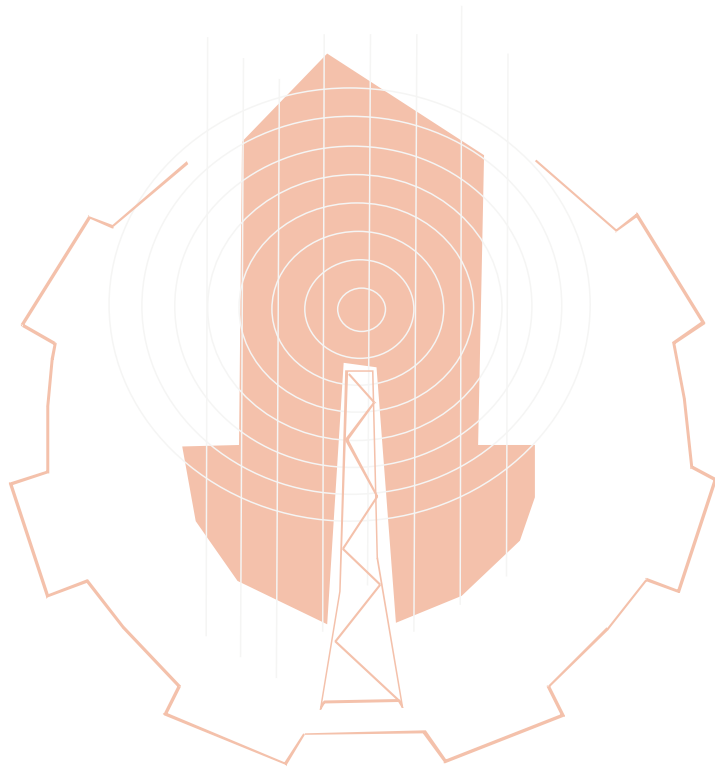




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EFFECT OF OPERATIONAL PARAMETERS ON CONTINUOUS-CURRENT ELECTRODEPOSITION OF Ni-Co ALLOYS

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المخلص

تم في هذا البحث ترسيب رقائق لسبيكة النيكل-كروم على الصلب الكربوني بطريقة التيار المستمر باستخدام خلية وات عند درجتي حرارة 40، 50^oم تحت الظروف الساكنة، وبقيم متفاوتة لكثافة التيار. تعرض البحث لدراسة اعتمادية خصائص رقائق هذا الطلاء على نوع الأنود والرقم الهيدروجيني وكثافة تيار الترسيب. كما تم تقييم كفاءة الترسيب عند استخدام أنودات قابلة للإذابة وأخرى غير قابلة للإذابة. أدى استخدام الأنودات الغير قابلة للإذابة الى انخفاض تدريجي للرقم الهيدروجيني لمحلول الترسيب إلى قيم حمضية منخفضة جداً، بسبب أكسدة جزئيات الماء عند أسطح الأنود، في حين أدى استخدام أنودات النيكل القابلة للإذابة إلى ضبط الرقم الهيدروجيني لخلية الترسيب بسبب التعويض لأيونات النيكل المفقودة أثناء الترسيب. لوحظ من نتائج الدراسة أن ارتفاع قيم كثافة تيار الترسيب يؤدي إلى تحسين كمية الرقائق المترسبة، وبالتالي زيادة سمك الطبقة المترسبة. واعتماداً على نتائج حيود أشعة أكس تبين أن الطبقة المترسبة تتميز ببنية بلورية تنتمي إلى النظام المكعبي. أخيراً بينت القياسات الكهروكيميائية أن جهد التآكل للمعدن المطلي انحرف إلى الاتجاه الموجب بمقدار 400 ملي فولت على الأقل مما يشير إلى تحقيق درجة عالية من الحماية من التآكل للصلب الكربوني في وسط ملحي بتركيز 3% كلوريد الصوديوم.

