Interfacial investigation and strengthening behaviour of Zn–Ni multifacial TEA/MEA thin films induced by electrodeposition

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Abstract Zinc–nickel films were obtained by electrocodeposition using electrolytic deposition techniques in the presence of TEOA ($C_6H_{15}NO_3$) and a surfactants consisting of triethylamine and monoethylamine with other bath additives. The modified structure of the films was analysed with scanning electron microscopy attached to energy-dispersive spectrometer, atomic force microscope and X-ray diffraction. Micro-hardness and corrosion of the coated body was examined and used as a criterion to justify the adhesion of the crystal deposited. The corrosion resistance of the coated and uncoated composites was studied in 3.5 % sodium chloride static solution using linear polarization technique. The hardness value increased from 38HV—substrate to 180HV—coated body, indicating a 78.89 % improvement. Equally, the corrosion resistance of the deposited matrix was enhanced by 84.62 %.

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1 Introduction

Steel is a widely used material in the industry due to its excellent properties. However, one of the major limitations of this alloy is the corrosion tendency in some aggressive environment [1]. Accordingly, methods for protecting the steel in such service condition becomes a research focus. In that direction, alloy coatings have been reported as a means of surface protection. Among the protective methods, electrodeposition of metals/alloys as surface coating provides smoother and harder surfaces, better bonding between particles and metal, easy control of the coating thickness, the ability to deposit metallic alloys and composite coatings and suitability for automation [2]. The use of Zn alone as coatings has been reported to be limited [3], leading to effort directed towards alloying it with nobler metals such as Ni, Co, Fe and Cd [4]. Some authors have reported that good deposition depends mainly on the nature of bath composition [5–7]. Thus, formation of Zn–Ni coatings was necessary. Zn–Ni alloy has been applied on steel, resulting excellent results [1, 8]. However, in recent time, addition of surfactant-induced bath constituent is important to further enhance the physicochemical and thermomechanical properties of coated composite. In our previous study [9], the use of ceramic admixture in the bath formation was employed with significant improvement in the studied properties. However, in an attempt to further optimize the deposition process, the bath constituent was prepared without the ceramic powder, leading to a binary-induced bath formation of Zn–Ni films. Equally, in that direction, the present research was aimed at evaluating the effect of plating parameters on the polarization stability and strengthening behaviour of Zn–Ni thin films induced with triethylamine (TEA) and monoethylamine (MEA) surfactants by chemical bath deposition.

Table 1 Chemical composition of mild steel used (wt%)

Element	C	Mn	Si	P	S	Al	Ni	Fe
Composition	0.15	0.45	0.18	0.01	0.031	0.005	0.008	Balance

2 Experimental procedure

2.1 Preparation of substrate and the coatings

The dimension of the mild steel (substrate) used was 40 mm × 20 mm × 1 mm sheet, and zinc sheets of 30 mm × 20 mm × 1 mm were prepared as anodes. The mild steel specimens' chemical composition is shown in Table 1. The cathode was mild steel coupons, and anode was commercially pure zinc (99.99 %). The mild steel specimens were polished mechanically, degreased and rinsed with water as described elsewhere [10]. The prepared Zn–Ni composite in the presence of TEA and MEA was heated for 2 h and periodically stirred for 200 rpm to obtain a homogenous solution before electrolytic deposition process. The prepared cathode and anodes were connected to the D.C. power supply through a rectifier at a current of 2 A/dm^2 with varying applied voltage: 0.5 and 1.0 V for dwell time of 10 and 15 min. The distance between the anode and the cathode and the immersion depth were kept constant. Thereafter, the samples were rinsed in distilled water and dried.

2.2 Bath constituents admixture

The mild steel substrate earlier prepared was actuated by dipping into 10 % HCl solution for 10 s followed by rinsing in distilled water. Analar grade chemicals and distilled water were used to prepare the plating solution at room temperature. Prior to plating, the TEA and MEA were added to the prepared Zn–Ni particles electrolytic solution as shown in Table 2. The formulations were then heated at 40 °C to easy admix and dissolution of any agglomerate in the bath solution. The bath produced was stirred continuously as heating trend lasted for hours before plating (Table 3).

