Influence of additives on electrodeposition of bright Zn–Ni alloy on mild steel from acid sulphate bath

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Abstract. The influence of a condensation product (CP) of veratraldehyde (VRTD) and *p*-amino benzoic acid (PABA) on Zn–Ni alloy electrodeposited onto mild steel was studied in acidic sulphate solutions. Ethylenediaminetetraaceticacid (EDTA) and cetyltrimethylammoniumbromide (CTAB) were used as complexing and wetting agents, respectively. The effect of bath constituents, pH, current density and temperature on nature of deposit were studied through Hull cell experiments. The bath constituents and operating parameters were optimized. Deposit properties and corrosion resistance were discussed. Throwing power, current efficiency and polarization studies were carried out. SEM photomicrographs of the deposit obtained from optimum bath revealed fine-grained deposit of the alloy in the presence of condensation product and hence modified the morphology of zinc–nickel alloy deposit. IR spectrum of the scrapped deposit showed inclusion of addition agent.

Keywords. Additives; cathode current efficiency; Hull cell studies; throwing power; zinc–nickel alloys.

1. Introduction

Electroplated zinc coatings are considered as one of the main methods used for the corrosion protection of steel. Recently, the interest on Zn–Ni alloy coating has increased owing to its better mechanical and corrosion properties compared with pure zinc coatings (Bajat *et al* 2000; Brooks and Erb 2001; Beltowska-Lehman *et al* 2002; Muller *et al* 2002). Developing and studying electrolytes of deposits of Zn–Ni alloys is a high priority problem in electroplating. The use of zinc and its alloys for improving the corrosion resistance of coated steel has been growing world wide (Shears 1989; Sharples 1990) and as a substitute for toxic and high cost cadmium coatings (Alfantagi *et al* 1996). In the automotive industry, for example, its use has been growing in search of increasing the corrosion resistance of chassis. The Zn–Ni alloys obtained by electrodeposition processes, with amount of nickel varying between 8% and 14% by weight, give corrosion protection of five to six times superior to that obtained with pure zinc deposit (Anicai *et al* 1992). Many studies have been carried out to understand the characteristics of the deposition process of Zn–Ni alloy (Barcelo *et al* 1994; Elkhatabi *et al* 1996a, b; Fabri Miranda *et al* 1997; Roventi *et al* 2000; Muller *et al* 2001; Koura *et al* 2003). The electrodeposition of Zn–Ni alloys is classified by Brenner (1963) as an anomalous codeposition where zinc is a less noble metal which is preferentially deposited. Al-

though this phenomenon (Shoch and Hirsch 1907) has been known since 1907, the codeposition mechanisms of zinc and nickel are not well understood (Swathirajan 1987; Mathias and Chapman 1990). There are some proportions to explain the anomalous codeposition of the Zn–Ni alloys. The first one attributes the anomalous codeposition to a local pH increase, which would induce zinc hydroxide precipitation and would inhibit the nickel deposition (Higashi *et al* 1981; Fukushima *et al* 1988; Akiyama *et al* 1989). It was, however, later that anomalous codeposition occurred even at low current densities (Horans 1981), where hydrogen formation was unable to cause large alkalinization effects. Another proportion is based on the underpotential deposition of zinc on nickel-rich alloys on nickel nuclei (Nicol and Philip 1976; Swathirajan 1986).

Zinc alloy deposition has been of interest recently since these alloys provide better corrosion protection than pure zinc coatings (Rajagopalan 1972; Fratesi *et al* 1997). It is known, in particular, that the mechanical, physical and electrochemical properties can be improved by alloying zinc with nickel (Hall 1983; Pushpavanam *et al* 1991; Fratesi and Roventi 1992; Kantek *et al* 1994). Electrochemically deposited Zn–Ni alloys have greater corrosion stability as compared to thermally obtained Zn–Ni alloys (Srivastava and Mukerjee 1976).

Zinc–nickel alloys exist in various phases and its structure and morphology (Swathirajan 1986,1987) also determine the corrosion resistance of a deposit. However, it is well known that surface modification can significantly improve the stability of a metal system against corrosion (Rammelt and Reinhard 1992).

