Cyclicvoltammetry and Morphology studies on Zn – Co alloy in the presence of additives

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***Abstract*: The Voltammetric studies reveal the combined interaction of additives on plating surface during electrodeposition. The effects of different combination of additives namely Vanillin (Vn), Saccharin (Sa) and Rochellesalt (Rs) were studied with respect to micro hardness, SEM and AFM on zinc –cobalt alloy deposition. The oxidation potentials and the reduction potentials during deposition from zinc and zinc – cobalt alloy bath in presence of additives were analyzed at different scan rate by cyclicvoltammetric studies. The deposition obtained from zinc – cobalt alloy bath at different current densities using various additives has improved the nature of the deposit revealed from microhardness, SEM and AFM, when compared to zinc bath. Cyclicvoltammetry analysis showed very low reduction potential in zinc – cobalt alloy bath with vanillin and rochellesalt.**

***Keywords*: Zn-Co alloy, Electrodeposition, Micro hardness, Morphology, Cyclic voltammetry.**

1. Introduction

Cyclic voltammetry is the most widely used electrochemical technique to acquire quantitative information about electrochemical reactions. The Cyclic voltammetry results are useful in the study of thermodynamics of heterogeneous electron – transfer reaction, coupled chemical reaction and adsorption processes. Electrodeposited metals and alloys invariably exhibit a crystalline microstructure and hence their properties depend mainly on the composition of the electrolyte and the operating parameters such as bath temperature, current density, pH of electrolyte, presence of additives etc.

An important aspect, from a practical and technological stand point, is that these coatings must still have a high zinc content to maintain the cathodic protection of the steel substrate while still remaining less active than just zinc coatings. B.Kavitha and R.Renuga have reported the role of organic additives in zinc bath solution [1,2].

J.C.Hsieh et.al.[3,4] studied the most important effects of additives on electrodeposition are morphological and microstructural changes, refinement of grain size of deposit and formation of oriented grain structure [5] and electrochemical change (current – potential relations for zinc reduction). Soo Jung et. al [6] have reported the reduction in anodic and cathodic currents in presence of vanillin in zinc deposition

Few researchers in their work have considered synergistic interaction between the additives, to explain their role in producing bright or quality deposit [7,5,8]. Decroly and Coworkers [9,10] proposed a mechanism for zinc – cobalt codeposition involving the formation of the zinc hydroxide layer on the electrode surface, which suppresses cobalt reduction. Tsuru et al [11] showed the effect of solvent has on zinc – cobalt codeposition. Normal codeposition of Zn –Co alloy occurs in alkaline medium [12]. Recently, Fractici and Coworkers [13] studied the electrodeposition of Zn –Co alloy using acid chloride bath. The presence of organic additives can also change the deposit type from anomalous to normal [14,15].

J.L. Ortiz – Aparicio and coworkers [16] have found that glycine is used as a complexing agent in the electrodeposition of Zn – Co alloy. Peech-canul .et al.[17] has explained the concept of hydroxide oscillation and anomalous deposition of zinc in Zn – Co alloy bath . Zinc hydroxide layer is depletes the reduction of both H^+ and cobalt occurs preferentially over Zn. G. Trejo et al [18] have studied the effect of benzilidine acetone on Zn – Co alloy deposition. They have shown that in the presence of this addition agent, oxidation and reduction peaks are slightly shifted towards more negative and positive potentials respectively.

M. Mouanga, L.Ricq, P. Berçot have studied [19] the electrodeposition of zinc–cobalt alloys from chloride bath under continuous current and in the presence of coumarin. The deposit morphology was analyzed using SEM and XRD was used to determine the preferred crystallographic orientations of the deposits. Voltammetric studies show that coumarin affects the reduction of zinc but it has no effect on cobalt reduction explaining the decrease of cobalt percentage in the alloy in the presence of coumarin.

Cyclicvoltammetry curves are recorded for characterizing the deposition properties. These plots are recorded from solution containing different addition agents using microelectrode. The zinc and its alloy coating are produced on cathode during cathodic potentiodynamic (Cathodic part of the cyclicvoltammetry) and the anodic potentiodynamic (anodic part of the cyclicvoltammetry) conditions in the same plating bath. The cyclicvoltammogram is obtained at different scan rate. The different scan rate gives the information on nature of deposit, corrosion resistance properties of coatings etc.