2.3 Characterization of the coated composite

The surface appearance and morphology of the coating and thin films were characterized with TESCAN scanning electron microscope equipped with energy-dispersive X-ray (SEM/EDX). The adhesion profile, topography and morphology of sample surface after coating were observed with atomic force microscope (AFM). Equally, the X-ray diffraction (XRD) spectra of some plated sample were assessed.

Table 2 Bath composition of Zn–Ni alloy codeposition in the presence of TEA and MEA

Composition	Mass concentration (g/l)
ZnCl	100
Ni$_2$Cl	100
KCl	80
Boric acid	10
Glycerine	10
TEA	2
MEA	2
pH	4.8
Voltage	0.5 and 1.0 V
Time	15 min
Temperature	40 °C

2.4 Micro-hardness and corrosion measurement

Vickers micro-hardness tester under a load of 100 g and a spacing of 150 μm with a dwell time of 15 s with an average of four measurements was used to evaluate the hardness of the developed composite using a Dura-scan inventor-EMCOTEST. The indentations started at the surface of the coated body through the base of the mild steel substrate. The electrochemical studies were performed with Autolab PGSTAT 101 Metrohm Potentiostat using a three-electrode cell assembly in a 3.65 % NaCl static solution at 40 °C. The developed composite was the working electrode, platinum electrode was used as the counter electrode, and Ag/AgCl was used as the reference electrode. The anodic and cathodic polarization curves were recorded by a constant scan rate of 0.012 V/s which was fixed from ±1.5 mV. From the Tafel corrosion analysis, the corrosion rate, potential and linear polarization resistance were obtained.

3 Results and discussion

3.1 Effect of TEA and MEA additives and electrolytic bath constituents

In some report, coarse and dull deposit was obtained without the use of any bath additives [11], since additive especially surfactant has proven to provide good adhesion strength and refined grains. TEA and MEA were used as an intermediate surfactant and as a neutralizer for acid

Table 3 Formulated bath composition of Zn–Ni in the presence of TEA/MEA

Sample order	Material sample	Time of deposition (min)	Potential (V)	Current density (A/dm^2)
Blank	–	–	–	–
Sample 1	Zn–Ni + TEA/MEA	10	0.5	2
Sample 2	Zn–Ni + TEA/MEA	10	1.0	2
Sample 3	Zn–Ni + TEA/MEA	15	0.5	2
Sample 4	Zn–Ni + TEA/MEA	15	1.0	2

component in the corrosion prevention and emulsifiers. Equally, with 2 ml of each surfactant, a bright and adorable deposit was observed at 0.5 V for 10 min. Accordingly, the coatings were found to display excellent properties in the presence TEA and MEA surfactant additives. The influence of KCl was to increase the conductance capacities of the bath formulation. In a homogeneous dispersion of the thin film formation over the interfaces, complexes are needed and boric acid/glycine tends to function as such. This complexes act with ions of Zn^{2+}, Ni^{2+} to reduce ionic tension of the cathode, provide grain refine and offer better adsorption on the cathode resulting to significant adherent and improved surface morphology.

3.2 Micro-hardness and corrosion characteristics of the developed composite

The micro-hardness variability of Zn–Ni + TEA/MEA addition at different plating parameters with applied voltage of 0.5 and 1.0 V in 10 and 15 min on mild steel is shown in Fig. 1. From the result, the micro-hardness of the coated body increased with the additives being dispersed into the bath. Equally, the increment in the hardness is such that the control sample with 38HV improved up to 185HV, indicating a 78.89 % improvement by the developed composite coating when those bath constituents were induced. The improvement in the hardness of all the coated

