

Electrodeposition and characterization of Nickel from Gluconate baths in presence of Some Additives

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Abstract: Electrodeposition of nickel from solutions containing nickel sulfate, boric acid, ammonium sulfate and sodium gluconate on copper substrate has been investigated. The study dealt with the influence of bath composition, current density, pH and temperature on cathodic current efficiency as well as the effect of urea, aniline sulfate and chloramine B as additives on the corrosion behavior using Potentiodynamic polarization curve and morphology of the deposited nickel using scanning electron microscopy (SEM). The optimum conditions for producing nickel deposits from the free additives baths were: 0.2 mol/l NiSO₄·6H₂O, 0.2 mol/l sodium gluconate, boric acid 0.4 mol/l, ammonium sulfate 0.4 mol/l, pH 8, current density of 2.5 A/dm² and at 25 °C. The same conditions were used in the presence of additives, under these conditions the cathodic current efficiency was 96.5% which decreased sharply with increasing temperature. These coatings have high corrosion resistance in comparison with Cu-substrate. However the surface morphology of the deposits varies from spherical grain to columnar in the absence and presence of additives, respectively.

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Key words: Electrodeposition of nickel, copper substrates, additives, potentiodynamic polarization, cathodic current efficiency.

1. Introduction:

Electrochemical nickel plating is a widely used process. Applications comprise functional coatings, for example, for corrosion protection, increase of wear resistance and decorative coatings such as bright Ni mostly in combination with chromium. Many electrolyte formulations are based on the classical composition proposed by Watts, which yields dull Ni deposits. To obtain decorative deposits with a mirror-like surface finish special additive formulations have been developed, which contain organic substances like surfactants, brighteners and levelers. The current efficiency is nearly 100% over a wide range of current densities [WEHNER et al., 2003].

The majority of metal electrodeposition processes are carried out from baths containing complexing agents such as sulfamates, tartrates, Citrates, glycinate and gluconates have been used. These complexing agents are non-toxic, easily obtained and their degradation products offer easier treatment [Rashwan et al., 2003]. A survey of literature shows that gluconate electrolytes were used to electroplate metals such as nickel [Abd El Meguid. E. A et al., 1999], copper [Abd El Rehim et al., 2000], tin [Abd El Rehim et al., 2000] and zinc [Rashwan et al., 2000]. Organic additives have been found to affect the

electrothrowing power of nickel from sulfate, chloride and Watts's bath. High purity nickel was produced by electroplating from sulfate and chloride solutions in the presence of high concentration of boric acid as a buffer [Lupi et al., 2006]. The effect of acetone on the current efficiency, morphology and particle size of the deposited nickel from an ammonical sulfate bath have been studied [Borikar et al., 2006]. The morphology of the nickel deposited with a high concentration of organic additive TBAC (tri benzyl ammonium chloride) have been reported and the average particle size of the deposited powder decreased with the concentration of acetone. More recently, performed of nickel electrodeposition at a constant current density to determine the optimum concentration of chloride and an organic additive used for industrial nickel electroplating were studied [Malevich et al., 2008]. Selenious oxide and certain dyes have been used in conjunction with naphthalene sulfonic acids in nickel baths for improving the brightness and leveling of the nickel deposits. While saccharin, p-toluene sulfonamide, sodium m-benzene disulfonate, o-sulfo benzaldehyde have been used as stress reducers in Watts or sulfamate bath to obtain the desired hardness without tensile stress [Lowenheim, 1974]. Certain anionic wetting agents are used in nickel baths to

prevent bubbles of hydrogen from adhering to the cathode and causing pits in the deposit. Sulfates of normal primary alcohols containing 8–18 carbon atoms at concentrations of 0.1–0.5 g/l were the first successful wetting agents used commercially in bright electrodeposited nickel baths. However, sodium lauryl sulfate (SLS) free from lauryl alcohol is the most extensively used wetting agent of this class for ductile dull nickel plating. Sodium lauryl sulfate and sodium lauryl ethoxy sulfonates, otherwise called or known as anionic surfactants have been widely used commercially in the electroplating of nickel [Shinochiro et al., 1979]. The objective of the present study is to obtain nickel deposits from alkaline-gluconate bath, in order to determine the dependence of coating characteristics on several electroplating variables and the effects of urea, analinium sulfate and chloralamine B in its structure and corrosion resistance.

