

Nano-nickel–copper alloy deposit for improved corrosion resistance in marine environment

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Abstract The nickel–copper alloy (70:30) prepared by metallurgical route is currently employed in marine environments because of its good resistance to corrosion. This alloy forms a thin protective surface layer when exposed to marine atmosphere and thus provides its corrosion resistance. Electrodeposition of nickel–copper alloy from sulphamate acetate-based electrolyte is a new and novel approach and was experimented. The detailed study was performed on the effect of electrolyte composition, current density and pH on the preparation of alloy deposit; the prepared alloy deposit particle size is of 78 nm, and the surface morphology of the alloy deposit was characterized with X-ray diffraction, scanning electron microscopy, EDAX, and atomic force microscope. Nickel–copper alloy deposited from the sulphamate acetate-based electrolyte operated at a temperature of 30 °C, with a pH of 6.6 and at 3 A/dm², produces nickel–copper (70:30) alloy deposit. The corrosion behaviour of this alloy deposit was studied by potentiodynamic polarization method; the corrosion current of nickel is 8.67 $\mu\text{A cm}^{-2}$ and the nickel–copper alloy is 2.65 $\mu\text{A cm}^{-2}$.

Keywords Nickel–copper alloy deposition · Nano-nickel–copper alloy coating · Corrosion protection alloy · Marine protection coating

Introduction

Electrodeposited alloys are gaining importance than wrought metal alloys produced either by molten technique

or other techniques such as doping or mixing powders because of possessing improved chemical and mechanical properties. Because of industrial developments, the installed steel structures are to be protected even in severe marine conditions; for this conventional deposition of single metal does not serve the purpose, somehow bimetallic alloy deposit does the purpose. Electrodeposition of nickel–copper alloy is known for its good and improved corrosion protection for the steel structural's in marine atmosphere. Even though conventional nickel–copper alloy, i.e. monel metal, is familiar for coinage, corrosion protection, and filament for electrical heaters, this electrodeposited alloy finds wide usage in marine structures, oil refineries, oil wells located in mid-sea, and rocket launch platforms located near sea.

Falke et al. (1979) developed the nickel–copper alloy deposit from acetate bath. Bradley et al. (1996) studied the nickel–copper alloy deposit from sulphamate electrolyte; Vu Quang et al. (1985) and Abd El Rehim et al. (1999) investigated the electrodeposition of nickel–copper alloy from citrate-based formulation and studied the effects of current, agitation, and temperature. Green et al. (1998) also investigated the stability of citrate electrolyte and the effect of pH on alloy deposition. Dube et al. (1995) made a detailed study on electroreduction of heterotetranuclear complexes during alloy deposition. Chassaing and Vu Quang (1987) studied the co-deposition kinetics of nickel–copper alloy in complexing citrate ammonia electrolyte. Horkans et al. (1991) explained the usage of rotating disc electrode and the effect of nickel–copper alloy deposits. Ishikawa et al. (1995) informed the deposition process from pyrophosphate-based electrolyte and studied the effects of bath composition and operating conditions of pyrophosphate tetraborate-based electrolyte on nickel–copper alloy deposition. Sobha et al. (1996)