sample is in the following order 1 > 2 > 4 > 3 > as-received. This is, however, similar to the result obtained for the electrochemical corrosion of the coated composite. Accordingly, this observation in the micro-hardness with the binary Zn–Ni alloy coating formation with the help of the TEA and MEA surfactant additives showed some strengthening phases such as Zn_4NiO_2, $ZnNi_2$, NiO_2, ZnO, Zn_3Ni_8 and Zn_3Ni_7 which might have contributed to the improved properties obtained in this study. However, the improvement in the hardness was less than the value obtained with $Zn–Ni–Al_2O_3$-coated composite in our previous study [9]. Equally, the structural properties of the alloy indicate a refined surface morphology which might have led to its better hardness value than others (Fig. 4a). The significant increase in the micro-hardness with all samples upon variable plating conditions suggests that TEA/MEA have a positive strengthening effect. These were believed to have altered the morphology and cause smaller grain, hence providing structural modification which enhanced the hardness of the composite coatings [12].

The electrochemical corrosion of the coated and uncoated composite was evaluated in 3.65 % NaCl solution with the corrosion rate analysis using the Tafel extrapolation, which is shown in Fig. 2. The linear polarization data of coated and uncoated samples in 3.65 % NaCl static solution are shown in Table 4. The corrosion potentials for
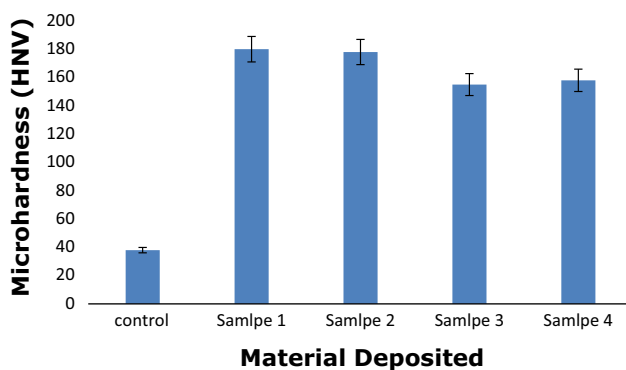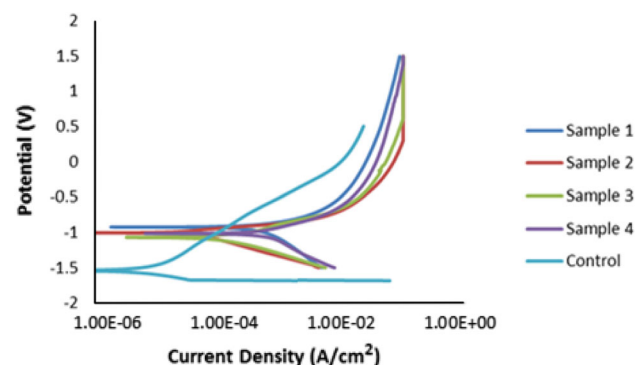

Fig. 1 Variation of micro-hardness for all the deposited materials

Fig. 2 Linear polarization curve for the coated and uncoated mild steel samples in 3.65 % NaCl solution

Table 4 Polarization data of coated and uncoated mild steel in a static 3.65 % NaCl solution

Sample no.	Ecorr [obs (V)]	jcorr (A/cm^2)	icorr (A)	CR (mm/year)	R_p (Ω)
1	−1.0665	5.43E−05	5.43E−05	0.6307	435.91
2	−1.0121	8.28E−05	8.28E−05	0.9626	276.79
3	−0.9212	1.30E−04	1.30E−04	1.5122	80.92
4	−1.0022	1.09E−04	1.09E−04	1.2624	129.06
As-received	−1.5390	7.04E−02	2.04E−03	4.1000	27.60

the entire coated composite increased with a significant reduction in the corrosion rate as compared to the as-received sample. It can be said that the developed binary coatings on mild steel improved its corrosion resistance with a noticeable increase in the polarization resistance value. Equally, the corrosion resistance of the deposited matrix was found to be enhanced by 84.62 %. This, however, suggests that the developed coatings were able to bring about a good bonding and adhesion with the substrate material. The films developed as a result of the binary coatings on to the mild steel substrate as a high surface resistance to corrosion process, which in turn lowers the corrosion rate. The polarization resistance of the coated sample is in the order of 1 > 2 > 4 > 3 > as-received.

