Cu-Ni Alloys Coatings For Corrosion Protection On Mild Steel In 0.5 M NaCl Solution

Mohammad Hafizudden Mohd Zaki, Yusairie Mohd*, Nik Norziehana Che Isa

Abstract - **Mild steel is the most common metal used in industry. However, mild steel easily corrodes when exposed to environment. One way to protect mild steel from corrodes is by coating it with more noble metal like copper and its alloys. In this study, copper and Cu-Ni alloys were successfully coated on the mild steel substrate by electrodeposition technique using alkaline citrate solutions containing Cu and Ni ions precursors. The reaction and mechanisms of the electrodeposition of copper and Cu-Ni alloys on the mild steel substrate were investigated by cyclic voltammetry and chronoamperometry methods. Surface morphology of the coatings was examined by FESEM. The elemental compositions of the coatings were confirmed by EDAX analysis. The molar ratios of Cu-Ni solutions have affected the formation of the coatings. Corrosion study shows that copper coated mild steel can improve the corrosion resistance of the mild steel in 0.5 M NaCl. Cu-Ni coating prepared from Cu60-Ni40 showed the highest corrosion resistance. The order of the corrosion resistance of the samples in 0.5 M NaCl at 25 ^{o}C is Cu60-Ni40> Cu75-Ni25> Cu90-Ni10> Cu100> mild steel.**

Keywords **-** Copper, Copper nickel, Corrosion Protection, Electrodeposition, Metallic coating.

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Received : 12 November 2017
Accepted : 31 December 2017
Published : 31 December 2017

I. INTRODUCTION

Mild steel is a remarkably cheap material, with good tensile strength and easy to weld using gas, arc or resistance welding, widely used metal for both domestic and industrial applications. However, one of the foremost weaknesses of mild steel is its low corrosion resistance [9]. Corrosion-related problems have a major impact on the safety, environmental preservation and the economic factors that required a lot of cost. This cost includes critical failures, property losses, repair and restoration costs, decorative losses and even losses of life [3][4][12]. A big portion of these losses can be prevented by planning and implementing proactive and systematic corrosion prevention practices and programs. The process of corrosion is due to the electrochemical reaction of the metal surface with corrosive environments, thus one of the most effective strategies is to effectively isolate the metal surfaces the corrosive environment by covering it with a protective layer, or coating.

Surface coating technique is usually used in most critical protective applications. The main function of the surface coating is to act as a protective barrier that eliminates the possibility of a substrate to be connected with electrolytes in the working environment, thus preventing the likely electrochemical reactions that can cause corrosion. Noble metal coating can form an effective barrier between the solid mild steel substrate and its working environment like sea water [12]. Many coating methods have been adopted in order to improve the service life of mild steel against corrosion attack, including electroplating or electrodeposition, cladding, spray coatings, hot dipping and diffusion coatings [12]. The electrodeposition technique has recently attracted considerable attention because it offered a variety of advantages over other methods. The economical electrodeposition technique can produce coatings with adequate thickness, structure and adhesion by altering deposition conditions carefully [1][7][8].

The interest of producing copper and its alloy coatings for the protection of mild steel is enormous in the engineering industries [6]. Copper is widely used as metallic coatings applied to mild steel surfaces in order to protect mild steel from corrosion since copper is a noble metal. However, pure copper can easily oxidize and the addition of the second metal like nickel in order to alloy the copper can be considered as a good idea in improving the corrosion resistance of mild steel [5][14][16]. Nickel is chosen as the second metal to be alloyed with copper because; Cu-Ni alloy is extensively used in marine applications. It is a material selection for condensers and heat exchangers, where seawater is used as a coolant and in desalination plants. It is also resistant to stress corrosion cracking by ammonia and sulphide ions and has good resistance to biofouling due to the release of copper ions [5].

In this study, the electrodeposition of pure copper and Cu-Ni coatings on mild steel have been investigated in alkaline citrate solution. Examination of the corrosion behavior of the copper coatings in 0.5 M NaCl solution has been carried out.