In the present investigation studies have been made on micro hardness, SEM, AFM and cyclicvoltammety for various scan rate to find the effect of additives namely vanillin, saccharin and rochellesalt on Zn - Co alloy bath.

2. Experimental

2.1. Electrolyte preparation

The experimental solution is made up of ZnO – 10g/l (merck) and NaOH -110g/l (merck) are shown in the table.1. All the solutions were prepared by using double distilled milli Q water. The current and potential were measured using digital multimeter. A rectifier (L3210) was used as the current source for electrodeposition. A digital balance (Wenzar) was used for weight measurements to determine the current efficiency, thickness etc. A digital pH meter (Elico, Hyderabad) provided with a glass and saturated calomel electrode was used to measure the pH of each of the experimental solutions. The pH of the solution was maintained at pH – 13.

For any electroplating operation, proper method for preparing electrolytes and preconditioning the solutions to remove impurities are essential parts to get good deposits of required physical and chemical properties. High purity (99.99%) soluble zinc anodes were used. The anode was degreased with trichloroethylene and treated with dilute sulphuric acid followed with a rinse before use.

2.2. Electrodeposit Characterization

Micro indentation hardness test was performed using a calibrated microhardness tester Hitachi model (SHIMADZU, Japan) by forcing a diamond indenter of specific geometry under test loads .Vickers indenter is a highly polished, pointed, square based pyramidal diamond with face angles of 136 degrees.

$$H_v = \frac{1.854P}{d^2}$$

Where d = length of the diagonal of the indentation and P = load applied

In the present study, Vickers microhardness was measured with applied loads of 50gm. The final microhardness values quoted were an average of 5-6 measurements performed on different locations on the each coating surface.

SEM photomicrographs of the deposits obtained in absence and in presence of different addition agents were taken. The plated specimens were cut into $1cm^2$ size, mounted suitably and examined under the electron microscope SEM (JOEL-JEM-1200-EX I),CECRI, Karaikudi.

The AFM is a very high resolution type of scanning probe microscope, with resolution of fractions of nanometer, more than 1000 times compared to the optical diffraction limit. The AFM used was model Pico scan 2100 molecular imaging, USA (CECRI, Karaikudi). Specimens were studied in a contact mode with silicon nitride tip to reveal the 3D surface and topography.

2.3. Cyclicvoltammetry Analysis

The cyclicvoltammetry studies were carried out in a three electrode cell. The electrodes used for the cyclicvoltammetry, are mild steel as working electrode, platinum electrode as counter electrode, calomel electrode as reference electrode. The experiments were performed in Soltran Electrochemical Measurement unit (SI1280B) potentiostat. The geometrical area of the electrodes was $1cm^2$, trials were carried out under Nitrogen atmosphere. The temperature was maintained as 30^0C. Cyclicvoltammetry studies were carried out various with scan rates at 20, 40, 50, 60,80,100 mVs^{-1}.

Cyclicvoltammety studies show the quantitative effect of plating potential during electrodeposition from zinc and Zn – Co alloy bath with additives and Voltammograms were recorded after obtaining reproducible traces on repeated cycling.

3. Result and discussion

3.1. Microhardness

The results of micro hardness of 35 µm thickness deposit obtained from the zinc and zinc- cobalt alloy bath with combined additives images are shown in the fig.1. The hardness was measured at load of 50gm. The hardness of zinc deposit was found to 120.77 Hv and that of zinc – cobalt alloy deposit was found to be 276.38Hv. Bath III, IV and V have enhanced the values to 359.32, 400.97 and 530.18Hv is shown in the fig.2. Thus the bath II to V deposit showed 1.5 to 4.5 times harder than zinc deposit (bath I).