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studied the electrolyte with hull cell studies and other parameters. Mizushima et al. (1996) used glycine as a complexing agent for the electrodeposited nickel–copper alloy. Cherkaoui et al. (1988) and Roy and Landolt (1995) explained the effect of pulse plating parameters on nickel–copper alloy coating. Toth-Kadar et al. (2000) experimented galvanostatic deposition to produce nickel–copper alloy deposit multilayer by employing DC and pulse current. Alper et al. (2004) discussed the preparation and characterization of nickel–copper alloy multilayers and studied the effect of copper in the deposit with respect to giant magneto resistance (GMR). Ismail et al. (2004) investigated electrochemical behaviour of nickel–copper alloy deposit with different nickel content in sulphamate electrolyte. Priscott et al. (Priscott 1958) and Ogden (1986) informed the preparation of alloy deposit from citrate electrolyte and its mechanical properties. Baskaran et al. (2006) evaluated the characterization of nano-crystalline Ni–Cu alloy by pulse electrodeposition. Ying et al. (1988) developed a mathematical modelling for electrodeposition of nickel–copper alloy from citrate-based solution; Podlaha et al. (1994) also developed a mathematical modelling on influence of citrate complex in alloy deposition. Roy et al. (1994), Bonou et al. (1994) and Ghosh et al. (1999) explained the corrosion resistance of the nickel–copper alloy deposited from both DC, pulse and reverse pulse techniques. Mohan and Rajasekaran (2011) studied the influence of electrolyte pH on the composition, corrosion resistance, and morphology of the nickel–copper alloy by brush plating. The present investigation explained about the preparation of nickel–copper alloy deposit from sulphamate acetate electrolyte and the effects of the bath composition, current density, pH, and temperature on the cathodic current efficiency, surface morphology, and corrosion resistance of the alloy deposit.

Materials and methods

The electrolyte was initially prepared from the nickel sulphamate formulation that contains nickel sulphamate 100 g/l, ammonium acetate 150 g/l, copper concentration 8–16 g/l, and Glue 0.05 g/l. Mechanically polished brass plates of size 25 × 75 mm of thickness 0.8 mm were used as the cathode and titanium substrate insoluble anode (TSIA) was employed for this study; for salt spray studies, steel panels of 50 × 75 mm were employed.

The copper acetate concentration was varied from 8, 12, and 16 g/l in the prepared electrolyte, and the electrolyte containing 16 g/l of copper acetate was chosen for nickel–copper deposition of the desired alloy composition (70:30.) By using this electrolyte (that contains 16 g/l of

copper acetate), further deposition was carried out at various current densities 1, 2, 3, and 4 A/dm². Among these, the deposit produced at a current density 3 A/dm² is having desired composition with maximum cathode current efficiency; so this current density was fixed for further studies. This alloy deposition was further carried out at various pH 4.6, 6.6, and 8 by maintaining the current density at 3 A/dm² in the electrolyte. The deposit produced at pH 4.6 and 8 is of good appearance, but the alloy deposition efficiency is of lower value; hence, the pH of the electrolyte has fixed at 6.6. When the electrolyte temperature is raised from 20 to 30 °C, the cathode current efficiency is increased and further raised to 40 °C, and the fall in current efficiency was noticed. Further at the temperature 40 °C, no alloy deposition is produced, and hence, the temperature is limited at 30 °C for further studies. The composition of nickel and copper in the alloy is analysed by EDAX and in the electrolyte by AAS Varian Model SpectraAA220.

Surface morphology and the crystal structure

The surface morphology and grain size of the alloy deposits prepared from the electrolyte at various conditions were examined at a magnification (2000 x) by using scanning electron microscopy (SEM) of model S-3000H, HITACHI, JAPAN. X-ray diffraction (XRD) (Model-PW3040/60 X'pert PRO, make-PANalytical, the Netherlands) with copper target radiation was used to understand phase orientation and lattice parameters of the deposit. The particle size of the deposit was calculated from the XRD data using Scherrer formula. The surface morphology of the alloy deposit as well as the particle size of the deposit obtained at the current density of 3 and 4 A/dm² was confirmed by atomic force microscope (AFM) (Model Picoscan 2000 Make: Molecular Imaging).

Corrosion studies

The corrosion resistance of the coating, prepared from the electrolyte that contain various concentration of copper, at different current densities, temperature, and pH value in 5 % sodium chloride solution was estimated by potentiodynamic polarization method using BAS-IM6 Impedance analyzer. The potentials were scanned over 200 mV in both cathodic and anodic direction from the open circuit potentials using platinum as counter electrode and standard calomel electrode (SCE) as reference electrode. The interception of the linear portion of the two polarization curves offers I_{corr} and E_{corr} values. Further, standard panels were coated with this alloy deposit, and salt spray test was carried out as per ASTM B117 and compared with bare nickel deposit.