ABSTRACT

Ni-Co coatings on carbon steel substrate were prepared by conventional continuous-current electrodeposition in watt's bath at 40 and 50°C. The deposition process was done without electrolyte agitation at different current densities. The dependence of coating properties on type of anode, pH and current density was investigated. The deposition efficiency was evaluated in relation to current density with use of soluble and insoluble anodes. It was found that using the insoluble anode material has led to a gradual decrease in the pH of the deposition bath down to very acidic values. This was affected by the oxidation of water molecules at the anode surface. However, using the soluble Ni-anode gave good control over the pH of deposition bath due to compensation for the loss of consumed Ni-ions in solution. Under both of test regimes, i.e., with use of soluble and insoluble anodes, increasing current density has improved the amount of electrodeposited Nickel; which led to increased thickness of electrodeposited layer.

Based on x-ray diffraction data, the recorded diffraction pattern has proved the crystalline nature of the electrodeposited Ni-Co alloy. Moreover, electrochemical measurement using a modern electrochemical system showed that coating with Ni-Co alloy has shifted the corrosion potential of steel substrate (in 3% NaCl solution) by more than 400 mV in the noble direction; which means a high degree of protection against corrosion has been achieved.

KEYWORDS: Ni-Co Alloys; Continuous Electrodeposition; Current Density; Anode Type.

INTRODUCTION

In most engineering applications, it is the functional properties that are of interest for improvement and development of structural materials. For instance, it is very important to raise the surface hardness of a metal or alloy in order to improve its wear resistance. Similarly, in chemical and petrochemical processes, the corrosion resistance is the most important property. Wear and corrosion are considered as some important phenomena of energy and material losses in mechanical and chemical processes [1-3]. For these reasons, electro-deposition of alloy coatings is widely used in the field of surface engineering in order to fulfill the continued demand for increasing the surface quality of both decorative and functional coatings [4,5]. Coating application by electrodeposition provides means to prolong the lifespan of mechanical parts that are subject to wear and/or corrosion. Moreover, in practice it reduces the cost of maintenance. Electrodeposition has the advantage of low working temperatures and most importantly, the possibility of producing composite coatings with different properties just by changing the electrodeposition operating conditions.

In contrast with other coating techniques such as sputtering and chemical vapor deposition, electro-deposition (or electroplating) offers a more versatile technique for producing single or multi-layer coatings due to its low cost [6]. This method can also be used at ordinary conditions of temperature and pressure. In particular, electrodeposition of nickel and Ni-Co alloy coatings are most attractive due to their low porosity content and high corrosion resistance [7,8]. This coating system has found much attention when it was observed to be an important potential candidate to be a substitute of toxic hexavalent chromium electroplating [9]

Over the years, electroplated nickel alloys have been found attractive mainly because of their unique physical and chemical properties and wide range of applications [10]. However, there is still lack of data on corrosion and wear resistance properties of this surface treatment method. Therefore, the purpose of this paper is to investigate the optimum conditions for the conventional Co-deposition of nickel-cobalt alloy on carbon steel substrate. In addition, the corrosion performance of the deposited layer will be evaluated by electrochemical corrosion test methods.

MATERIALS & METHODS

A commercial quality AISI 1021 carbon steel rods 40-50 cm long were the test material used in this investigation. Disc-shaped samples 24 mm in diameter and 6 mm thick were cut from these rods. The samples were then abraded on emery paper down to a 1000 grit size. Following this step, samples were cleaned under running water, washed with distilled water and ultrasonically cleaned in 5 Wt.% NaOH solution. Final cleaning was then done by immersion in 10% HCl solution, washing with acetone and drying just before immersion in plating bath. The electro-deposition cell used in this investigation consisted of a half-liter Pyrex glass beaker, anode and the steel disc samples (cathode). The anode and the cathode(substrate) were disposed within the bath at a distance of 25 mm apart. The cell and its contents were thermo-stated in a WNB 22 Memmert, thermal bath with a temperature control to within $\pm 0.1^\circ\text{C}$. Continuous electrodeposition of Ni and Ni-Co alloy was carried out in fresh solutions at 40, 50 and 60°C without electrolyte

agitation, at different current densities. Table (1) gives the bath composition of plating bath

Table 1: Bath composition of Ni and Ni-Co alloy electrodeposition [5]

component	Concentration (M)	
	Ni-plating	Ni-Co alloy plating
NiSO ₄	1.3	1.3
NiCl ₂	0.3	0.3
HBO ₃	0.48	0.48
CoSO ₄	-	0.071