3.2. Studies on surface morphology

In present study , the SEM images were recorded for each deposit plated at 12 µm. The studies on surface morphology were carried out at 10Kx magnifications in bath I to V are shown in the fig.3. In the presence of 0.7 g/l cobalt in the zinc bath, an appreciable change was observed in the morphology with decrease in grain size, when compared to zinc deposit from bath I. The presence of cobalt due to modifies the growth of zinc neuclei and the deposit is compact and fine grained codeposition. Fig .3a. shows the SEM image of plate like structure. Fig.3b. shows tube like clear images. The zinc-cobalt alloy deposits appear sufficiently well distributed compact and continuous. In presence of vanillin in zinc-cobalt alloy (bath III) the deposit is dull with hexagonal crystal of uniform size (Fig. 3c). In presence of combined additives (vanillin and saccharin) in bath IV, the deposits are hexagonal, compact, spongy with dull appearance having a few white spots on them (fig.3d). But in the presence of vanillin and rochellesalt (bath V) , fig.3e the SEM images of the deposit obtained are fine grained with uniform size, bright matte coloured having tube like structure. The analysis of SEM images reveal the conversion of polycrystalline deposit into fine grained Nano crystalline bright deposit in the presence of all three additives in the bath. Vanillin acts as grain refiner and leveler in the deposit. Vanillin and saccharin mixture in the Zn-Co alloy bath increases the compactness and refines grain size. But the combined additives of vanillin and rochellesalt (Bath V) refine the grain size and produces smooth, compact and leveled deposit.

3.3. Atomic Force Microscopy

The 3D microstructure of zinc and zinc-cobalt deposits with additives are shown in fig. 4. From the figure, it can be observed that size of the grains and surface roughness are in nanometer level during deposition from bath I to V.

3.4. Cyclicvoltammetry studies

1. Voltammetric studies in the absence of additives (bath I& II)

The cyclicvoltammogram recorded for bath I in the potential range from – 0.2 to 0.2V at different scan rate (20,40,60,80 100 mV S^{-1}) is shown in the figure.5. From the figure, the anodic peak potential decreased at -1.695V to-1.685V and the peak current is also negative value at -153.25 mA to -260.95 mA. A cathodic peak was observed in the voltammogram recorded at different scan rate at peak potential (-1.223V to -1.67V) and the increased peak current (324.457mA to 374.751mA). It was diffusion controlled in this peak region. The formation of ZnOH due to follow on reduction Zn metal was observed. It is clear that zinc

deposit occurs at more negative potential, as calculated from Nernst equation. This can be explained by charge transfer of electrodeposition process, based on Fletchers theory [20].

Fig.6. represents the anodic and cathodic potential peaks of Zn-Co alloy deposition from bath II at various scan rate 20,40,60,80,100 mV s-1. In anodic region, oxidation potential is followed by the potential ranges from -1.671V to -1.640 V and the peak current at -176.38 mA to -301.708mA. ZnO and CoO are oxidized ZnOH and CoOH layers are formed. In cathodic region, the reduction potential is decrease from -1.313V to -1.289V and hydrogen gas evolution is followed by reduction of Zn^{2+} and Co^{2+}.

2. Voltammetric studies in the presence of vanillin

Table 2. shows the cyclicvoltammogram recorded for bath III in the presence of vanillin. The anodic potential and peak current decreased during deposition from alloy bath in the presence of vanillin. The more negative peak potentials are due to absorption of additives on active sites of cathodic surface [21].

3. Voltammetric studies with combined additives

In presence of combined additives vanillin and saccharin in bath IV, the cathodic and anodic potential and peak current are more negative compared to the presence of vanillin (bath III). The oxidation potential is -1.543V to -1.611V and peak current is -118.661mA to -225.177 mA shown in the Table.3.

In presence of combined additives, vanillin and rochellesalt in bath V, the oxidation potential ranges from -1.527V to -1.555V and the reduction potential ranges from -1.328V to -1.282V. It has more negative potential at various scan rate (Table.4).

Fig.7. represents the charge densities estimated for peaks obtained from bath I to V at 50mVs $^{-1}$ scan rate. It was noticed that in cathodic peak the maximum charge density value was found for bath in absence of additive. In presence of additives charge density value decreases. The maximum decrease is observed in presence of vanillin and rochelle salt the potential range is -1.308 V and the decreased peak current is 44.605 mA. It can be related to change in morphology electrodeposits [22,23,].

4. Conclusions

It is clear that presence of additives in zinc – cobalt alloy bath shows the favorable action of additives on zinc – cobalt alloy deposit compared to zinc deposit. The cobalt present in the zinc bath modifies the growth of deposit and formation of smaller grains. The deposit of zinc-cobalt alloy with additives (Rochelle salt and Vanillin) has increased fine grained nature of the deposit. When the current density is increased the hardness of the deposit increased with modification morphology. AFM studies confirm the formation of smooth surface. Low current potentials were observed at a scan rate of 50 mVs^{-1} for the Zn –Co alloy bath with roschellesalt and vanillin.