Results and discussion

Effect of variables

After the preparation of electrolyte, the nickel–copper alloy deposits are prepared on polished brass plates. The foremost importance is given on copper concentration in the deposit as this is the deciding factor of alloy composition. The copper acetate is added to the electrolyte as the copper metal concentration as 8, 12, and 16 g/l, and the prepared deposits are analysed by employing EDAX. The deposit obtained from the electrolyte that contains 8 g/l copper metal produces alloy containing 85.31 and 14.69 % of nickel and copper. Further addition of copper metal as 12 g/l yields 80.8 and 19.18 % and 16 g/l gives 72.80 and 27.2 % of nickel and copper, respectively, in the deposit. Hence, the deposit obtained from the addition of 16 g/l copper in the electrolyte is considered for further experiments as it matches the conventional 70:30 composition of nickel with copper. Wilbert and Lee et al. (1949) patented the electrodeposition of nickel–copper alloy from acetate-based electrolyte. Whereas in the present investigation presented, the nickel–copper alloy coating was prepared from nickel sulphamate- and copper acetate-based electrolyte; insoluble anode was employed for easy maintenance of the electrolyte. Then, the other parameters such as current density, pH, and temperature are also varied by maintaining 16 g/l concentration of copper is the electrolyte, and data are given in Table 1.

Surface morphology

Scanning electron microscope

The surface morphology of nickel–copper alloy deposits are analysed by SEM and presented in Fig. 2. The SEM figure of alloy deposit produced at 1 A/dm² could not be

produced as it is in the powder form. Fig. 1a represents the deposit prepared at 2 A/dm² and predicted the three-dimensional growth as the grain size is of lamellar one; Fig. 1b shows the grain refinement has taken place in the deposit that was prepared at 2 A/dm² and that fine grain deposit was noticed. Fig. 1c shows further reduction in grain size, but many cracks have been observed which is not suitable for corrosion resistance. Fig. 1d, e shows the hydroxide/oxide deposition has taken place after the initial fine grain deposit and is not desirable for corrosion resistance. From Fig. 1f, g, it was observed that alloy deposit produced at a temperature of 20 °C is mostly of two-dimensional one and further raise in temperature to 25 °C; the growth of the deposit is refined into three-dimensional orientation; however, the nickel content in the deposit linearly goes up with further increase in temperature, and hence, the deposit produced at 30 °C is taken for further corrosion studies.

X-ray diffraction

The XRD patterns of nickel–copper alloy deposits presented in Fig. 2 are polycrystalline in nature. The pattern 2A and 2B shows the deposit prepared at current densities of 2 and 3 A/dm², in which nickel–copper alloy is predominantly deposited with a particle size 78 nm with the lattice orientation of [111], whereas from the Fig. 2c, the deposit prepared at a current density of 4 A/dm², oxide of nickel–copper alloy is predominantly deposited with a lower particle size 65 nm. In Fig. 2d, the deposit prepared at a pH of 4.6 also indicated oxide of nickel–copper alloy is predominantly deposited with a particle size 43 nm; then, by raising pH to 8.0, the peak of nickel–copper alloy is of [111] orientation of particle size 52 nm, and alloy efficiency is lower. So, the deposit represented by Fig. 2b is suitable for the marine application as the predominant peak is nickel–copper in alloy form as well as the particle nano size.

Atomic force microscope

Fig. 3a, b clearly confirms the particle size of 78 and 65 nm as the deposit is prepared at current density of 3 and 4 A/dm², which is of coincidence with the XRD results.