2. Materials and Method:

Two solutions baths listed in two tables (1) and (2) used were freshly prepared from analar chemicals and doubly distilled water. Copper sheet cathode and pure nickel sheet anode both of dimensions 2X2 cm² were used. The copper sheet cathodes were mechanically polished with different grade emery papers and then immersed in pickling solution (300ml H₂SO₄+100ml HNO₃+5ml HCl+595ml doubly distilled water) for 1min, washed with distilled water, rinsed with acetone, dried and finely weighted. The pH was measured using Microprocessor pH/mV/^oC Meter (Model CP 5943-45USA) and adjusted by NaOH 20% addition, the temperature was controlled by using hot plate-magnetic stirrer (Philip Harris Ltd). Direct current was supplied by a d.c power supply unit (GP-4303D). Cathodic current efficiency (CCE) of the deposits were calculated as $Q_{Ni}/Q_{tot} \times 100$, where Q_{Ni} is the real charge estimated from the quantity of deposited nickel and Q_{tot} is the theoretical charge calculated from Faraday's Law. The surface of the as-deposited nickel on copper substrates was morphologically inspected using scanning electron microscopy (SEM). (JEOL-5410 attached to an EDX unit). The electrochemical experiments were performed using A VOLTA LAB 40 (Model PGZ301) with the aid of commercial software (Volta Master 4 version 7.08). A saturated calomel electrode (SCE) and a platinized platinum black were used as the reference and auxiliary electrodes, respectively with different deposited plates as the working electrode and the electrochemical cell was filled by 3.5% NaCl. Volta Master 4 calculates and displays the corrosion rate, Corr. in $\mu\text{m}/\text{year}$: this rate is calculated from the i_{cor} the corrosion current density found, the D density and the M atomic mass

and V valence entered in the Tafel dialogue box. The calculation is performed as follows:

$$\text{Corrosion } \mu\text{m}/\text{year} = (i_{cor} \text{ (A/cm}^2\text{)} \times M \text{ (g)}) / (D \text{ (g/cm}^3\text{)} \times V) \times 3270$$

with: 3270 = 0.01 x [1 year (in seconds) / 96497.8] and 96497.8 = 1 Faraday in Coulombs.

3. Results and Discussion:

3.1. Cathodic Current Efficiency (CCE):

The effect of pH on cathodic current efficiency, CCE, of nickel deposition from baths containing 0.2 mol/l NiSO₄.6H₂O and 0.2 mol/l C₆H₁₁NaO₇ with 0.4 mol/l boric acid and 0.4 mol/l ammonium sulfate at 25 ^oC and current density of 2.5 A/dm² is illustrated in Figure (1). It's clear from the plot of Figure(1) that the CCE of nickel is very low at low pH values of (3-4) and abruptly increases at pH of 5 attaining steady state in the pH range 5-7 (CCE=70%). At a pH of 8 the CCE is a maxima value of about 97%. The increase in the CCE of nickel deposition with increasing the pH value is due to the increase in hydrogen overpotential. Moreover, the strong hydrogen evolution in acidic solution may inhibit the diffusion of Ni(II) species to cathodic diffusion layer possibly to concurrent hydrogen adsorption and bubbles formation [Ying and Ng, 1988, Abd El Rehim et al., 1997]. In these gluconate solutions, it has been suggested that the gluconate ion is attached to Ni

(II) ion by coordination through the carboxyl group and one of the adjacent hydroxyl groups [Joyce and Pickering, 1965]. Therefore, nickel may be obtained by electroreduction of either the complexed or uncomplexed ions with simultaneous hydrogen evolution as a side reaction and nickel may exist as [Ni C₆H₁₁O₇]⁺ complex ($K_f=74.43$) [Kouba A, 1975]. The influence of temperature on cathodic current during nickel electrodeposition in pH 8 was examined and the results are shown in Figure (2). An increase in temperature from 25 ^oC to 50 ^oC decreased the cathodic current efficiency and this can be explained by the enhancement of rate of hydrogen evolution which suppressed the metal deposition [Ying and Ng, 1988]. One of the most important operating conditions in electroplating process is the current density, as shown in Figure (3). Increasing the current density to 2.5 A/dm² increased the efficiency and after that decreased sharply and this is also due to hydrogen evolution at high current densities. It is found that the efficiency of nickel plating increases with increasing plating time from 10 to 20 min Figure (4). With further increase in plating time the efficiency decreased and the increasing of the efficiency with plating time may be attributed to the fact that hydrogen evolution takes place simultaneously with nickel deposition. Hydrogen evolution decreases with increasing plating time as a

result of increasing pH in the vicinity of the cathode surface [ABD EL REHIM et al., 2002].

From Figure (5). Cathodic current efficiency of Nickel electrodeposition increased with increasing gluconate concentration up to 0.2 mol/l and then decreased with increasing gluconate content in the bath. These results are expected due to the inhibiting effect of gluconate ions [Abd El Meguid et al., 2003]. The data of Figure (6). Show that the cathodic current is increased with increasing Ni(II) ion up to 0.2 mol/l and then slightly decreases which may be due to that increase in nickel content tends to oppose its depletion in the cathodic diffusion layer [Abd El-Halim and Fawzy, 1993]. The effect of urea, analinium sulfate and chloramine B as additives in nickel electroplating from alkaline gluconate was shown in Figure (7). The cathodic current of nickel electrodeposition is decreased as the additive content in the bath is increased and this can be explained by the fact that larger aliphatic or aromatic compounds with positively charged amine groups generally blocked the active side in cathodic substrate at high concentration and it may cause pitting corrosion at higher or lower concentration [Hackerman and Snavely, 1984].