The quality of the deposited layers was assessed visually and by using optical microscopy. Further investigation of morphology was done by scanning electron microscopy. The phase constituents in the Ni-deposited layer were analyzed with APD2000 x-radiation diffractometer using Cu-K α radiation (0.154 nm). The diffraction patterns obtained were analyzed and indexed using SAX[®] analytical software. Systematic error has been accounted for by making sure that the sample surface lies exactly on the reference plane of the XRD specimen holder. This was achieved by using plasticine at the back of the sample and pressing hard till the sample surface stood exactly on the same plane as the reference plane of the sample holder.

The electrochemical behavior of bare and coated steel was investigated in 3% NaCl solution at room temperature using Reference 600 Potentiostat/Galvanostat equipment.

DISCUSSION OF RESULTS

Continuous nickel and Ni-Co alloy electrodeposition on carbon steel substrate was carried out in two stages. In the first stage nickel metal was deposited on steel in watt's bath at 40 & 60°C as Ni was the only available material at that time. After procurement of nickel and cobalt salts, thin-films of this Ni-Co alloy were grown on carbon steel substrate using continuous electrodeposition method and the results are given in the following sections.

Ni thin-film deposition:

The data presented in Table (2) is for the electrodeposition of nickel on carbon steel substrate using insoluble Pt-anode at 40 and 60°C. The range of current density used for this set of deposition experiments was between 30 and 180 mA/cm². The time of deposition was fixed at 30 minutes. According to these data, as the current density increases from 30 to 180 mA/cm², the deposition rate on the exposed specimen surface increases from 1.5 to 10.2 mg/min at 40°C and from 1.52 to 10.88 mg/min at 60°C. This implies no appreciable change in rates of deposition were recorded although the temperature was raised from 40 to 60°C without bath agitation. By using the insoluble anode material in the electrodeposition cell, a gradual decrease in the bath pH from 3.5 at the beginning of the experiments to pH= 1.1 in the last run was noted. This change in the pH of plating solution to a very acidic value can be explained by the oxidation of

water molecules at the anode surface according to the following electrochemical reaction:

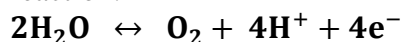


Table 2: Ni electrodeposition using insoluble Pt-Anode at 40 and 60°C and 30 minutes fixed deposition time

Run No.	Current density, mA/cm ²	40°C		60°C	
		pH	Rate of deposition, mg/min.	pH	Rate of deposition, mg/min.
1	30	3.5	1.5	3.5	1.52
2	60	2.3	4.25	3.3	3.38
3	90	1.8	5.72	2	5.04
4	120	1.6	7.11	1.6	7.03
5	150	1.2	8.43	1.4	8.66
6	180	1.1	10.20	1.0	10.88

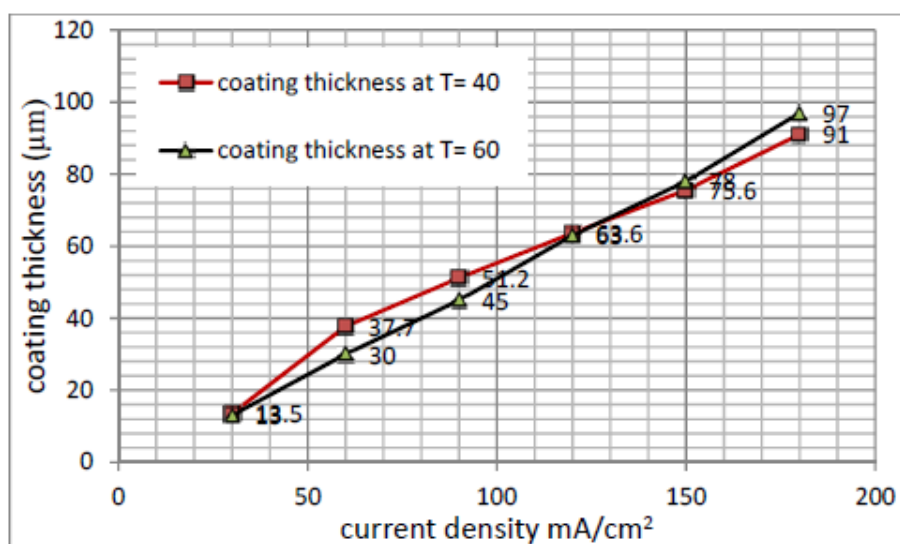


Figure 1: Variation of Ni-coating thickness with current density at two bath temperatures