II. MATERIALS AND METHOD

The electrodeposition of copper and Cu-Ni was performed in a typical three-electrochemical cell with mild steel (20 mm x 20 mm x 1 mm) coupon was used as working electrode, a platinum rod as a counter electrode and silver-silver chloride (Ag/AgCl) as a reference electrode. The electrodeposition process was controlled using an Autolab Potentiostat (Aut302 FRA2), interfaced with a PC running NOVA software. Before electrodeposition begin, mild steel was polished with silica carbide papers from P800 to P1200 grit, followed by ultrasonically cleaned with acetone and dried at room temperature. Chemical reagents were used $CuSO_4$, $NiSO_4$, sodium citrate ($C_6H_5Na_3O_7.2H_2O$), and NaOH. Alkaline bath solutions (pH 8) based on citrate, as a complexing agent was used containing precursors of pure copper, Cu90-Ni10, Cu75-Ni25 and Cu60-Ni40, in order to deposit pure copper and Cu-Ni, respectively. The process of copper and Cu-Ni deposition on the mild steel in an alkaline citrate solution was studied by cyclic voltammetry (CV) and chronoamperometry (CA). Deposition was carried out at a constant applied potential (based on CV) for 15 min. The surface morphology, elemental composition and crystalinity of the prepared coatings were examined using a Field Emission Scanning Electron Microscope (FESEM, Carl Zeiss SMT Supra 40VP) combined with EDAX measurements and Thin Film X-Ray diffraction (TF-XRD), repectively. Then, the corrosion resistance of the prepared coatings was investigated in 0.5 M NaCl solution using linear polarization method.

III. RESULTS AND DISCUSSION

A. Surface Pre-Treatment of Mild Steel

Surface pre-treatment of the substrates is the critical step before electrodeposition process in order to remove contaminants and to produce a rough surface for better mechanical bonding between the coating and substrate. Contaminants and films interfere with bonding, which can cause poor adhesion, coating failure and even prevent deposition. Mild steel substrate is naturally covered with a passive oxide layer which formed spontaneously in air on bare substrate. Oxide layer has a high electrical resistivity and creates a high potential barrier to electron transfer. Therefore, with the presence of the oxide layer, the voltage loss within the electrode is high and its practical application is not good. Hence, mechanical surface pre-treatment was done by polishing the substrate surface with silica carbide (SiC) paper.

Fig. 1 and 2 show the visual observation and surface morphology, respectively, of (a) as-received and (b) polished mild steel surface. As-received mild steel seems too rough with imperfections covered with corrosion products representing the insulation of the native oxide layer. After polishing process, the mild steel surface became more smooth and free from the larger imperfections since small amounts of metal removed by means of abrasives. The removal of the contaminants and oxide layer will make the deposition process possible and increase the adhesion of the coatings.

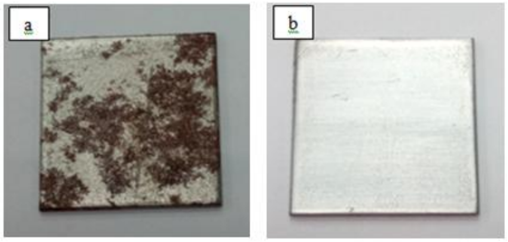

Fig. 1: Visual observation of a mild steel substrate (a) as-received and (b) after polished with SiC paper.

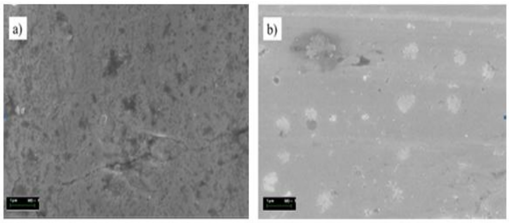

Fig. 2: SEM images of the mild steel substrate (a) as-received and (b) after polished with SiC paper. Magnification 5000x.

B. Cyclic Voltammetry Analysis

Fig. 3 shows the cyclic voltammogram of mild steel substrate that performed in a typical three-electrode electrochemical cell over a range of 0.5 V to – 2.0 V vs Ag/AgCl with 100 mV/s scanning at room temperature in the solutions containing precursor of (a) pure copper and (b) pure nickel.