3.2. Potentiodynamic Polarization Curves:

Linear polarization technique was carried out by subjecting the working electrode to a potential range of 205 mV below and above corrosion potential (E_{corr}) at a scan rate of 5 mV/sec, corrosion rate were evaluated from the polarization curves by Tafel extrapolation with the aid of commercial software (Volta Master 4 version 7.08). The results in Figure (8). and table (3) Show the corrosion behavior of the deposited plates with nickel gluconate layer and nickel gluconate plated with addition of urea, aniline sulfate and chloramine B and from the data one could say that nickel gluconate layer alone and with additives was decreased the corrosion rate of cu-substrate in order

Aniline sulfate> urea> Ni-Gluconate> chloramine B> cu-substrate

With protection efficiency of:

96.15%> 95.12%> 91.21%> 83%, respectively

Organic additives protect the entire surface of a corroding metal when present in sufficient concentration both anodic and cathodic reactions are suppressed in the presence of organic additives, the film formed protect the metal surface through a hydrophobic film and the film formed provides a barrier to the dissolution of the metal [Hackerman and Snavely, 1984] and the reason that aniline sulfate and urea showed greatest protection efficiency can be explain by the fact that larger aliphatic or aromatic compounds with positively charged amine groups generally form active portions in organic cationic

inhibitors [Hackerman and Snavely, 1984, Pierre R, 1999].

3.3. Surface Morphology of The deposits:

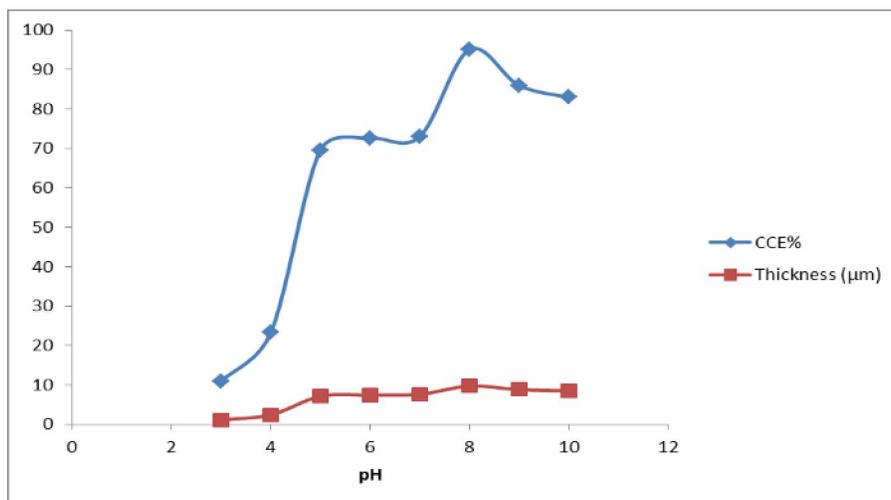
The surface morphology of the as-deposited nickel on Cu-substrate was examined by scanning electron microscopy. Figure (9 a, b, c, d) shows the morphological details of some nickel deposits obtained from the optimum bath conditions for nickel gluconate deposited alone and with aniline sulfate, urea, chloramine B as additives. The deposits are generally adherent, bright and smooth and cover all substrate surface and the obtained deposits from the optimum free additives solutions is essentially differ from those which obtained in the presence of additives; as it is compact fine spherical grain shape which reflect in the presence of additives to compact fine columnar shape as in the presence of aniline sulfate and urea and mixture of spherical grain to predominately columnar shape in the presence of chloramine B, this transition from spherical to columnar reflect the presence of microcracks in the deposits as result of highly stress. The stress could be due to the blocking sites which found by the action of additives .The result of EDX Figure.10. Indicate that the Ni% is high (97.5-98%) in these baths.