As can be seen in Figure (1) no appreciable changes in the rate of deposition and consequently in coating thickness, can be observed as the bath temperature changes from 40 to 60°C.

Ni-Co alloy electro-deposition

After the initial successful runs of electrodeposition from Ni-plating bath and after procurement of nickel anode which was imported from UK, the testing program was directed towards the electrodeposition of Ni-Co alloy on carbon steel substrate which was the intention of the testing program. The chosen set of parameters for the continuous electrodeposition of this alloy system were 10 to 50 mA/cm² current density, 40 and 50 °C as the test temperatures. Under this testing regime the pH of the electroplating bath was controlled to within 0.1 variation as can be read in columns (3 and 5) of Table (3). This was achieved by the use of soluble anode material. As noted in the previous testing

program, oxidation of water bath could not be controlled when using the insoluble anode material. The use of soluble Ni-anode material did compensate for the loss of consumed Ni-ions in solution. Under these test conditions the obtained rate of deposition varied between 0.5 to 2 mg/min.

In Ni-Co alloy continuous electrodeposition, a similar observation was made on the effect of temperature on deposition rate as in the case of pure nickel electrodeposition as can be seen in Table (3). In other words, raising the test temperature by about ten degrees did not affect the deposition rate appreciably.

Table 3: Ni-Co alloy electrodeposition using soluble Anodes at 40 and 50°C at a fixed deposition time of 30 minutes

Run No.	Current density, mA/cm ²	40°C		50°C	
		pH	Rate of deposition, mg/min.	pH	Rate of deposition, mg/min.
8	10	3.7	0.46	3.6	0.61
9	20	3.7	0.73	3.7	0.82
10	30	3.8	1.71	3.6	1.76
11	40	3.8	1.86	3.7	2.10
12	50	3.7	2.10	3.6	2.26

On the other hand, it was interesting to note that under the new bath test parameters a sharp increase in coating thickness was recorded above the current density of 20 mA/cm² as can be seen in Figure (2). The increase in current density improved the amount of the electro-deposited Nickel, thus led to increased thickness of deposited layer. The surface morphology of deposited layer was also influenced by current density. For this reason, it appeared to be convenient to suggest 30 mA/cm² as the optimum current density for electrodeposition of Ni-Co layers on carbon steel substrate for getting electrodeposits of about 15 microns' thickness, which is quite reasonable coating for many practical applications [10].