Corrosion resistance

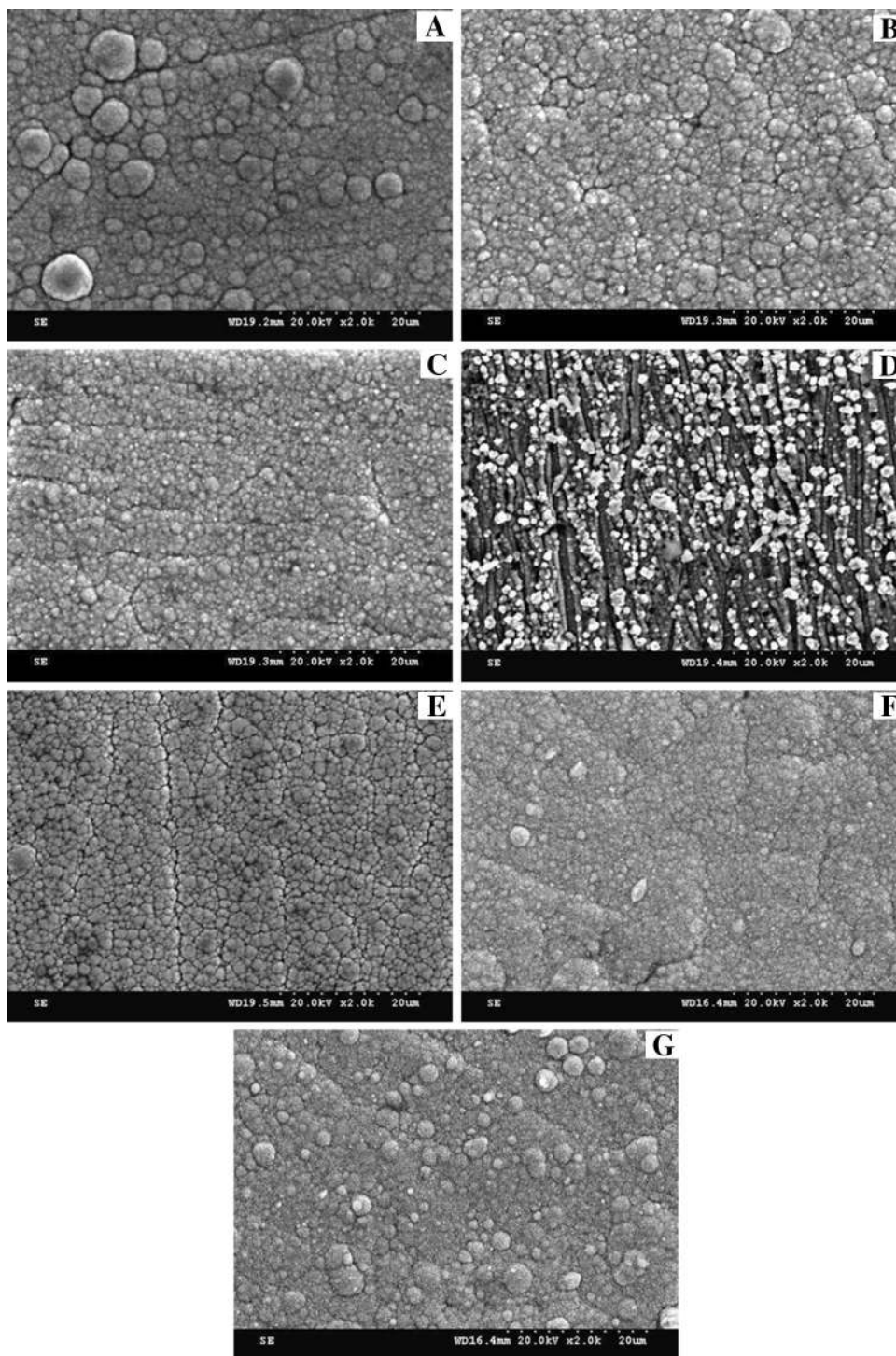
It was observed from Fig. 4a that there is no change in corrosion potential from minus 305 to minus 300 mV as well as corrosion current from 2.81 to 2.65 $\mu\text{A cm}^{-2}$ as the coating is prepared from the current density 2–4 A/dm². Fig. 4b indicates that as the alloy deposit prepared at pH 4.6 is mostly of oxides, the corrosion potential (minus