Table (1): Materials and Operating Conditions of Nickel Gluconate Baths

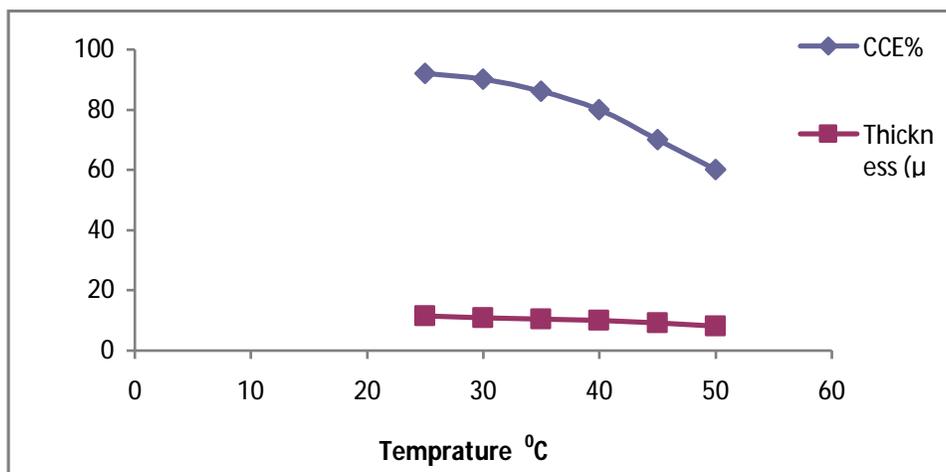
NiSO ₄ .6H ₂ O	0.025-0.25 mol/l
C ₆ H ₁₁ NaO ₇	0.05-0.4 mol/l
H ₃ BO ₃	0.4 mol/l
(NH ₄) ₂ SO ₄	0.4 mol/l
Current	1-4 A/dm ²
pH	3-10
Time	10-60 min
Temperature	25-50 °C
Stirring	150 rpm

Table (2): Materials and Operating Conditions of Nickel Gluconate Additives Baths

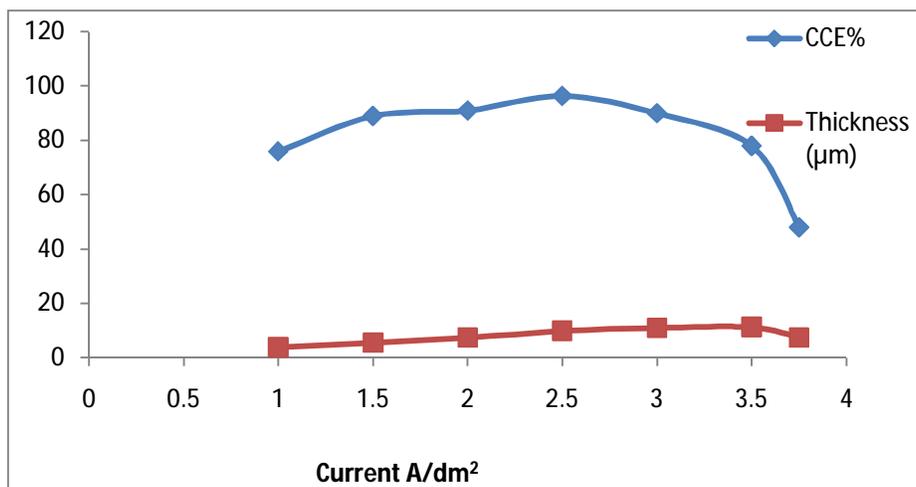
NiSO ₄ .6H ₂ O	0.2 mol/l
C ₆ H ₁₁ NaO ₇	0.2 mol/l
H ₃ BO ₃	0.4 mol/l
(NH ₄) ₂ SO ₄	0.4 mol/l
Urea	0.5-2 g/l
Aniline Sulfate	0.5-2.5 g/l
Chloramine B	0.5-2.5 g/l
Current	2.5 A/dm ²
pH	8
Time	20 min
Temperature	25 °C
Stirring	150 rpm



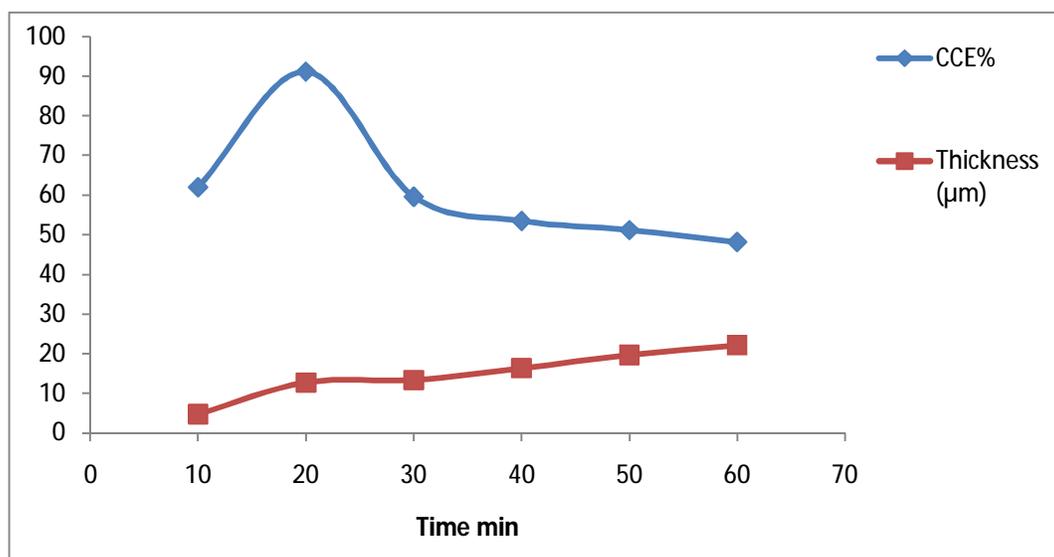
Fig(1) .Effect of pH on cathodic current efficiency, CCE, of nickel deposition from baths containing 0.2 mol/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 0.2 mol/l $\text{C}_6\text{H}_{11}\text{NaO}_7$ with 0.4 mol/l boric acid and 0.4 mol/l ammonium sulfate at 25°C , time 20 min and current density 2.5 A/dm^2 .