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References

[1]. B. Kavitha Surface & Coating Technology 201, 6 Dec. 2006, 3438-3442.
[2]. R. Renuga, Ramamurthy, S.K. Muralidharan Journal of power sources 76, 1998, 197-209
[3]. J.-C. Hsieh, Chu-Chang, Tai-Chou Lee, J. Electrochem. Soc. 155, 2008, D675–D681.
[4]. L. Oniciu, L. Muresan, J. Appl. Electrochem. 21, 1991, 565–574.
[5]. M.S. Chandrasekara, Shanmugasigamani, M. Pushpavanam, Mater. Chem.Phys. 124, 2010, 516–528.
[6]. Soo Jung Kim, Hyun Tae Kim. Su Moon park Journal of Electrochemical Society 151, 2004, 850
[7]. N.D. Nikolic, Z. Rakocevic, K.I. Popov, J. Electroanal. Chem. 514, 2001, 56-66.
[8]. M.C. Li, Li Li Jiang, W.Q. Zhang, Y H Qian, Su Zhen Luo, Jia Nian Shen, J. Solid State Electrochem. 11, 2007, 549–553.
[9]. Boshkov, N; Petrov, K; Vitikova, S; Met Fin. 2002, 100, 8.
[10]. Boshkov, N; Nemska, S; Vitikova, S; Met Fin. 2002, 100, 14.
[11]. Arun Prasad, K; Giridhar, P; Ravindran, V; Muralidharam, V.S; Solid State Electrochem. 2001, 6, 63.
[12]. Swathirajan, S; J Electrochem. Soc 1986, 133, 671.
[13]. Gomez, E; Valles, E; J Electronal. Chem. 1995, 397, 177.
[14]. Peulon, S; Lincot D; J. Electrochem. Soc. 1998, 145, 864.
[15]. Falk, T; Svensson, J.E; Johannsson, L.G; J Electrochem.Soc.1998,145,39 and references 20, 28 and 29 cited therein.
[16]. Presul-Moreno, F; Jakab, M.A; Scully, J.R; J Electrochem. Soc 2005, 152, B376.
[17]. Peech-Canul, M A. Ramanauskas, R .Maldonado, L; Electrochem. Acta 22, 1997, 6.
[18]. G Trejo. R Ortega. Y Meas, E Chainet. P Ozil Journal of applied electrochemistry 33, 2003, 373.
[19]. M. Mouanga, L. Ricq, P. Berçot, Surface & Coatings Technology 202 (2008) 1645–1651.
[20]. S. Fletcher, C.S.Halliday, D.Gates, M.Westcott, T. Lwin, G. Nelson, J. Electroanal. Chem. 159, 1983, 267-285.
[21]. F.J. Barry, V.J. Cunnane, J. Electroanal. Chem. 537, 2002, 151-163.
[22]. M.M. Abou-Krisha, H.M. Rageh, E.A. Matter, Surf. Coat. Technol. 202, 2008, 3739-3746.
[23]. G. Roventi, T. Bellezze, R. Fratesi, Electrochim. Acta 51, 2006, 2691-2697.

Table 1 Plating bath composition

Components	Bath I g/l	Bath II g/l	Bath III g/l	Bath IV g/l	Bath V g/l

ZnO	10	10	10	10	10
NaOH	110	110	110	110	110
CoO	-	0.7	0.7	0.7	0.7
Vanillin	-	-	1.0	1.0	1.0
Saccharin	-	-	-	1.0	-
Roschellesalt	-	-	-	-	0.5

Table 2 Cyclicvoltammetry data in Zn-Co alloy with vanillin

Scan rate	**Reduction Potential**		**Oxidation Potential**	
	Ep (V)	***Ip (mA)***	***Ep (V)***	***Ip (mA)***
20	-1.2694	381.7784	-1.5276	-106.461
40	-1.2579	395.335	-1.5601	-153.597
60	-1.2524	403.790	-1.577	-188.123
80	-1.2468	408.812	-1.5850	-214.827
100	-1.2383	415.597	-1.5974	-233.641