Table 1 Effect of various parameters with nickel–copper alloy deposit

S. No	Current density (A/dm ²)	pH	Temperature (°C)	Copper (%)	Nickel (%)	Alloy efficiency (%)
1	1	6.6	30	61.87	38.13	82.96
2	2			32.00	67.99	76.34
3	3			27.20	72.80	97.34
4	4			21.64	78.36	87.90
5	3	4.6	30	78.23	21.77	34.04
6		8.0		47.09	52.91	65.22
7	3	6.6	20	40.56	59.44	80.80
8			25	34.77	62.56	91.37



Fig. 1 SEM image of nickel–copper alloy deposit. **a** 2 A/dm², **b** 3 A/dm², pH 6.6, 30 °C, **c** 4 A/dm², **d** at pH 4.6, **e** at pH 8, **f** 20 °C, **g** 25 °C



279 mV) is in the positive side and current is in higher range ($9.7 \mu\text{A cm}^{-2}$); alloy deposit prepared at pH 6.6 and 8.0 is of alloy form, and the corrosion potential (minus 302) is shifted towards negative direction (minus 330 mV), and the corrosion current is of falling trend ($3.0 \mu\text{A cm}^{-2}$). Fig. 4c explains the change of two-dimensional growths into three-dimensional growth of the deposit with the

enhanced corrosion current of the alloy deposit prepared at 20 and 30 °C. From Fig. 4d, the corrosion current for nickel deposit alone is $8.67 \mu\text{A cm}^{-2}$, and corrosion potential is minus 504 mV that implies fast dissolution occurs in chlorine or marine atmosphere. But El-sayed sherif et al. (2011) reported the corrosion current $5.6\text{--}2.9 \mu\text{A cm}^{-2}$, and the corrosion potential from minus 250 to