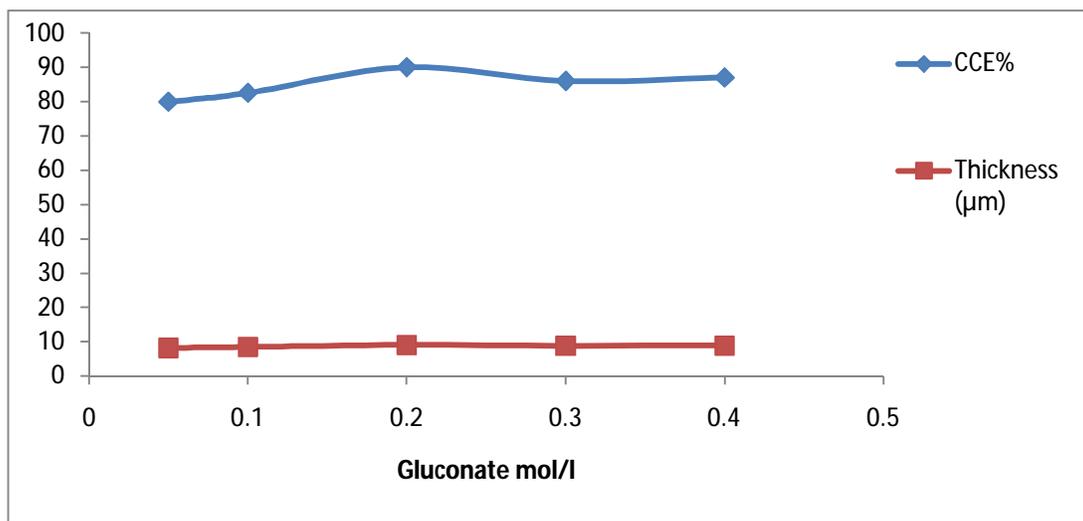
Fig(2) .Effect of temperature on cathodic current efficiency, CCE, of nickel deposition from baths containing 0.2 mol/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 0.2 mol/l $\text{C}_6\text{H}_{11}\text{NaO}_7$ with 0.4 mol/l boric acid and 0.4 mol/l ammonium sulfate at pH 8, time 20 min and current density 2.5 A/dm^2 .



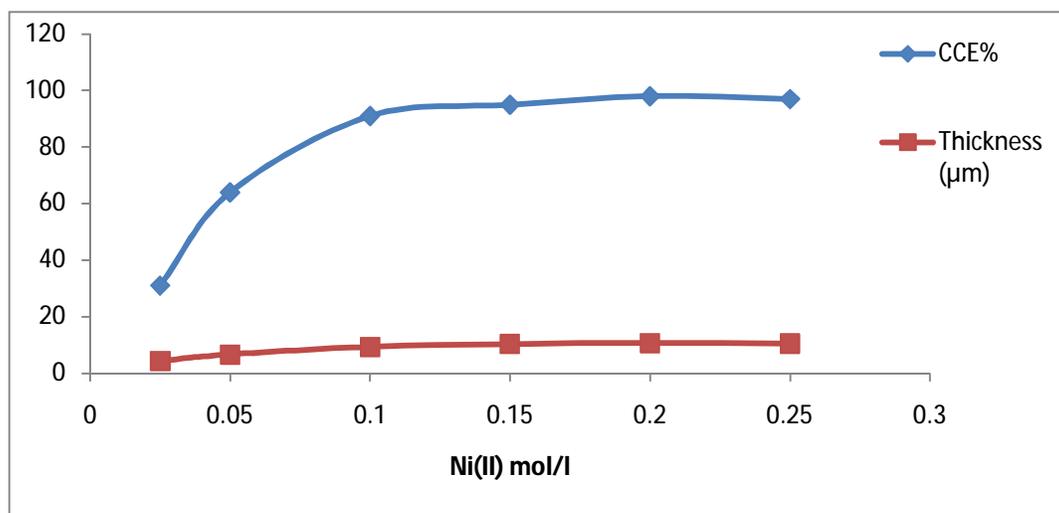
Fig(3) .Effect of current densities A/dm² on cathodic current efficiency, CCE, of nickel deposition from baths containing 0.2 mol/l NiSO₄.6H₂O and 0.2 mol/l C₆H₁₁NaO₇ with 0.4 mol/l boric acid and 0.4 mol/l ammonium sulfate at pH 8, time 20 min and temperature 25⁰C.



