRD patterns of the copper coatings prepared on the 304 stainless steel substrate from pH 8 solution containing 0.01 M Cu^{2+} ions at -1.1 V for (a) 60 s, (b) 120 s, (c) 180 s, (d) 300 s, (e) 600 s and (f) 900 s.

The adhesion quality of the copper coatings on stainless steel surface was investigated by tape test. The copper coatings have excellent adhesion on the stainless steel substrate as indicated by 100 % of retainment of the coatings on the stainless surface after the adhesive tape was removed. All coatings also adhered strongly on the stainless steel surface even after rubbing aggressively with tissue.

Conclusion

Electrodeposition of copper on stainless steel substrate was successfully done from pH 8 EDTA solution containing 0.01 M Cu^{2+} ions. Cyclic voltammetry (CV) was used to determine the nature of stainless steel electrode reactions in the solutions with and without Cu^{2+} ions. Suitable potentials related to the Cu^{2+} ions reduction was determined from the CV. Nucleation and growth of the copper coatings on the stainless steel surface at -1.1 V were dependent on deposition time. The copper coatings with good surface coverage and adhesion can be prepared on the stainless steel substrate by choosing the right

deposition potential and deposition time. Further investigations are underway to test antimicrobial activity of the copper coatings for possible applications such as touch surface material in healthcare setting.

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