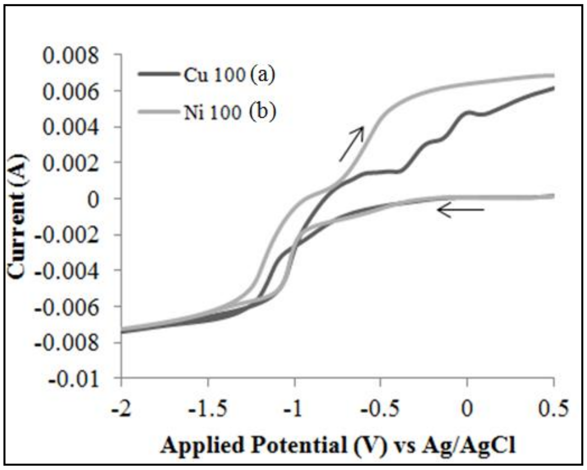

Fig. 3: Cyclic voltammograms of mild steel substrate in alkaline citrate solution (pH 8) containing (a) pure copper and (b) pure nickel. Scan rate: 100 mV/s. The arrows indicate the direction of the cycle scan.

From the voltammograms, it can be seen that the pattern of both curves is quite similar with the only slightly different in current values and crossover potential. The reduction of the electroactive species, either Cu^{2+} of Ni^{2+}, in the solutions started to occur at about – 0.4 V. On forward scan (negative direction), cathodic current slowly increased during scanning indicated the nucleation and growth of the stable nucleus of either copper or nickel on the mild steel surface. At potential higher than – 1.3 V to – 2.0 V, the hydrogen evolution reaction (HER) is starting to occur which is the production of H_2 bubbles can be seen clearly by naked eye during the scanning. At reverse scan, there is a potential range where the cathodic current is lower compared to the forward scan. Since the nucleus of the electroactive species already exists on the mild steel surface, the growth of nuclei can be continued as long as the current is still in cathodic direction. The suitable potential range of deposition of copper or nickel on the mild steel surface is suggested between – 0.4 V to – 1.3 V without the interference of HER.

The effect of molar ratios of Cu-Ni solutions on CV scan is given in Figure 4. CV curves showed that the crossover potential for co-reduction of Cu-Ni is about – 1.0 V. Instead of making copper or nickel ions stable in alkaline solution, citrate also function in bringing the electrode potentials of the metals (i.e.: Cu and Ni) closer in the binary alloy electrolyte (standard electrode potentials of Cu + 0.34 V and Ni – 0.25 V). The copper and nickel are deposited at more negative potentials in the presence of citrate in the electrolyte compared to the standard potential. Since, copper is a noble metal than nickel (reduce at more positive potential), the co-deposition of Cu-Ni started with the reduction of copper and followed by the reduction of nickel, leading to the co-reduction of Cu-Ni. So, for further chronoamperometric study, the potential of – 1.0 V was applied for all solutions.

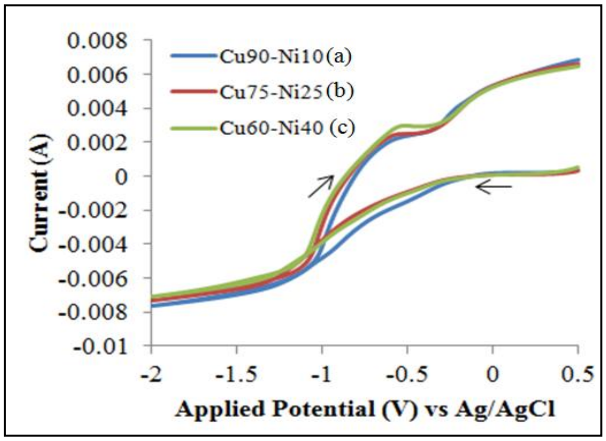

Fig. 4: Cyclic voltmmograms of mild steel substrate in alkaline citrate solution (pH 8) containing (a) Cu90-Ni10, (b) Cu75-Ni25 and (c) Cu60-Ni40. Scan rate: 100 mV/s. The arrows indicate the direction of the cycle scan.