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In the present work, an attempt has been made to develop a bright zinc–nickel alloy deposition on mild steel. For the preparation of CP, various primary amines and aldehydes are subjected to condensation reaction. Among these, the CP formed between veratraldehyde (VRTD) and *p*-amino benzoic acid (PABA) gave bright deposit and was used for the deposition process. Hull cell experiment was employed to optimize the current density, bath constituents and pH. Throwing power and current efficiency of the bath solution were determined at various current densities.

2. Experimental

The chemicals used were of AR grade and easily soluble in water. For the preparation of solutions, distilled water was used. The acid zinc–nickel alloy bath was prepared by using $ZnSO_4$, $NiSO_4$ and boric acid (basic electrolyte = BE) (table 1). Due pretreatments were given to the bath to remove the metallic and organic impurities. The CP was prepared by dissolving 1·2 g of VRTD in 10 ml acetic acid, this solution was heated to activate the aldehyde and 2·1 g PABA in 10 ml ethanol was added drop by drop to the solution and refluxed for about 3 h at 70°C, then an yellow coloured solution was obtained. The solution as such was used for the Hull cell studies. A known amount of the condensation product in ml was added to the bath solution. The bath solution was stirred for 30 min and then used for Hull cell experiments.

Hull cell studies were carried out using a 267 ml cell at current, $I = 1$ A and duration, $t = 10$ min (Ramachandran and Mayanna 1992). Suitably pretreated mild steel cathode panels and zinc anode (99·99%) were used. After the plating experiment, the plates were subjected to bright dip in 1% nitric acid for 2 s followed by water wash. The nature and appearance of zinc–nickel alloy plating was carefully studied and recorded through Hull cell codes (figure 1a). All the experiments were conducted at 298 ± 1 K.

Cathode current efficiency (CCE) was estimated at different current densities. The operating current density range, deposit brightness etc were taken as the main criteria for selecting the additives. Haring–Blum cell was employed to determine the throwing power at different current densities (1–4 Adm^{-2}), at pH 3 and 298 K (figure 2). Plating was carried out for 10 min on mild steel cathodes, positioned at a distance ratio of 1 : 5 from the perforated zinc anode. From the weight of the deposit obtained at the nearer (W_n) and far cathodes (W_f), the throwing power

(TP) was calculated using Field's formula (Raub and Muller 1967)

$$\text{Throwing power (\%)} = \frac{L - M}{L + M - 2} \times 100, \qquad (1)$$

where L is the linear ratio and M the metal distribution ratio, W_n/W_f.

For corrosion resistance test, the coated steel plates of 3×4 cm^2 area were given bright dip followed by passivation in a solution containing 200 gL^{-1} sodium dichromate and 2 mLL^{-1} of sulphuric acid at 303 K for 5 s. These passivated samples were dried for 24 h in a clean atmosphere and subjected to neutral salt spray test in accordance with ASTM standard method, B-117, using 5% neutral sodium chloride solution at 303 K.

The effect of additives on cathode polarization was galvanostatically evaluated using a mild steel cathode ($S = 2$ cm^2), zinc anode and a saturated calomel reference electrode (SCE) (Mirkova *et al* 1995) in a three-compartment rectangular cell (figure 3). Constant current was applied in small increments using a controlled power supply unit and the corresponding potentials were recorded after allowing sufficient time to reach the steady state. Structural examination of the deposits was done using a scanning electron microscopy (SEM). IR spectroscopy was used to find out the inclusion of additive in the deposit.

3. Results

3.1 *Hull cell studies*

3.1a *Influence of condensation product*: Basic bath solution gave coarse dull deposit between the current density range of 1 and 7 Adm^{-2} at 2A cell current. To improve the nature of deposit, CP was added to the bath solution. With increase in the concentration of CP, the nature of deposition was improved and at a concentration of 10 mLL^{-1} of CP, the Hull cell panels were bright between the current density range of 0·2 and 5·8 Adm^{-2}. With further increase in the concentration of CP, the nature of deposit became brittle at high current density region. Therefore, on the basis of the above observations, the concentration of CP was kept at 10 mLL^{-1} as optimum. The Hull cell patterns are shown in figure 1b.