3.3 Structural characterization

In Figs. 3, 4 and 5, the SEM/EDS of the as-received sample, Zn–Ni + TEA/MEA at 0.5 and 1.0 V for 10 min, Zn–Ni + TEA/MEA at 0.5 and 1.0 V for 15 min, were shown, respectively. In general, it can be seen that the thin film formed on the mild steel plate resulted into a good appearance, better plating and good adhesion (Figs. 4, 5). The refined grain structures and surface morphology in Fig. 4a comprise of reduced small irregular-shaped crystallite size as compared to Fig. 4b, which confirmed the higher hardness value obtained. For that reason, the observed improvement may not be far from the possibility that the deposition behaviour and the adhesion strength of any particular plating process often depend on the potential, current density and most importantly the time of deposition [13].

In Fig. 1, the decrease in the hardness value may be attributed to the fact that the time of deposition involved (15 min) was too long for such plating in that condition as compare to Zn–Ni + TEA/MEA at 0.5 and 1.0 V for 10 min.

The addition of TEA and MEA as a surfactant via bath codeposition can be said to have eliminated the stress behaviour that can occur during the coating process. Equally, due to the relieve agent, better adhesion within the interface can be attributed to additive such as boric acid
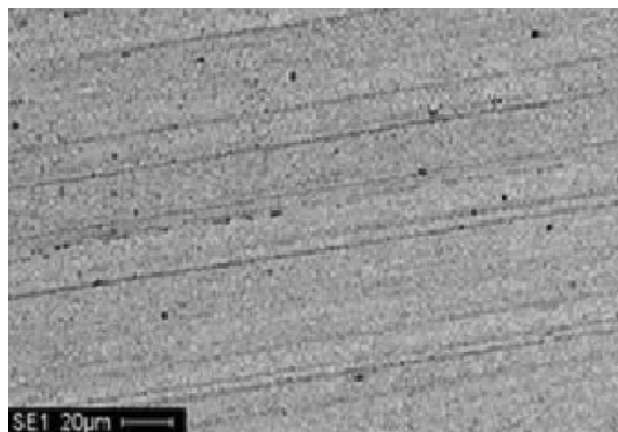
Fig. 3 SEM/EDS for the as-received mild steel

and glycine which act as the conductance. Evidence of few porous on the coatings could be seen (Figs. 4b, 5a, b). In general, all the micrographs indicated a moderate adhesion with EDS revealing the elemental plating constituent (Figs. 4, 5). There was a uniform and continue thickness in the matrix without flaws. The absence of this defects and flaws along the interface is significant in this study and is an indication of good coating matrix and good adhesion properties.