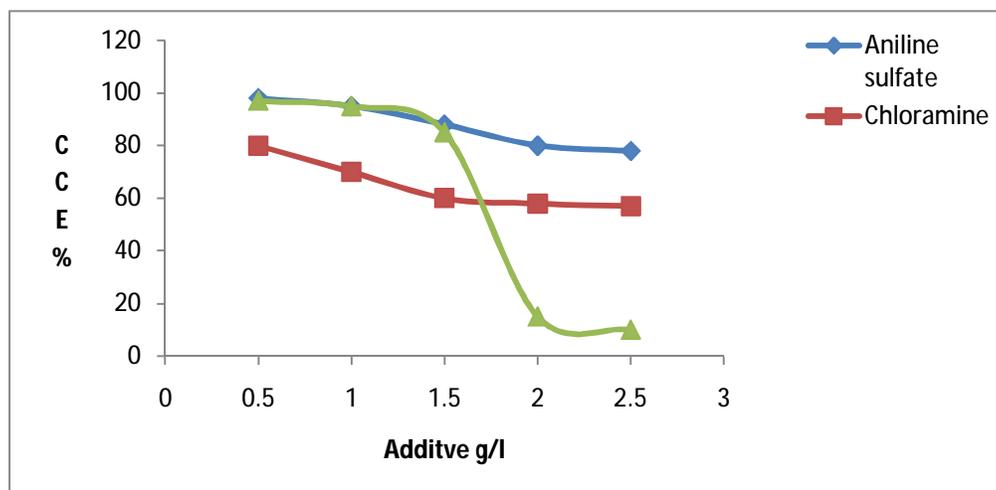
Fig(4) .Effect of plating time/min on cathodic current efficiency, CCE, of nickel deposition from baths containing 0.2 mol/l NiSO₄.6H₂O and 0.2 mol/l C₆H₁₁NaO₇ with 0.4 mol/l boric acid and 0.4 mol/l ammonium sulfate at pH 8 and temperature 25⁰C and current density 2.5 A/dm².



Fig(5) .Effect of gluconate mol/l on cathodic current efficiency, CCE, of nickel deposition from baths containing 0.2 mol/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 0.4 mol/l boric acid and 0.4 mol/l ammonium sulfate at pH 8, time 20 min and temperature 25°C , current density 2.5 A/dm^2 .



Fig(6) .Effect of Ni(II) mol/l on cathodic current efficiency, CCE, of nickel deposition from baths containing 0.2 mol/l $\text{C}_6\text{H}_{11}\text{NaO}_7$ with 0.4 mol/l boric acid and 0.4 mol/l ammonium sulfate at pH 8, time 20 min and temperature 25°C , current density 2.5 A/dm^2 .



Fig(7) .Effect of urea, aniline sulfate and chloramine B g/l on cathodic current efficiency, CCE, of nickel deposition from baths containing 0.2 mol/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 0.2 mol/l $\text{C}_6\text{H}_{11}\text{NaO}_7$ with 0.4 mol/l boric acid and 0.4 mol/l ammonium sulfate at pH 8, time 20 min and temperature 25°C , current density 2.5 A/dm^2 .