3.1b *Influence of zinc sulphate*: To find out the effect of zinc ion, the zinc sulphate concentration was varied

Table 1. Basic electrolyte composition used.

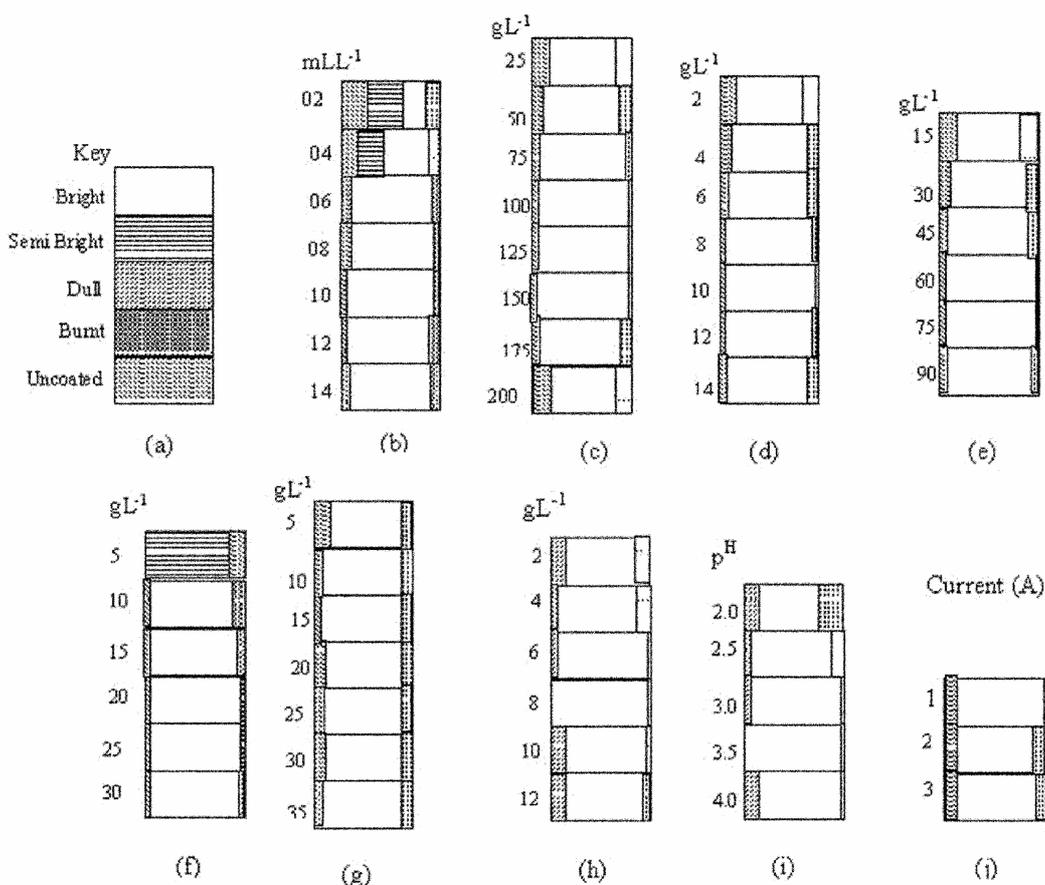| Bath composition	Conc. (gL^{-1})	Operating conditions
$ZnSO_4 \cdot 7H_2O$	130	Anode: zinc metal (99·99% pure)
$NiSO_4 \cdot 6H_2O$	15	Cathode: mild steel
Na_2SO_4	40	Temperature: 298 K
H_3BO_3	15	