Figures 6 and 7 indicate the X-ray diffraction spectra of some coated samples with various phases. These include phases such as Zn_4NiO_2, $ZnNi_2$, NiO_2, ZnO, Zn_3Ni_8 and Zn_3Ni_7 in Fig. 3 besides original Zn–Ni-based particulate which was observed within coating interface. Higher peak of the resulting phases is probably due to the surfactant induced into the bath during composite matrix codeposition. The interaction between these strengthening phases ultimately produces a crystal orientation of grain size rather than chemical dissolution. The resultant element from the EDS correlates with the strengthening phases observed in all the composites studied. Equally, the improvement of different crystal structures can be related to the growth of grains due to its compactness. In general, all the deposited samples provided a good reflection of surface structure expected in this study.
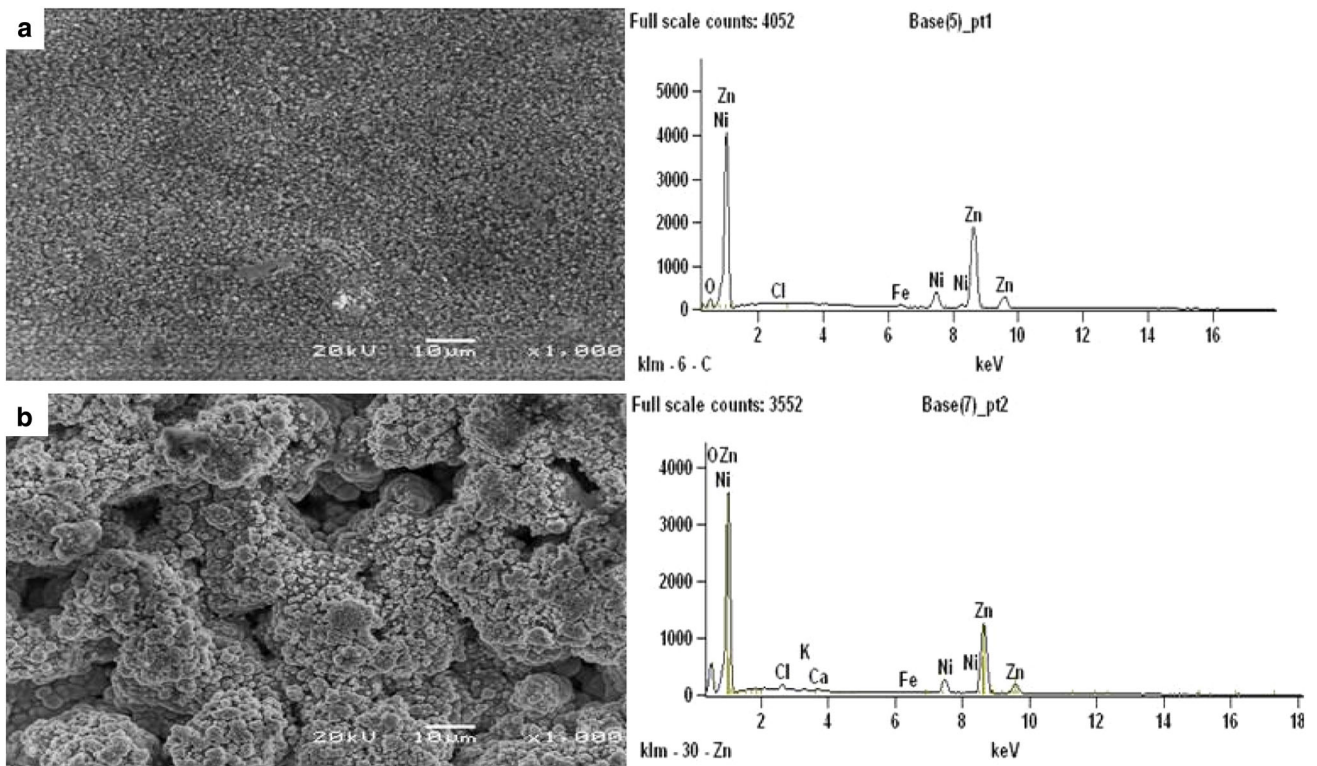
Fig. 4 SEM/EDS for Zn–Ni + TEA/MEA for 10-min plating time at **a** 0.5 V and **b** 1.0 V
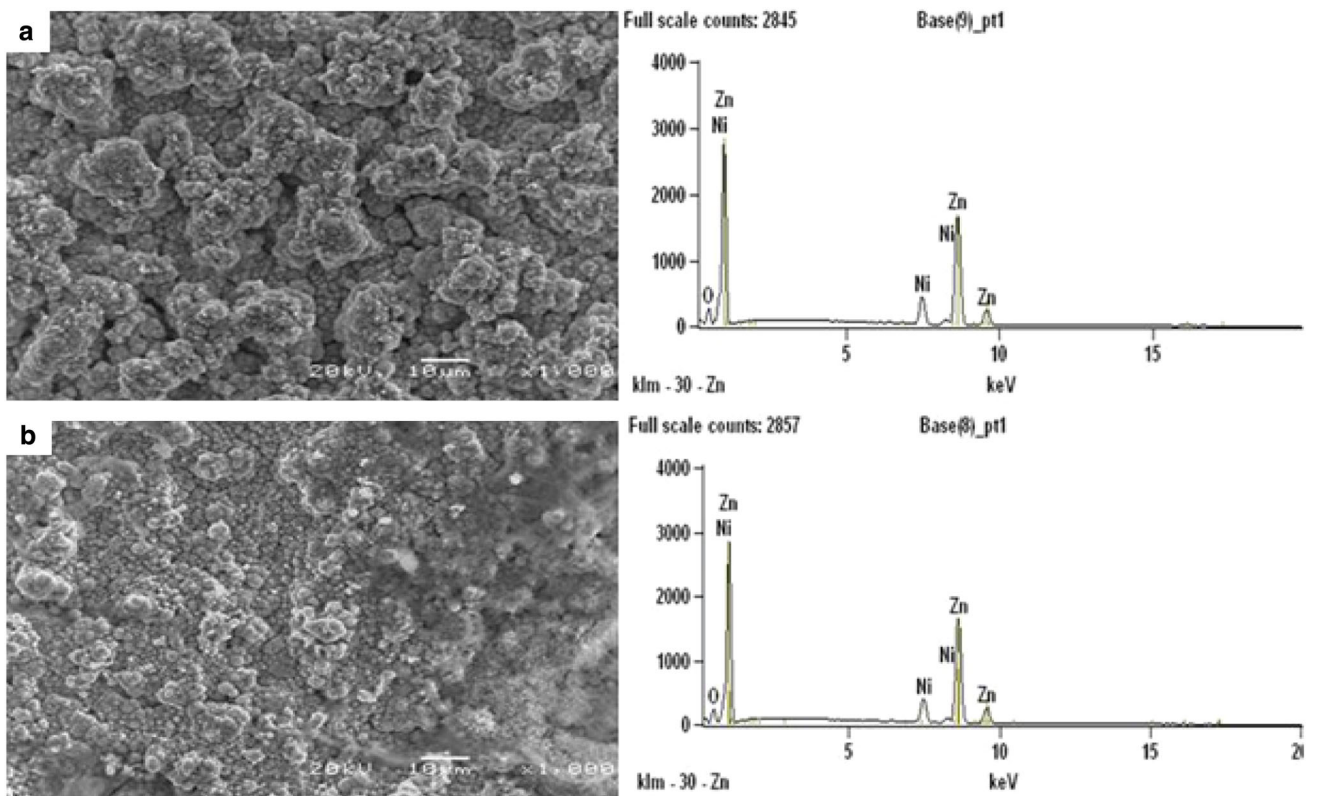