C. Chronoamperometric Analysis

Chronoamperometry (CA) was used as an experimental technique to study the electrodeposition process. A basic study interprets the deposition process in terms of nucleation followed by growth and generally relies on the use of current transient analysis. During CA experiments, the current-time transients are recorded as the potential is stepped from the OCP to the potential at which the electrodeposition of metals or alloys would occur. Fig. 5 shows the chronoamperometric curves for the electrodeposition of (a) pure copper, (b) Cu90-Ni10, (c) Cu75-Ni25 and (d) Cu60-Ni40 on the mild steel substrate for 15 min. The cathodic current showed an abrupt decrease for short times, indicated that, at the beginning of the electrodeposition process, charging of double layer occurred. Taking no account of this current because at this time, the structure of the interface may change and there is no involvement of reduction process. After that, Faradaic current takes place indicating the nucleation and growth of the coating nucleus on the mild steel surface. Steady-state current indicates further development of the coating nucleus on the substrate surface. Once all of the nucleation sites are occupied, further increase in the deposition time would only increase the size of the crystals since no new nucleation sites are created, theoretically.

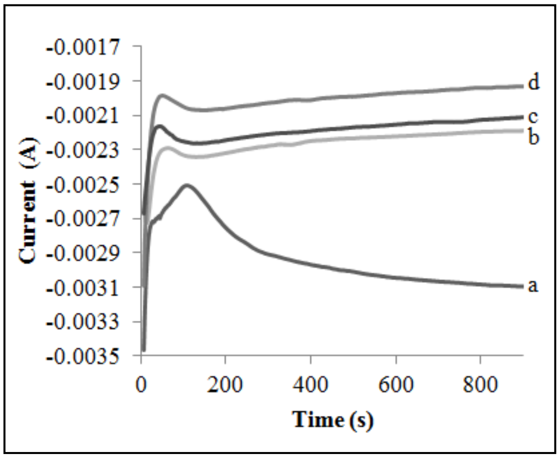

Fig. 5: Chronoamperometric curves of the coatings on the mild steel substrate from alkaline citrate solution (pH 8) containing (a) pure copper (b) Cu90-Ni10, (c) Cu75-Ni25 and (d) Cu60-Ni40 at – 1.0 V at 25 ^{o}C for 15 min.

The suggested schematic mechanism of nucleation and growth of coatings on the mild steel surface is shown in Fig. 6.

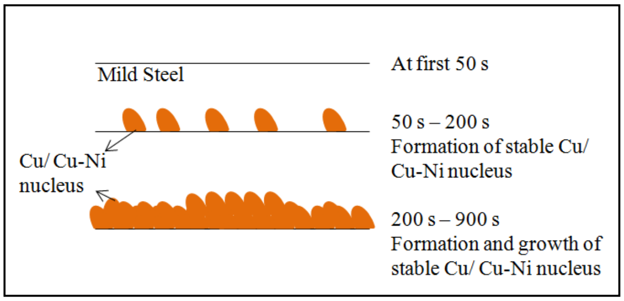

Fig. 6: Schematic diagram of nucleation and growth of coatings on the mild steel surface

Fig. 7 shows the visual observation of of the coatings formed on the mild steel surface electrodeposited from different solution compositions at – 1.0 V for 15 min of electrodeposition process. It can be seen obviously that the color of the coatings varies. The entire exposed mild steel surface was covered with smooth and uniform coatings with dark brown color (pure copper) and yellowish brown color (Cu-Ni).

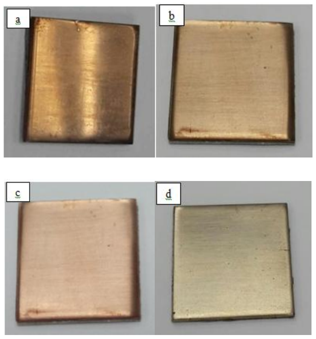

Fig. 7: Visual observation of (a) pure copper, (b) Cu90-Ni10, (c) Cu75-Ni25 and (d) Cu60-Ni40 coatings electrodeposited on mild steel substrate at – 1.0 V after 15 min electrodeposition process.