Figure 1. Hull cell figures: (**a**) Key, (**b**) effect of condensation product, (**c**) effect of $ZnSO_4$, (**d**) effect of $NiSO_4$, (**e**) effect of Na_2SO_4, (**f**) effect of H_3BO_3, (**g**) effect of EDTA, (**h**) effect of CTAB, (**i**) effect of pH and (**j**) effect of cell current.
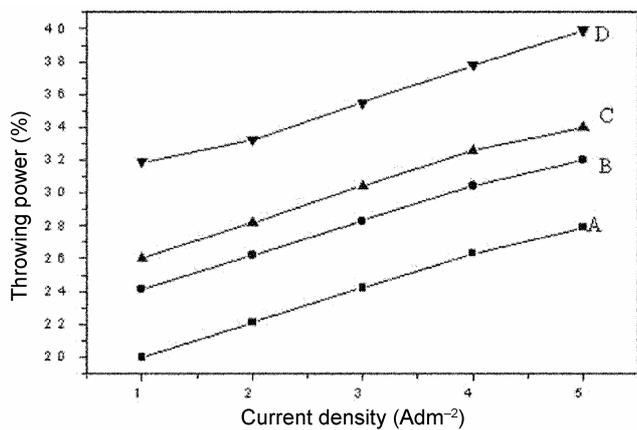

Figure 2. Throwing power by Haring and Blum cell: A. Basic bath (BB), B. BB + EDTA, C. BB + EDTA + CTAB and D. optimized bath.
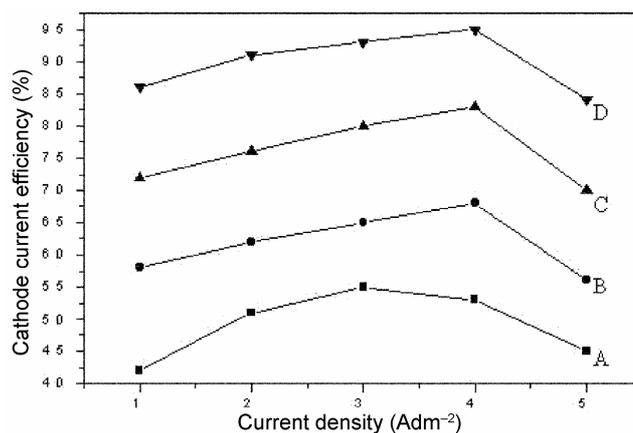

Figure 3. Effect of additives on cathode current efficiency of Zn–Ni alloy deposition: A. Basic bath (BB), B. BB + EDTA, C. BB + EDTA + CTAB and D. optimized bath.

from 25–200 gL^{-1} keeping CP at 10 mLL^{-1}. At lower concentrations, bright deposit was observed in the current density range between 1 and 6 Adm^{-2}. At low current density region, dull and at high current density region,

burnt deposits were obtained. With increase in the concentration of zinc sulphate, the brightness range was extended to higher and lower current density regions. Satisfactory bright deposit was obtained at a concentration of

150 gL^{-1}. Above this concentration, no improvement in the nature of deposit was observed. The concentration of zinc sulphate was fixed at 150 gL^{-1} as optimum (figure 1c).

3.1c *Influence of nickel sulphate*: The concentration of nickel sulphate was varied from 2–14 gL^{-1}. At very low concentration, the Hull cell panels suffer burnt deposit at high current density region and dull deposit at low current density region. The burnt and dull deposit regions were found to be reduced and at 10 gL^{-1}, the deposit was bright over a current density range of 0·2–5·9 Adm^{-2}. Further increase in the concentration (>10 gL^{-1}) did not show any improvement in the bright current density region. The Hull cell patterns showing the effect of nickel sulphate are shown in figure 1d.

3.1d *Influence of sodium sulphate*: Sodium sulphate was added to increase the conductance of the bath solution. The concentration of sodium sulphate was varied from 15–90 gL^{-1}. At 60 gL^{-1} of sodium sulphate in the bath solution, the deposit was bright over the current density range 0·2–5·8 Adm^{-2}. The concentration of sodium sulphate was fixed at 60 gL^{-1} in the bath solution (figure 1e).

3.1e *Influence of boric acid*: The role of boric acid has been of great interest in the electrodeposition of Ni (Rajagopalan 1972; Fratesi and Roventi 1992) and Zn–Ni alloy (Hall 1983). It is now believed that boric acid either complexes with Ni^{2+}, acting as a homogeneous catalyst, or adsorbs on the electrode surface, and has a significant role in morphology and compositional characteristics. The presence of boric acid results in an increase of current efficiency of deposition process, amount of zinc in the deposited alloy, and nucleation density of the deposit (Hall 1983). These effects have been attributed to the adsorptive interactions of boric acid at the electrode surface. Also, boric acid acts as a buffer to maintain pH of the electrolyte bath (Pushpavanam *et al* 1991; Kantek *et al* 1994). Similar effects of boric acid were observed in the present work during Zn–Ni deposition from suggested sulphate bath.