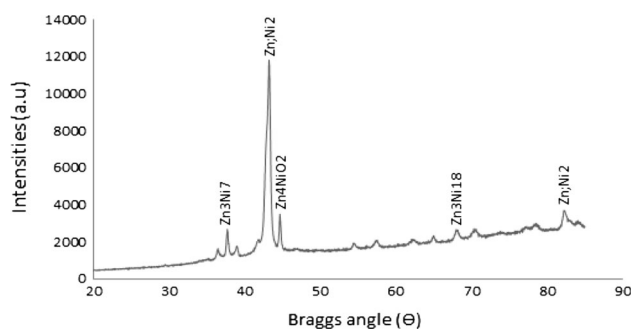Fig. 5 SEM/EDS for Zn–Ni + TEA/MEA at 15-min plating time at **a** 0.5 V and **b** 1.0 V

Fig. 6 XRD spectra for Zn–Ni + Tea/Mea at 0.5 V in 10-min plating time

AFM images of Zn–Ni films obtained at 0.5 V for 10 and 15 min deposition condition are shown in Fig. 8a, b. These show that uniform crystallites coalesced along with smaller grains were found affirming the result obtained from scanning electron micrograph. Fig. 8a indicate a smoother and uniform topography of the Zn–Ni film on the mild steel substrate, which demonstrated better adhesion of

the resultant coatings. This also affirmed the significant result obtained for this coated sample.