D. Characterization of the Prepared Coatings

1. Surface Morphology Analysis

The surface morphology of the coatings was investigated using FESEM for pure Cu and Cu-Ni alloys coatings prepared at constant potential -1.0V for 15 min. Fig. 8 shows the morphologies of the coatings formed on the mild steel surface electrodeposited from different solution compositions. The pure copper solution has produced agglomerates coatings covered the entire surface on the mild steel as shown in Fig.8(a).The addition of the nickel on the copper solution has significantly changed the morphology of the Cu alloy coatings. The solution containing Cu90: Ni10 has slightly changed the morphology of the coatings as compared to pure copper coatings with smooth crystals coatings (see Fig. 8(b)). When the solution was adjusted to Cu75: Ni25 (Fig. 8(c)), the coatings appeared to continually change which prefer to be more pyramidal rice-like structure. Whilst, deposition using solution containing Cu60:Ni40 has produced morphology of heterogeneous coatings consists of rice-like structure and spherical structure on the mild steel surface as can be seen in **Fig. 8(d)**. The morphology is attributed to the aggregation of the copper and nickel during electrodeposition process. Small crystallites are more obviously seen compared to Cu90:Ni10 and Cu75:Ni25 coatings due to its higher concentration of the nickel in the solution. The higher nickel content in the solution will produce more compact and uniform coatings with smaller crystallites structure.

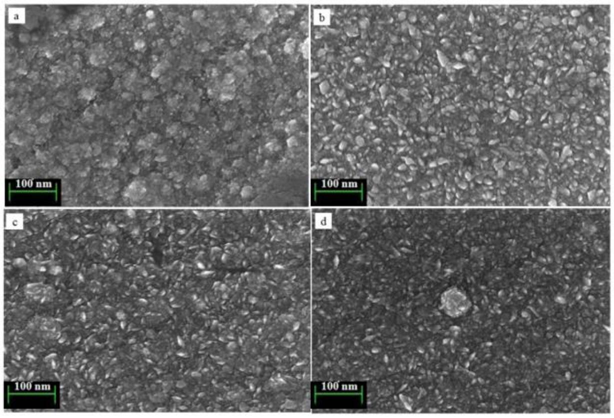

Fig. 8: SEM images of (a) pure Cu, (b) Cu90-Ni10, (c) Cu75-Ni25 and (d) Cu60-Ni40 deposited on mild steel substrate at -1.0V for 15 min. Magnification 25000x.

2. Elemental Composition Analysis

The elemental compositions of the pure copper and Cu90-Ni10, Cu75-Ni25 and Cu60-Ni40 coatings were confirmed by EDX. It can be concluded that the agglomerates structure is owing to copper nucleus whereas the pyramidal rice-like structure due to the nickel nucleus. Table 1 shows the weight percent (wt %) of the elements present on the mild steel surface before and after coatings.

Table 1: Composition of elements (wt %) present on the mild steel surface before and after coating.

Sample	Element (wt %)				
	Cu	Ni	Fe	C	O
Mild steel	ND	ND	98.23	1.77	ND
Cu-100	83.15	ND	ND	11.03	5.82
Cu90-Ni10	77.70	3.38	ND	12.50	6.50
Cu75-Ni25	82.57	11.61	2.42	2.13	1.27
Cu60-Ni40	79.89	11.88	ND	6.68	1.55

The results show that the uncoated mild steel contained 98.23 wt% of Fe and 1.77 wt% of C. For pure Cu, the composition of Cu element are 88.27 wt% and no Fe element was detected due to the complete coverage of Cu on the mild steel. The C and O are present with 11.03 wt% and 5.82% respectively. O is attributed by the oxidation product of copper. For Cu-Ni alloys, the composition of elements obviously different but the formation of alloys can be confirmed when the Cu and Ni are identified coated on the mild steel surface. However, EDX analysis did not show a good correlation between ratios of molar concentration used and Cu-Ni on the mild steel surface.

3. Crystallographic Structural Porperties Analysis

Fig. 9 shows typical X-Ray diffraction (XRD) patterns of the crystallographic structure of bare mild steel (a), pure Cu coated mild steel (c), respectively. The intensity of peaks for all patterns was compared with the peaks described in reference database to display preferential orientations (Refer Appendices C (2a), C (2b), and C (2c) for Fe, Cu and Ni respectively). The most intense and sharp peaks are observed in the 2ϴ angle range between 40^o to 85^o for all samples. The peak related to the oriented direction of (111) plane from Fe (Fig. 9,(a)) ($2ϴ = 45^o$) indicates that the structural and crystals are triangular pyramidal [15]. Whilst for pure Ni coated mild steel (b) and pure Cu coated mild steel (c), the peak formed at $2\Theta = 44^{o}$, indicates that the Ni and Cu crystals are also gradually oriented along (111) direction. Figure 4.12 shows the diffraction patterns of pure Cu and Cu-Ni alloys coatings formed on the mild steel substrate. All the peak patterns resulted in the same position with only small differences in intensity and this results are in good agreement from previous studied [15]. Pure Cu (a) has the highest peak at 2Θ which is 44^{o}. By the addition of Ni into Cu which is Cu-Ni alloys, there is a decrease of the (111) peak for Cu90:Ni10 (b), Cu75:Ni25 (c) and Cu60:Ni40 (d) respectively.