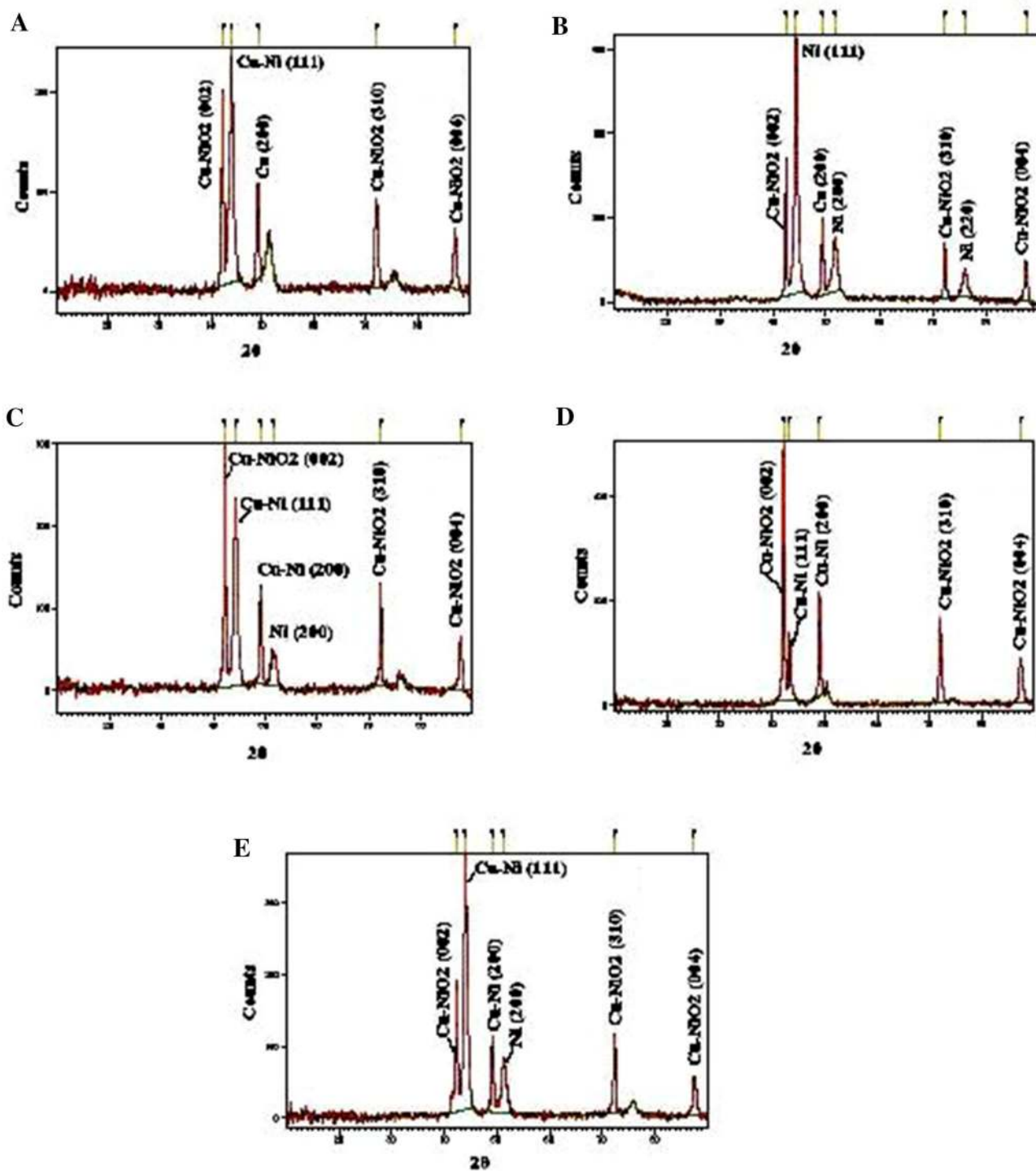


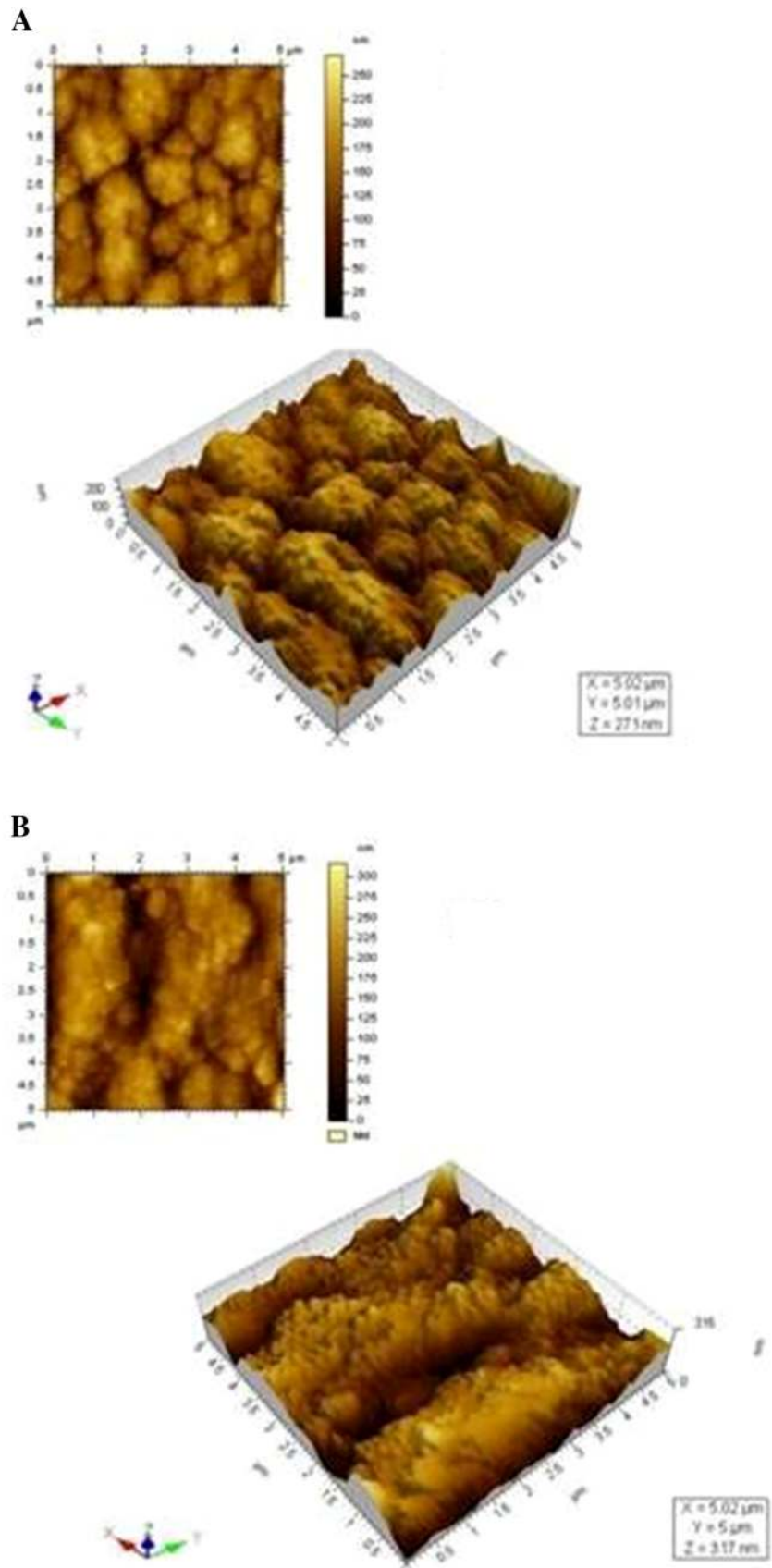
Fig. 2 XRD patterns of nickel–copper alloy deposit. **a** 2 A/dm², **b** 3 A/dm², pH 6.6, 30 °C, **c** 4 A/dm², **d** at pH 4.6, **e** at pH 8

minus 278 mV was reported for conventional nickel–copper alloy of composition 70:30. Hence, this nickel–copper alloy coating is comparable with the conventional alloy.

The nickel–copper alloy and nickel deposit on steel panels were tested in Salt spray chamber that contains

5 % of sodium chloride solution, and daily visual observation was carried out to notice the brown spot on the coated side. The nickel only deposit withstood only 72 h (Fig. 5) and nickel–copper alloy deposit panel extended the withstanding period up to 250 h (Fig. 6).