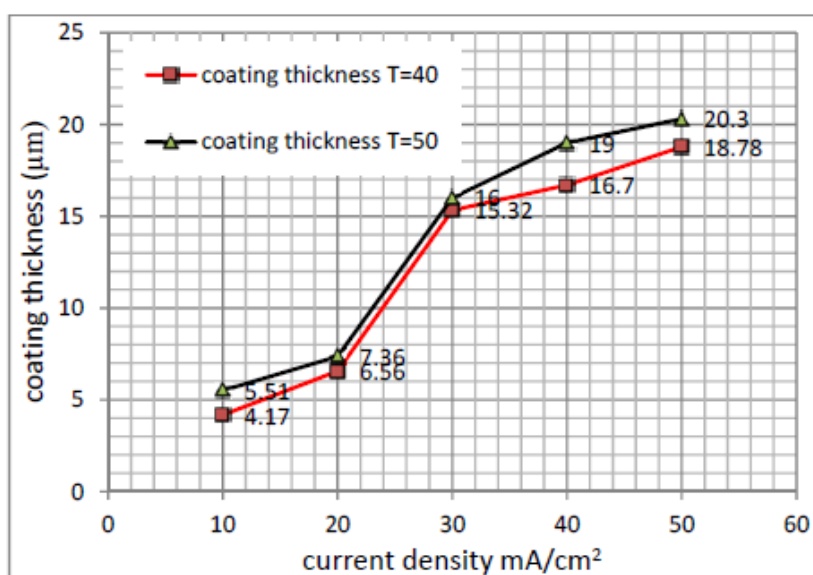


Figure 2: Current density versus thickness of Ni-Co coating alloy

The effect of deposition time on the thickness of deposited layer is given in Table (4) for three measured time periods. It is shown that as the time of deposition exceeded 30 minutes, thicker layers can be deposited. For example, at 30 minutes the thickness of deposited Ni-Co layer was about 20 microns. As the time of deposition was raised to 45 minutes the thickness of deposited layer was more than 3 times the thickness obtained at 30 minutes. This means thicker deposited coating could be obtained at longer operating times. The obtained result matched well to Koay and Zabri [11] results in their research work on electrodeposition of Fe-Ni-Co alloy on mild steel.

Table 4: Variation of rate of deposition with time using soluble Ni-anode at 40°C.

Run No.	Current Density (mA/cm ²)	pH	Deposition Time(min)	Deposition Rate (mg/min.)
18	30	2.8	15	1.34
19	30	2.8	30	1.71
20	30	2.8	45	6.53

Effect of Anode Type

At the beginning of test program, an inert type of anode was used. However, such use imposed a negative effect on the bath chemistry in terms of changes in pH values as explained in previous sections. Thus, for running electrodeposition of nickel on carbon steel substrate covering a current density range from 30 to 180 mA/cm², 150 minutes elapsed. The pH changes in this time period using platinum anode is shown in Figure (3a). A sharp decrease in the pH values were noted in the first hour. Following this, the pH continued to fall down to about pH = 1 by the end of experiment.

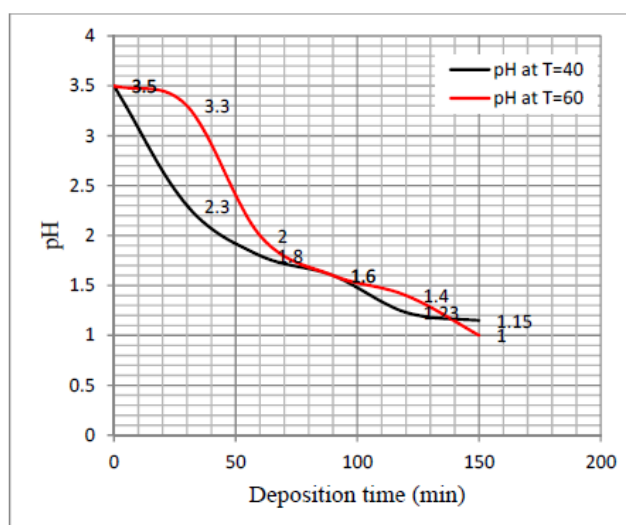


Figure 3a: pH variation with time of deposition using insoluble (Pt) anode

This behavior was similar at both testing temperatures, namely 40 and 60°C. After procurement of a new (soluble) type of anode material, these undesirable effects on the bath chemistry were avoided. The Ni-anode in the form of the plate was obtained and

installed in the electrodeposition cell. Monitoring of the pH during the electrodeposition runs of Ni-Co alloy showed more or less stable values of pH of the electrodeposition bath as shown in Figure (3b) where an average value of $\text{pH} = 3.7$ can be seen. This pH value agrees well with Sadiku-Agboola et. al. [12] who suggested a pH of 4 to 5 for good results.