The concentration of boric acid was varied from 5–30 gL^{-1}. At lower concentration of boric acid, the Hull cell panels suffered from dull deposit. With increase in the concentration of boric acid, the burnt deposit was reduced. At 20 gL^{-1} of boric acid, a bright deposit was observed in the current density region 0·2–5·5 Adm^{-2} at 1A cell current (figure 1f).

3.1f *Influence of EDTA*: The concentration of EDTA was varied from 5–35 gL^{-1}. At low concentration, the Hull cell panels suffered burnt deposit at high current density region and dull deposit at low current density region. At 15 gL^{-1} of EDTA in the bath solution, the deposit was bright over a current density range 0·2–5·5 Adm^{-2}. With further increase in the concentration (>15 gL^{-1}), no improvement in the deposit was observed. The concentration of EDTA was fixed at 15 gL^{-1} in the bath solution (figure 1g).

3.1g *Influence of CTAB*: In common practice, surfactants are used in electrodeposition to control the metallic crystal shape and size in order to produce smooth and bright deposits. Common effect of additives are changes in the preferred deposit orientation, morphology and an increase in the deposition over potential. The specific activity of the surfactants are generally understood in terms of adsorption at the cathode surface during deposition and depends on the concentration of the surfactant molecules. When the concentration approached the critical micelle concentration (CMC), the formation of bilayers or multilayers at the electrode surface occurred (Srivastava and Mukerjee 1976).

The concentration of CTAB was varied from 2–12 gL^{-1}. At low concentration, the Hull cell panels suffered burnt deposit at high current density region and dull at lower current density region. The bright deposit was obtained at a concentration of 6 gL^{-1}. The concentration of CTAB was fixed at 6 g^{L-1} in the bath solution (figure 1h).

3.1h *Effect of pH*: To know the effect of pH, the pH of the bath solution was varied from 2–4. At low pH, the Hull cell panels showed burnt deposit at high current density region. At pH 3·5, satisfactory deposit was obtained. From the observations, the pH of the bath solution was kept at 3·5 as optimum. The Hull cell patterns are as shown in figure 1i.

3.1i *Effect of cell current*: The Hull cell experiments were carried out at different cell currents (1–3 A) for 10 min using optimum bath solution. It was found that at a cell current of 1 A, the deposit was bright in the current
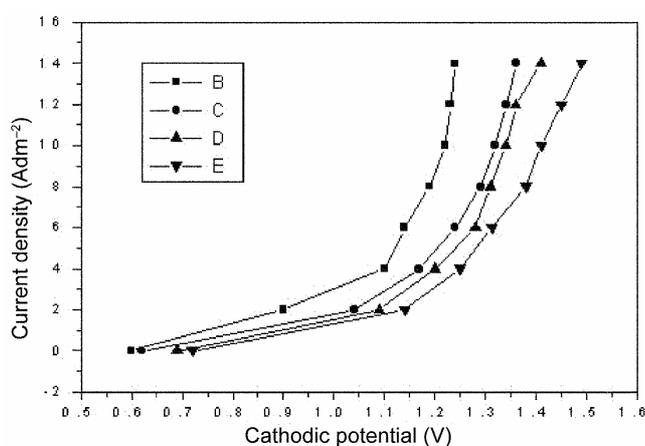

Figure 4. Effect of additives on cathodic polarization; B: Basic bath (BB), C. BB + EDTA, D. BB + EDTA + CTAB and E. BB + EDTA + CTAB + CP.

Table 2. Optimized bath composition.

Bath composition	Conc. (gL^{-1})	Operating conditions
$ZnSO_4 \cdot 7H_2O$	150	Anode: zinc metal (99·99% pure)
$NiSO_4 \cdot 6H_2O$	10	Cathode: mild steel
Na_2SO_4	60	Temperature: 298 K
H_3BO_3	20	pH: 3·5
EDTA	15	Plating time: 10 min
CTAB	8	Bright current density range: 0·2–8 Adm^{-2}
Condensation product (CP) (mLL^{-1})	10	

Table 3. Salt spray test conducted at different time intervals.