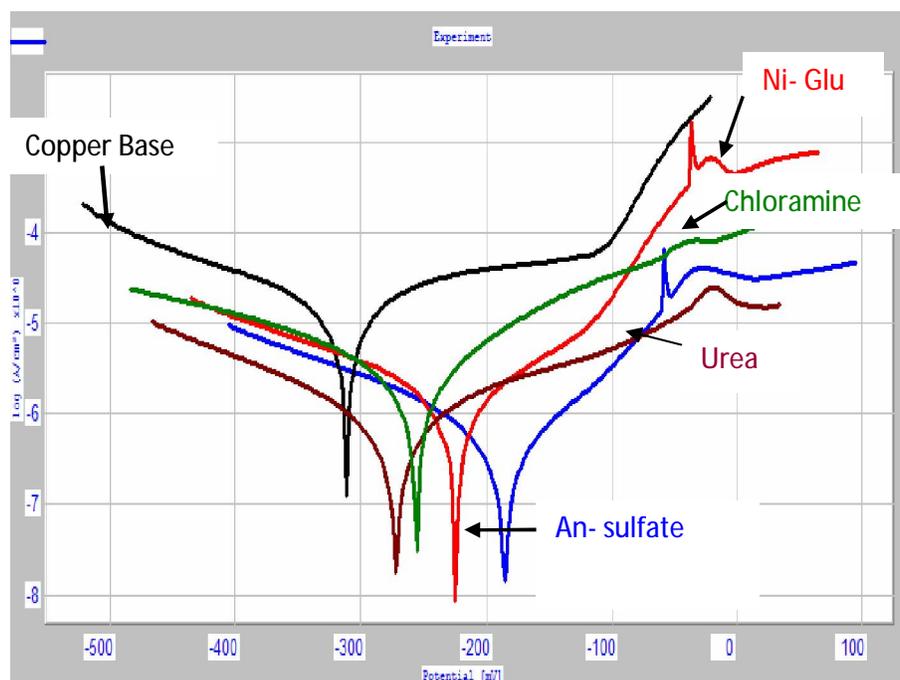


Fig. (8) Corrosion behavior of nickel deposited from gluconate baths alone (Ni-glu) and with aniline sulfate, urea, chloramine B, the samples was chosen from the optimum plating conditions.

Table (3): Data obtained from the corrosion behavior of nickel deposited from gluconate baths alone (Ni-glu) and with aniline sulfate, urea, chloramine B, the samples was chosen from the optimum plating conditions.

	E (i=0) corr. mV	i corr. $\mu\text{A/cm}^2$	Rp kohm.cm ²	Beta a mV	Beta c mV	Corrosion $\mu\text{m/Y}$
Cu Base	-315.0	6.2359	1.93	73.4	-82.7	72.40
Urea	-275.4	0.3045	38.09	66.6	-75.5	3.535
Chloramine B	-259.5	1.0579	11.06	57.6	-81.9	12.28
Ni-Glu	-228.7	0.5479	17.83	64.3	-66.2	6.362
An-sulphate	-189.9	0.2404	48.65	61.4	-75.7	2.791



Fig. (9a).SEM of nickel deposited from bath containing 0.2 mol/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 0.2 mol/l $\text{C}_6\text{H}_{11}\text{NaO}_7$ with 0.4 mol/l boric acid and 0.4 mol/l ammonium sulfate at pH 8, time 20 min and temperature 25°C , current density 2.5 A/dm^2 .

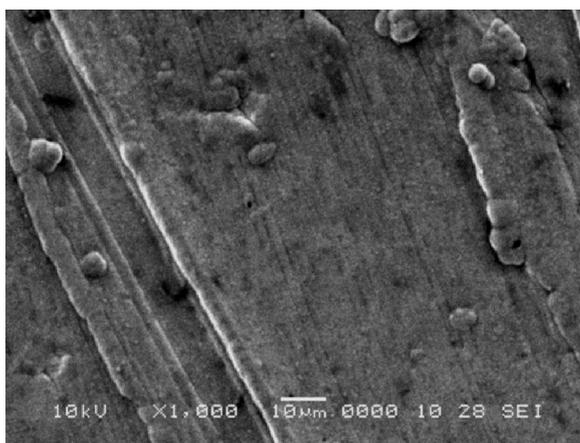


Fig. (9b). SEM of nickel deposited from bath containing 0.2 mol/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 0.2 mol/l $\text{C}_6\text{H}_{11}\text{NaO}_7$, 0.5 g/l aniline sulfate with 0.4 mol/l boric acid and 0.4 mol/l ammonium sulfate at pH 8, time 20 min and temperature 25°C , current density 2.5 A/dm^2 .

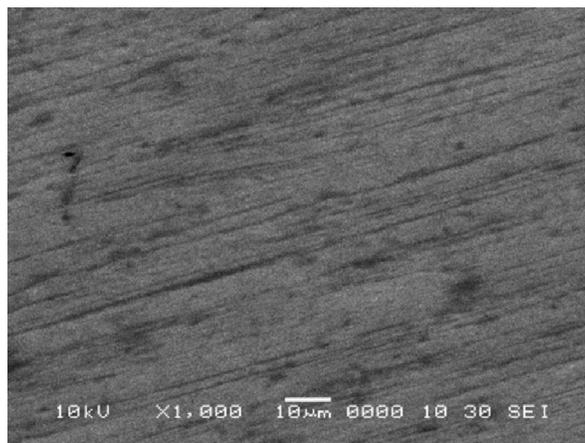


Fig. (9c). SEM of nickel deposited from bath containing 0.2 mol/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 0.2 mol/l $\text{C}_6\text{H}_{11}\text{NaO}_7$, 0.5 g/l urea with 0.4 mol/l boric acid and 0.4 mol/l ammonium sulfate at pH 8, time 20 min and temperature 25°C , current density 2.5 A/dm^2 .