Fig. 3 AFM images of nickel–copper alloy deposit. **a** 3 A/dm², **b** 4 A/dm²



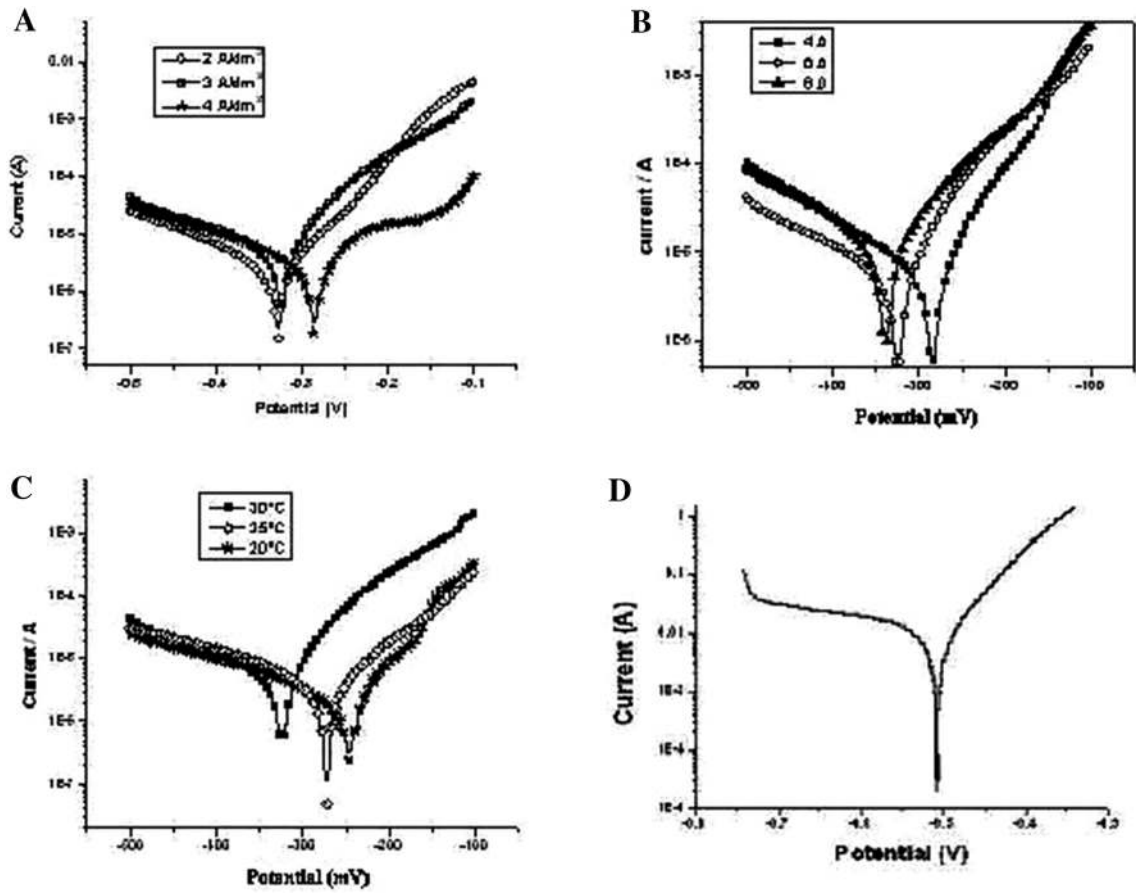


Fig. 4 Corrosion behaviour of nickel–copper alloy deposit **a** effect of current density **b** effect of pH **c** effect of temperature **d** corrosion behaviour of nickel alone deposit



Fig. 5 Salt spray tested nickel deposited panel

This clearly indicated that nickel–copper alloy deposit is having the improved corrosion resistance compared with nickel deposit alone.



Fig. 6 Salt spray tested nickel–copper alloy deposited panel

Conclusion

Nickel–copper alloy deposit was effectively prepared from the sulphamate acetate-based electrolyte, was operated at a

temperature of 30 °C, with a pH of 6.6 and at a current density of 3 A/dm² by employing insoluble anode TSIA, and produces nickel–copper alloy deposit (70:30); it is of metallic in nature with maximum alloy deposition efficiency of 97 %. Further, this alloy deposit is of nanocrystalline size of 78 nm that improves the corrosion resistance than the conventional nickel deposit in the marine atmosphere. Even though corrosion potential of nickel is more cathodic than nickel–copper alloy deposit, the corrosion current for nickel (8.67 $\mu\text{A cm}^{-2}$) is nearly three times higher than nickel–copper alloy (2.65 $\mu\text{A cm}^{-2}$), and the corrosion data of the alloy deposit is comparable with conventional nickel–copper alloy. By performing the salt spray test on these coatings, alloy deposit withstood a longer duration of 250 h than the nickel deposit 72 h. Hence, this nickel–copper alloy deposit is more suitable for the marine environment.

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