Plating bath composition	Hours of treatment	Observation
Basic bath (BB)	24	No white rust
	48	White rust
Optimized bath	24	No white rust
	48	No white rust
	72	No white rust
	96	White rust
Passivated deposit	24	No white rust
	48	No white rust
	72	No white rust
	96	No white rust
	>96	No white rust

density range 0·2–5·6 Adm^{-2}. At a cell current of 2 A, the deposit was bright in the current density range 1–8 Adm^{-2}. At a cell current of 3 A, the deposit was bright over the current density range between 2 and 8 Adm^{-2}. The Hull cell patterns are as shown in figure 1j.

4. Discussion

4.1 *Current efficiency and throwing power*

Current efficiency and throwing power were measured at different current densities by using optimum bath solution. The current efficiency was measured by taking a rectangular methacrylate cell. At low current density (1 Adm^{-2}), the current efficiency was found to be 86%. At a current density of 2 Adm^{-2}, the efficiency was increased to 91%. The maximum current efficiency of 95% was found at 4 Adm^{-2}. With increase in the current density above 4 Adm^{-2}, the current efficiency was found to be decreased.

Throwing power of the bath solutions were measured by using Haring and Blum cell at different current densities. At low current density (1 Adm^{-2}), the throwing power was 31·9% and with increase in the current density, it also increased and attained a maximum value of 39·9% at 4 Adm^{-2}.

4.2 *Polarization studies*

The steel cathode potential was measured galvanostatically with respect to saturated calomel electrode at different current densities. The variation of potential in the presence of different bath constituents is shown in figure 4. The shift in cathodic potential towards more negative direction was observed in presence of addition agents. This is attributed to the formation of more stable electrical double layer by the condensation product, which contains electroactive functional groups.

4.3 *Corrosion resistance*

For corrosion resistance study, the steel cathodes were given the deposit of varying thicknesses from 5–20 μm. The specimens after plating were subjected to bright dip in 1% nitric acid followed by passivation. The porosity of the deposit was tested with ferroxyl test. The test indicated pore free nature of the deposit. Further corrosion resistance test was carried out in a salt spray chamber. The deposited plates after passivation were subjected to a continuous spray of neutral 5% sodium chloride solution. The specimen deposited from optimum bath did not show any white rust even after 96 h of testing. This indicated good resistance of the deposit against corrosion (table 3).

4.4 *Adhesion properties*

Standard bend test was used to measure both adherence and ductility of zinc–nickel alloy deposits. Mild steel panels of 1 mm thick (1×10 cm^2 area) were electroplated with zinc–nickel alloy to different thicknesses (5–20 μm). These samples were subjected to bending test through 180°. No crack or peel off in the deposit was noticed even after 180° bending of the specimen. This indicated good adherence and ductility of the deposit.