4 Conclusions

The development of Zn–Ni coating induced with TEA and MEA organic additive by chemical bath deposition technique has been successfully deposited on mild steel substrates with non-existence of cracks, resulting to better hardness and corrosion resistance. The conditioning effect of the organic compound was found to stabilize the matrix formation and provide a preferential deposit. The hardness value increased from 38HV—substrate to 180HV—coated body, indicating a 78.89 % improvement. Equally, the corrosion resistances of the deposited matrix were found to be enhanced by 84.62 %. The XRD spectra of the developed thin film showed binary Zn–Ni alloy coatings, indicating some strengthening phases such as Zn_4NiO_2, $ZnNi_2$, NiO_2, ZnO, Zn_3Ni_8 and Zn_3Ni_7 predominantly.

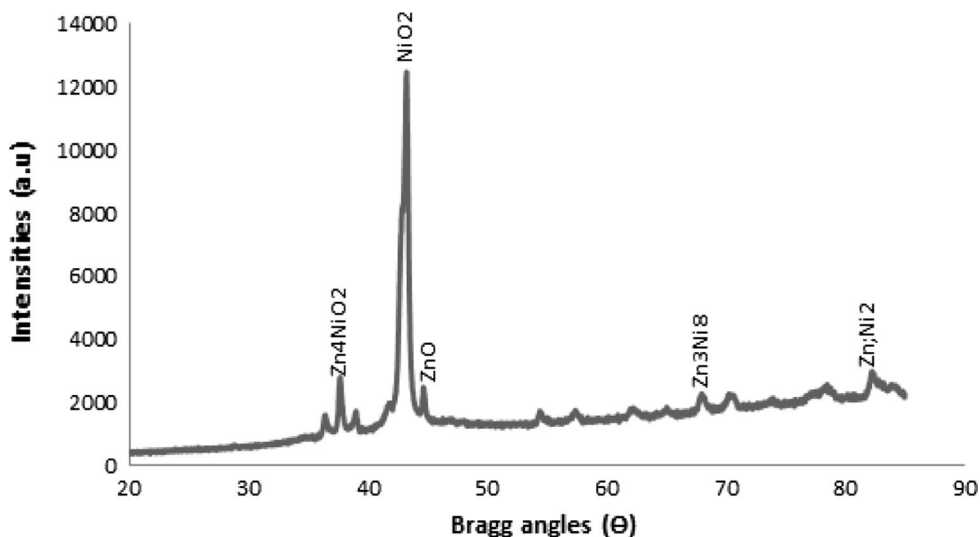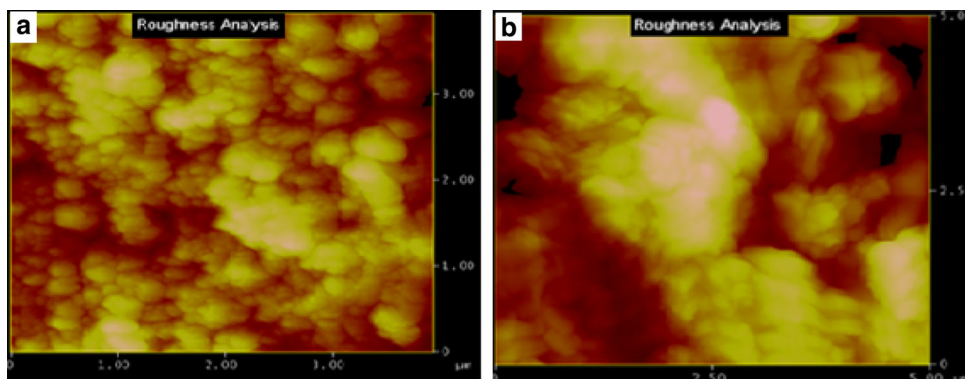Fig. 7 XRD spectra for Zn–Ni + Tea/Mea at 1.0 V in 15-min plating time

Fig. 8 AFM image of Zn–Ni thin film with TEA/MEA obtained at 0.5 V for **a** 10 min and **b** 15 min indicating the topography of the coated film

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