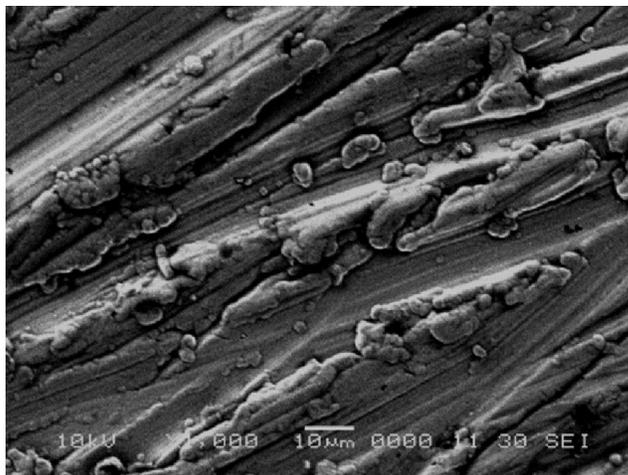


Fig. (9d). SEM of nickel deposited from bath containing 0.2 mol/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 0.2 mol/l $\text{C}_6\text{H}_{11}\text{NaO}_7$, 0.5 g/l chloramine B with 0.4 mol/l boric acid and 0.4 mol/L ammonium sulfate at pH 8, time 20 min and temperature 25°C , current density 2.5 A/dm^2 .

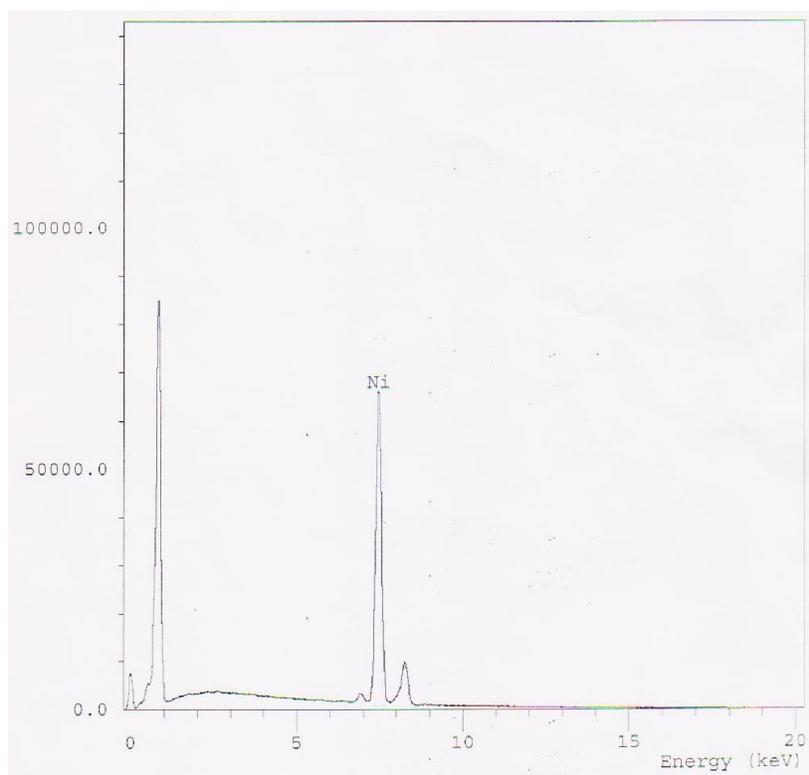


Fig.(10). Energy dispersive X-ray of nickel deposition from baths containing of 0.2 mol/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 0.2 mol/l $\text{C}_6\text{H}_{11}\text{NaO}_7$ with 0.4 mol/l boric acid and 0.4 mol/l ammonium sulfate at pH 8, time 20 min and temperature 25°C and current density 2.5 A/dm^2 .

4. Conclusion

This work studied electrodeposition of nickel in alkaline gluconate baths with and without of aniline sulfate, urea and chloramine B as additives and the influence of these additives in the corrosion behavior of

cu-substrate. It is found that the optimum operating condition for producing nickel deposits from the free additives bath are: 0.2 mol/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 0.2 mol/l sodium gluconate, pH 8, current density of 2.5 A/dm^2 and at 25°C . And the same condition was used in the

presence of additives, under these conditions the cathodic current efficiency is 96.4% which decreases sharply with increasing temperature. These coatings have high corrosion resistance in comparison with substrate. However the surface morphology of the deposits varies from spherical grain to columnar in the absence and presence of additives, respectively.

Acknowledgments

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