4.5 *Surface morphology and IR studies*

The nature of grains of the deposit in presence and absence of addition agent is explained with the help of SEM photomicrographs (figure 5). SEM photomicrograph of the deposit obtained from the basic bath shows coarse-grained deposit having irregular crystal size (figure 5a). The average grain size is ~2 μm. In presence of EDTA (figure 5b), the grain size in the deposit is comparatively smaller and regular with an average grain size of
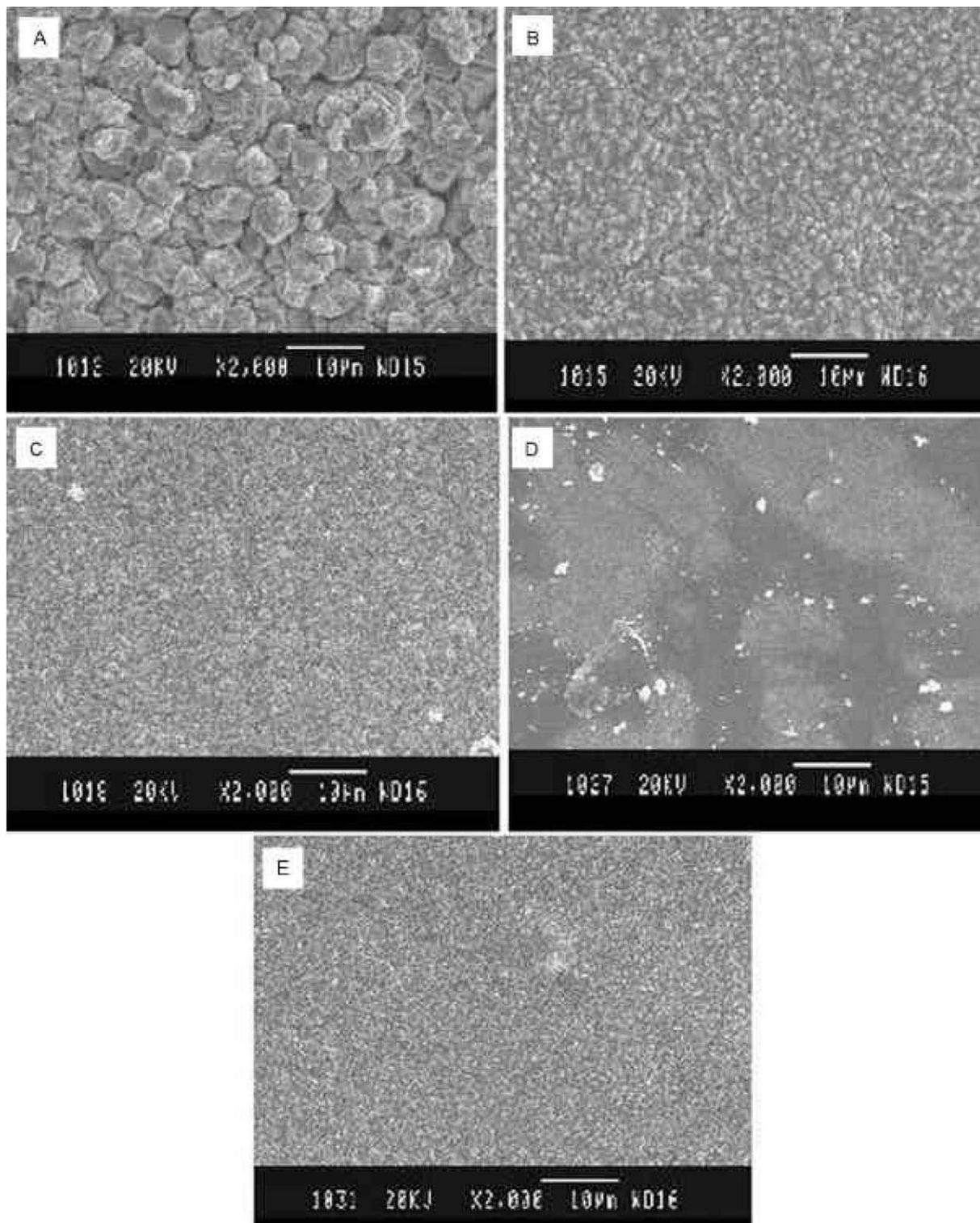
Figure 5. SEM photomicrographs of the deposits obtained at 4 Adm^{-2} in the presence and absence of addition agents at 298 K: A. BB, B. BB + EDTA, C. BB + EDTA + CTAB, D. optimized bath and E. passivated deposit.

~ 0.7 μm. In presence of CTAB (figure 5c), the grain size is smaller (~ 0.08 μm) indicating a modification in the rate of crystal growth. It is also noteworthy to mention the porous-free nature of the coating due to the smaller grain size. The change in morphology can be associated to a strong blocking effect of the cationic surfactant which causes an increased nuclei renewal rates leading to an increase in nucleation number and hence smaller grain

size. The SEM photomicrograph (figure 5d) of the deposit obtained from the optimum bath shows perfect crystal growth, uniform arrangement of crystals, refinement in crystal size and hence bright deposit. The average grain size of the deposit is ~0·04 μm and figure 5e shows the passivated deposit.