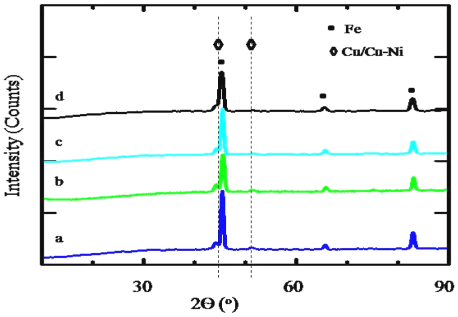

Fig. 9 : XRD patterns of crystallographic structure for (a) pure Cu, (b) Cu90:Ni10, (c) Cu75:Ni25 and (d) Cu60:Ni40.

E. Electrochemical Properties Measurement

In this study, the corrosion rate of pure Cu, pure Ni(used as a control) and Cu-Ni alloys coated on mild steel was measured using Tafel extrapolation (Linear polarization curve). Autolab Potentiostat instrument with NOVA software was used since it provides a convenient interface for Tafel plots, calculation of Tafel slopes and corrosion rate. The corrosion rate analysis of these samples was performed in 0.5M NaCl solution. Fig. 10 shows the Tafel extrapolation curves of the overlay of uncoated mild steel and coated mild steel with pure Cu, pure Ni (used as a control) and Cu-Ni alloys.The electrochemical parameters like corrosion potential (Ecorr), corrosion current density (icorr), polarization resistance (Ω), corrosion rate (mm/yr) and corrosion protection efficiency (η %) are summarized in Table 2.

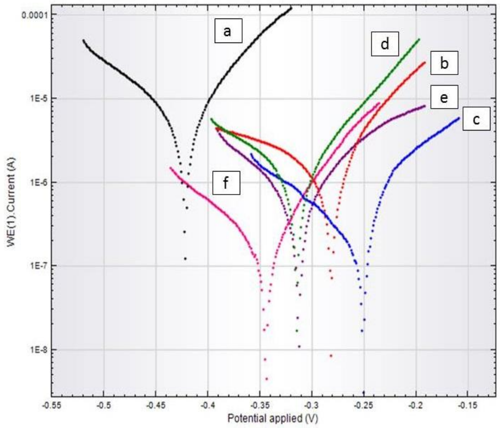

Fig. 10: Tafel curves of (a) uncoated mild steel, (b) pure Cu, (c) pure Ni (d) Cu90-Ni10, (e) Cu75-Ni25 and (f) Cu60-Ni40 coated mild steel in 0.5 M NaCl at 25 ^{o}C

Table 2: Corrosion parameters of the uncoated mild steel and coated mild steel

Substrate	E_{corr} (mV)	i_{corr} (μA/cm^2)	R_p (kΩ)	r (mm/year)	η %
Uncoated mild steel	- 422.730	7.565	2.870	0.87904	-
Cu-100	- 285.320	3.780	5.233	0.21906	75.08
Ni-100	- 222.340	0.166	268.040	0.01781	97.97
Cu90-Ni10	- 291.010	0.616	32.948	0.07092	91.93
Cu75-Ni25	- 273.270	0.389	41.666	0.04481	94.90
Cu60-Ni40	- 299.560	0.371	119.910	0.04184	95.00

From Figure 4.13, E_{corr} of uncoated mild steel curve (a) is at position of -0.422V. While, for pure Ni, the E_{corr} position is -0.222V about right due to compact with small crystallites coating as shown earlier in Figure 4.10 c. However, the E_{corr} for pure Cu is located at -0.285V more negative than Ni probably due to its structure and morphology of the coatings which is agglomerate with cracks coatings as in Figure 4.10 a. But the addition of Ni into Cu has shifter the E_{corr} values. The E_{corr} position for Cu-Ni alloys (d) (e) and (f) are at -0.291V, -0.273V and -0.299V respectively. The shifted potential for pure Cu, pure Ni, mild steel, and Cu-Ni alloys were compared with the shifted potential in sea water by John Wiley and Sons, Dissimilar metal corrosion, 1975 .