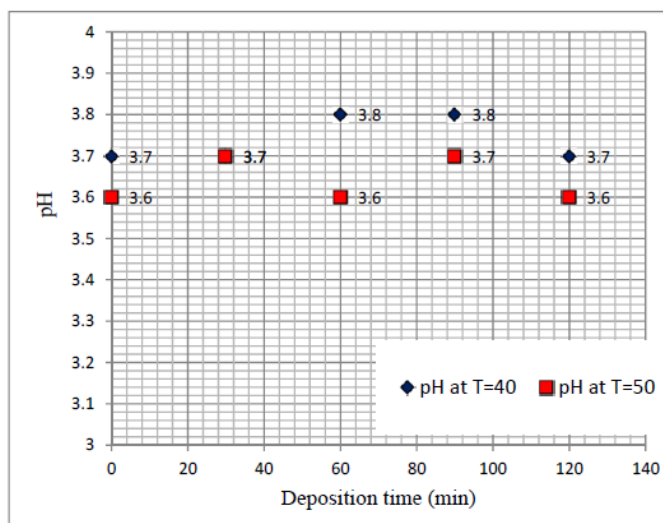


Figure 3b: pH variation with time of deposition using soluble(Ni) anode at 40 & 50°C

Surface morphology of Ni-Co electrodeposits

Figure (4) shows the surface morphology of Ni-Co films deposited on carbon steel substrate at 50 °C and a current density of 50 mA/cm² using nickel soluble anodes. As can be seen in the SEM image, a compact porosity-free layer was obtained. The coating was free of cracks and exhibited a good adhesion to the steel substrate. In most engineering applications, it is the functional properties (such as adhesion and coating integrity) that are of interest to designers.

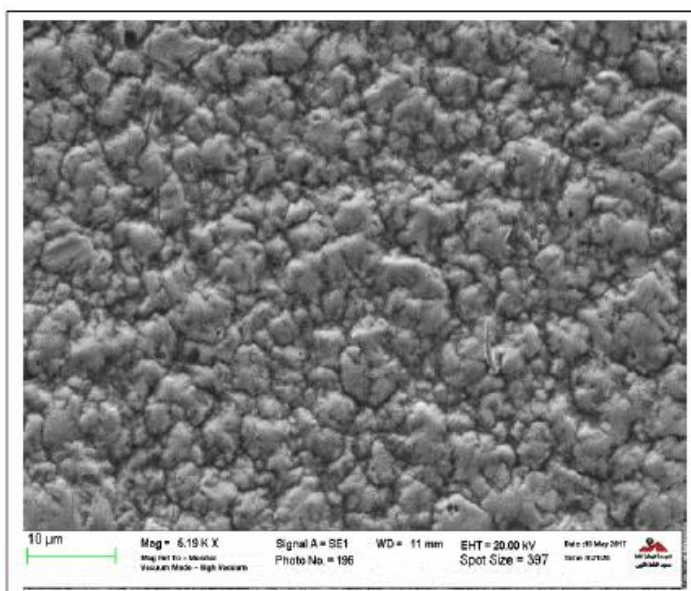


Figure 4: SEM micrograph showing the morphology of Ni-Co electrodeposits on carbon steel substrate

The coating should be pore-free to avoid a high cathode-to-anode area ratio which can lead to intense localized corrosion of steel because Nickel is noble with respect to steel. This is not the case for galvanized steel because zinc metal is active to steel and the presence of pores in zinc coating leads to a high anode-to-cathode area ratio. Thus galvanic corrosion current density is weak and no steel corrosion is expected.

XRD data

Figure (5) presents the surface X-ray diffraction pattern of Ni-Co electrodeposit coating deposited on carbon steel substrate a modified Watts bath electrolysis. Four peaks with (111), (200), (220) and (311) orientation have been recorded on Ni-Co alloy coating diffraction pattern. These were recorded at 2θ values of 45, 52, 77 and 93° respectively, corresponding to different crystal facets with the predominance of (200) which showed the highest peak intensity, this result has matched well with the standard Ni-Co structure in our data base. The deposited layer had a crystalline FCC structure.