The IR spectrum of scrapped deposit obtained from the optimum bath was used to test the inclusion of addition agent in the deposit. IR spectrum shows an absorption peak at 1636 cm^{-1} which corresponds to –C=N group of CP. This indicated the inclusion of CP in the deposit during electrodeposition. Also the position of the peaks indicated the changes in the bond strength of the addition agent during electrodeposition. Figure 6 shows IR spectrum of the scrapped deposit.

The brightness of the deposit improved which may be due to the adsorption of –OCH$_3$, –CH=N and –COOH groups present in CP on active sites. From this observation, we conclude that CP covers the steel surface with less than a single layer. We believe these molecules are preferentially adsorbed on the peak of the dendritic growth sites, preventing further growth of their peaks, leading to a smoother surface.

As a final check of the qualities of electrodeposits thus obtained, we used reflectance spectrum in the UV-vis region i.e. reflectance signals plotted as a function of wavelengths of incident light. In these experiments, the monochromatic light was brought to the surface of the electroplated zinc with one branch of the bifurcated optical fibre and the light reflected off the surface was detected with another branch, at the end of which a charge coupled device detector was attached. The brightness of the surface as measured in terms of the reflected light intensity from the surface obtained in the presence of CP over that of the electrodeposit without CP ranges from about
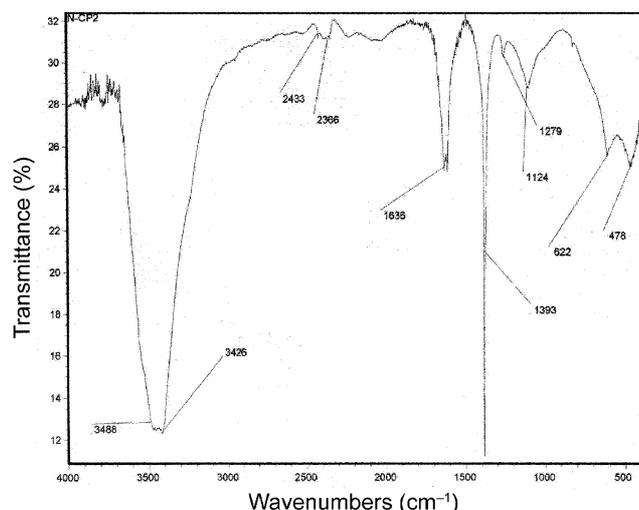
as small as 1·3 times at 560 nm to more than twice of those at 440 and 800 nm. In other words, how bright the surface depends on the wavelength. The difference in brightness results from the relative flatness of the surface obtained with and without the additive with regard to the wavelength of the incident light. Our result clearly shows that the grains making up the surface are much smaller, making the surface macroscopically flatter and more homogeneous, when CP is used as an additive during the electroplating of zinc–nickel alloy.

4.6 *Consumption of brightener*

In electroplating, the addition agents play an important role in producing lustrous deposits. The addition agents are consumed during plating and thus their concentration decreases. When this concentration goes below the optimum value, the deposit becomes dull in appearance. To know the amount of addition agents consumed in the present bath, 2·5 L of bath solution was taken and plating experiments were carried out at different current densities. The total number of coulombs passed on to the bath solution was recorded at the time when the bath just started to give semibright deposit. The used bath solution was Hull cell tested by adding different amounts of CP. The concentration of CP at which once again bright deposit was obtained, was determined. The amount of condensation product consumed for 1000 amps-h was 12 mLL^{-1}.

4.7 *Percentage of Ni in deposit*

The percentage of nickel in alloy deposit decreased with increase in the concentration of zinc sulphate. This characteristic behaviour is due to preferential deposition of zinc over nickel (anomalous deposition process). And also the percentage of nickel in alloy deposit increased with increase in concentration of nickel sulphate. The percentage of nickel in the optimum bath was 8%.

5. Conclusions

The optimized bath produces good deposit over a wide current density range. The optimized bath composition is shown in table 2. The deposit is pore free and corrosion resistant. The throwing power is reasonably good. The brightener can be easily synthesized. The addition agents are non-toxic, easily soluble in water and hence require no treatment of the effluent. The bath could be easily commercialized.

Figure 6. FTIR spectrum of the scrapped Zn–Ni alloy deposit.

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