The corrosion protection efficiency (η %) of mild steel coated with pure Cu, pure Ni and Cu-Ni alloys was measured using the formula from Equation 3.4. While the corrosion rate (mm/year) of the samples, it can be measured by referring the formula from Equation 3.1, Equation 3.2 and Equation 3.3. From the results obtained, it can be seen that the uncoated mild steel sample has the highest corrosion current density (i_{corr} 7.564µA/cm^2) and a highly corrosion rate with 0.8790 mm/yr in 0.5M NaCl solution. The electron discharge and the active dissolution of mild steel in NaCl solution give an impression that the native oxide film is unstable under the prevailing chloride environment as shown in equation 4.4 and 4.5. The mechanism of dissolution in chloride environment [13].

$Fe + H_2O + Cl^- \longrightarrow [FeClOH]\ ads + H^+ + e^-$ (Eq. 1)

$[FeClOH] + H^+ \longrightarrow Fe^{2+} + Cl^- + H_2O$ (Eq. 2)**Error! Reference source not found.**

From all indications, the severe attack of the metal by aggressive chloride anions occurs locally and uniformly. The rough surface observed was basically due to rapid corrosion reaction between the mild steel and chloride anions which almost cover the mild steel surface, revealing pits and uniform corrosion attack occurs [10][11]. There were a large number of pits can occur by iron oxide layer revealing that pit formations under these conditions which occurs continuously during exposure period whilst iron oxide builds up over the surface [2]. Meanwhile, i_{corr} for pure Cu was 3.780µA/cm^2 and the corrosion rate was 0.2190 mm/yr. These show that copper can protect mild steel with 75.08% corrosion protection efficiency. However, pure Ni showed lower i_{corr} with 0.1662µA/cm^2 and higher corrosion efficiency which was 97.97% and corrosion rate 0.0178mm/yr. The corrosion protection efficiency of mild steel significantly improved after plating with nickel. The nickel itself has higher corrosion efficiency which almost 100% compared to pure copper. Thus, nickel was added into Cu alloys to improve the corrosion rate of Cu with highly corrosion protection efficiency [11].

In this study, Cu60:Ni40 alloy has the lowest i_{corr} (0.3707µA/cm^2) and corrosion rate 0.0418mm/yr with corrosion protection efficiency 95% as compared to other Cu-Ni alloys (Cu90:Ni10 and Cu75:Ni25) due to the formation of fully covered Cu and Ni film which retarded the ingress of chloride ions fully into the plated region and down to the substrate. It was stated that the reduction of i_{corr} and increase of polarization resistance value compared to the uncoated mild steel was due to the presence of nickel in the copper coatings. Thus, Cu-Ni alloys decrease the corrosion rate of the mild steel. The order of corrosion rate can be arranged as follows:

Mild steel > pure Cu> Cu90:Ni10> Cu75:Ni25 >Cu60:Ni40

It can be assumed that the presence of Ni in Cu coating has significantly improved the corrosion protection of mild steel by lowering the i_{corr} and decreasing the corrosion rate.

Nickel was more corrosion resistance compared to copper in 0.5M NaCl solution by the formation of oxide layer.

IV. CONCLUSIONS

The electrodeposition of copper and Cu-Ni alloys on the mild steel substrate in alkaline citrate solution was studied by cyclic voltammetry and chronoamperometry techniques. The smooth and uniform coatings covered the entire surface of the mild steel surface observed by FESEM. While, EDAX analysis revealed that the coatings contained copper and nickel elements. Examination of corrosion behavior in 0.5 M NaCl proved that the copper coatings (pure and alloys) improved the corrosion resistance of mild steel. The order of corrosion resistance of the samples in 0.5 M NaCl at 25 ^{o}C is Cu60-Ni40> Cu75-Ni25> Cu90-Ni10> Cu100> mild steel. The addition of nickel into copper coatings has enhanced the corrosion protection of mild steel. The highest corrosion protection efficiency of steel (i.e.: 95 %) was achieved by copper alloys prepared from Cu60-Ni40 ratio.