Table 3 Cyclicvoltammetry data in Zn-Co alloy with vanillin and saccharin

Scan rate	**Reduction Potential**		**Oxidation Potential**	
	Ep (V)	***Ip (mA)***	***Ep (V)***	***Ip(mA)***
20	-1.2599	328.039	-1.5434	-118.661
40	-1.2599	337.6303	-1.5641	-155.6275
60	-1.2459	351.484	-1.5848	-183.765
80	-1.2418	356.93	-1.5997	-201.486
100	-1.2456	365.219	-1.6115	-225.1778

Table 4 Cyclicvoltammetry data in Zn-Co alloy with vanillin and rochellesalt

Scan rate	**Reduction Potential**		**Oxidation Potential**	
	Ep (V)	***Ip (mA)***	***Ep (V)***	***Ip (mA)***
20	-1.3284	39.4687	-1.5278	-17.6759
40	-1.3114	43.6870	-1.544	-24.596
60	-1.2965	45.9935	-1.5575	-30.726
80	-1.2839	48.696	-1.5491	-34.186
100	-1.2817	51.003	-1.555	-38.009

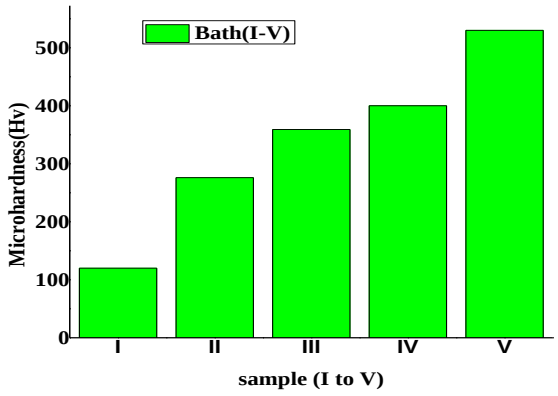

Fig. 1: Microhardness deposits from bath I , II, III, IV and V at 35µm

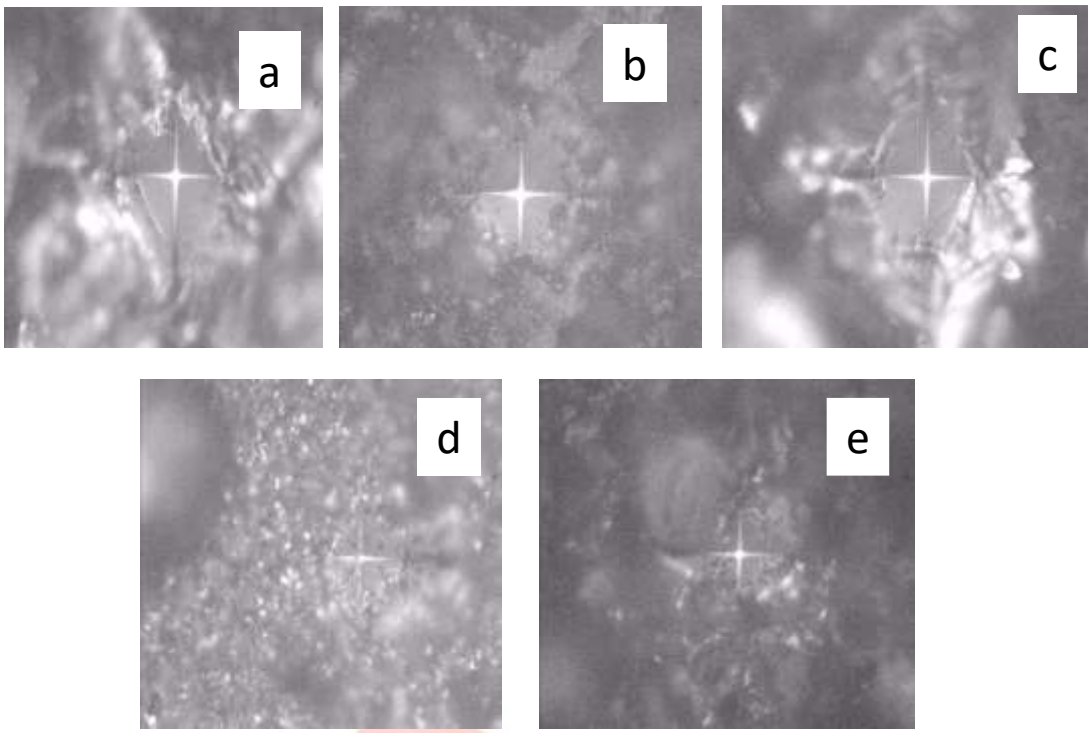

Fig. 2: Microhardness images of deposit obtained from bath I (a), II(b), III(c), IV(d) and V(e) at 35µm