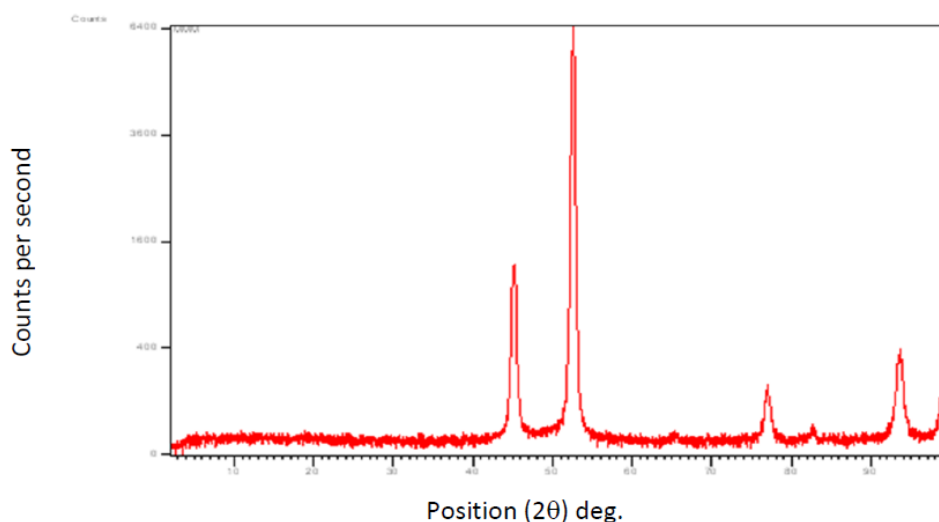


Figure 5: X-ray diffraction pattern of Ni-Co electrodeposit on carbon steel substrate

Corrosion Behavior Diagram:

The open circuit potential (OCP) measurement or corrosion behavior diagram were collected for bare and Ni-Co coated steel, in 3% NaCl solution. These data are presented in Figure (6). In both curves of Figure (6) the corrosion potential (E_{corr}) shifts rapidly in the active direction at the beginning of measurement. After this shift in the active direction, corrosion potential E_{corr} of coated steel kept decreasing slowly and does not approach steady state during one hour testing period. However, the final recorded potential of coated steel was nobler to -240 mV (SCE). On the other hand, Figure (6) shows that even the initial recorded E_{corr} of bare steel is active to -550 mV (SCE) indicating a profound active corrosion under these condition. It is obvious that coating with Ni-Co alloy has shifted the corrosion potential in the noble direction by more than 400 mV; which means a high degree of protection has been achieved.

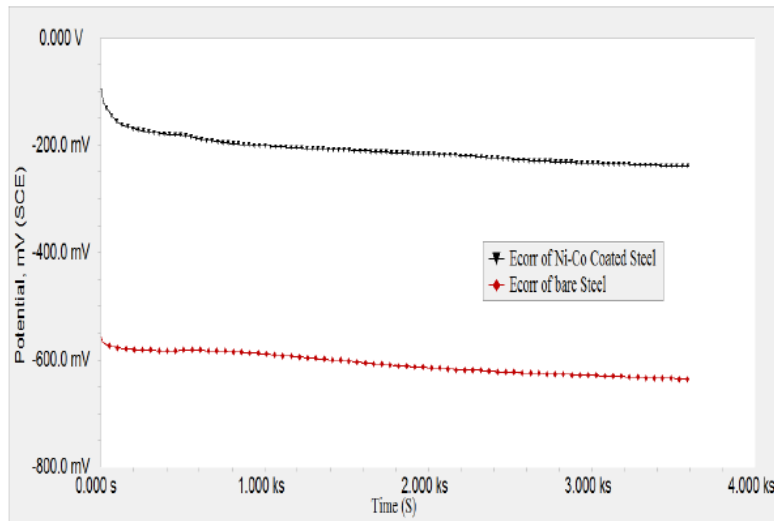


Figure 6: Corrosion behavior diagram of Ni-Co coated steel and bare steel in 3% NaCl solution at 25°C

CONCLUSIONS

Based on the results obtained from this study, the following conclusion can be drawn:

- Pure Ni and Ni-Co alloy thin films were successfully grown on carbon steel substrate using continuous electrodeposition process under stagnant conditions.
- Excessive decrease in the pH of the electrodeposition bath was caused by the usage of insoluble type anodes.
- A good control over the pH of the deposition bath was achieved using soluble Ni-anode due to compensation for the loss of consumed Ni-ions in solution
- The crystalline nature of the electrodeposited Ni-Co alloy layer was proved by XRD data analysis.
- A substantial shift of steel corrosion potential in the noble direction by Ni-Co alloy deposition consolidates the steel resistance against corrosion.

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