ACKNOWLEDGMENTS

The authors wish to acknowledge the Ministry of Higher Education (Malaysia) for the financial support through Fundamental Research Grant Scheme (FRGS) 600-RMI/FRGS 5/3 (139/2015) and Faculty of Applied Sciences, Universiti Teknologi MARA (UiTM) Shah Alam, Selangor for the facilities provided.

REFERENCES

[1] Almeida, M. R. H.; Barbano, E. P.; Carvalho, M. F.; Carlos, I. A.; Siqueira, J. L. P. and Barbosa, L. L.; 2011: Electrodeposition of Copper-Zinc from an Alkaline Bath Based on EDTA. Surface & Coatings Technology 206 : 95 – 102.

[2] Balasubramanian, A.; Srikumar, D. S.; Raja, G.; Saravanan, G. and Mohan, S.; 2008: Effect of Pulse Parameter on Pulsed Electrodeposition of Copper on Stainless Steel. DOI 10.1179/026708408X344680.

[3] Bonou, L.; Eyraund, M.; Denoyel, R. and Massiani, Y.; 2002: Influence of Additives on Cu Electrodeposition Mechanisms In Acid Solution: Direct Current Study Supported by Non-Electochemical Measurement. Electrochimica Acta 47 : 4139 – 4148.

[4] Boyapati, V. A. R. and Kanukula, C. K.; 2012: Corrosion Inhibition of Cu-Ni (90/10) Alloy is Seawater and Suilphide-polluted Seawater Environments by 1,2,3-benzotriazole. Hindawi Publishing Corporation, ISRN Corrosion, Vol. 2013, Article ID703929.

[5] Chong, A. L.; Mardel, J. I.; MacFarlane, D. R.; Forsyth, M. and Somers, A. E.; 2016: Synergistic Corrosion Inhibition of Mild Steel in Aqueous Chloride Solutions by an Imidazolinium Carboxylate Salt. ACS Sustainable Chemistry & Engineering, 4 : 1746 – 1755.

[6] Davis, J. R.; 2011: Copper and Copper Alloys, ASM Specialty Handbook. ASM International.

[7] Estrella-Gutiérrez, M. A.; Lizama-Tzec, F. I.; Arés-Muzio and Oskam, G.; 2016: Influence of A Metallic Nickel Interlayer on The Performance of Solar Absorber Coatings Based on Black Nickel Electrodeposited onto Copper. Electrochimica Acta 213 : 460 – 468.

[8] Goranova, D.; Avdeev, G. and Rashkov, R.; 2014: Electrodeposition and characterization of Ni-Cu alloys. Surface & Coatings Technology 240 : 204 – 210.

[9] Ismail, M. K.; Fathi, M. A. and Badawy, A. W.; 2005: Electrochemical Behavior of Copper-Nickel Alloys In Acidic Chloride Solutions. Corrosion Science 48 : 1912 – 1915.

[10] Panagopoules, C. N. and Tsoutsouvaa. M. G.; 2011: Corrosion Engineering Science and Technology 46 : 513.

[11] Popoola, A. P. I.; Olorunniwo, O. E. and Ige, O. O.; 2014: Corrosion Resistance Through The Application of Anti-Corrosion Coatings. In Developments in Corrosion Protection. InTech.

[12] Popoola, A. P. I. and Fayomi, O. S.; 2011: Performance Evaluation of Zinc Deposited Mild Steel In Chloride Medium. Int. J. Electrochem. Sci, 6 : 3254 – 3263.

[13]Rahmani, K.; Jadidian, R. and Haghtalab, S.; 2016: Evaluation of Inhibitors and Biocides on The Corrosion, Scaling and Biofouling Control of Carbon Steel and Copper–Nickel Alloys In A Power Plant Cooling Water System. Desalination 393 : 174 – 185.

[14] Silaimani, S. M.; Vivekanandan, G. and Veeramani, P.; 2015: Nano-nickel–Copper Alloy Deposit for Improved Corrosion Resistance In Marine Environment. International Journal of Environmental Science and Technology 12 : 2299 – 2306.

[15] Simons, M. R.; 2008: Report of Offshore Technology Conference (OTC) Presentation, NACE International Oil and Gas Production.

[16] Xu, W.; Rayment, T. and Davenport, A.; 2017: The Effect of Carbon Within Corrosion Pits of Iron in Chloride Solutions. Corrosion Engineering, Science and Technology 1 – 8.