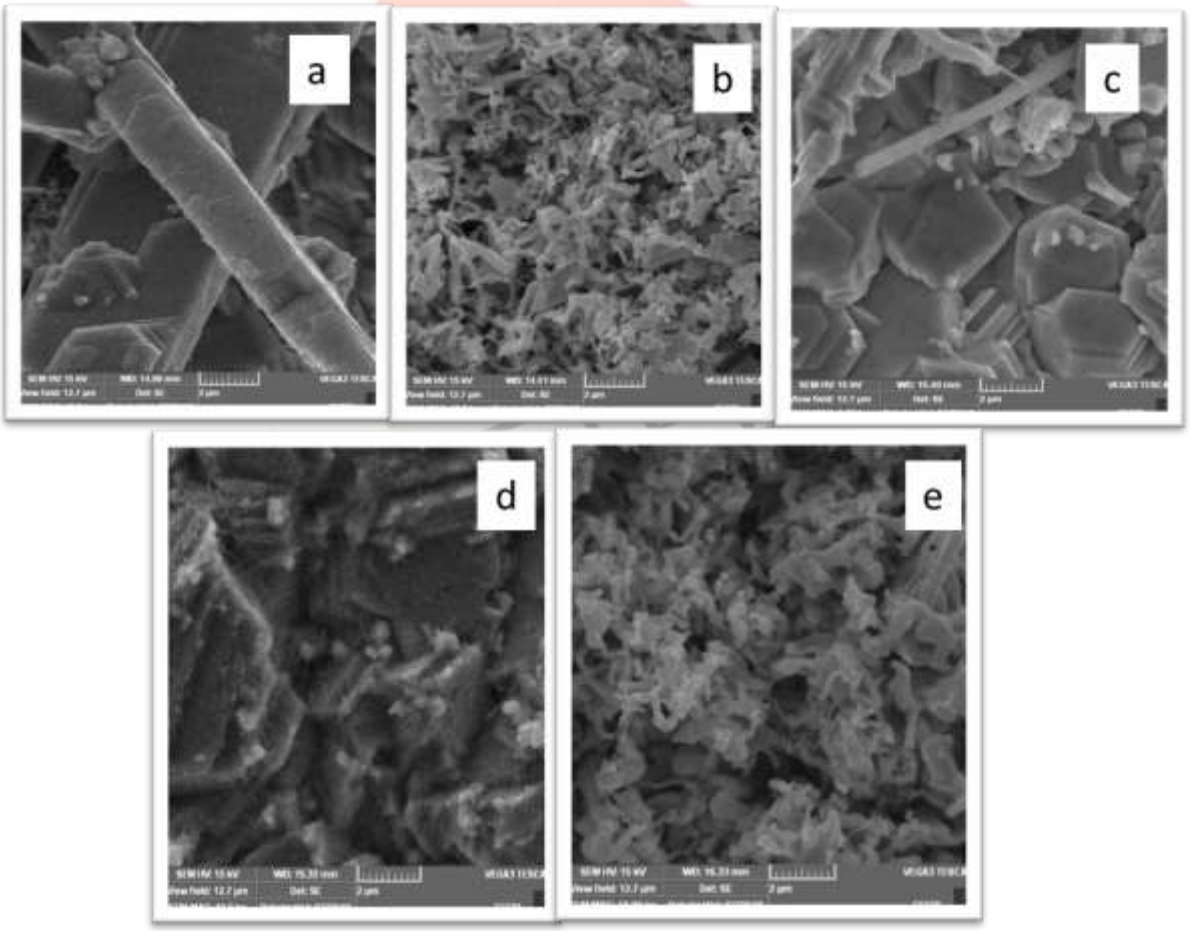

Fig.3: SEM images of deposit obtained from bath I (a), II(b), III(c), IV(d) and V(e) at 12µm

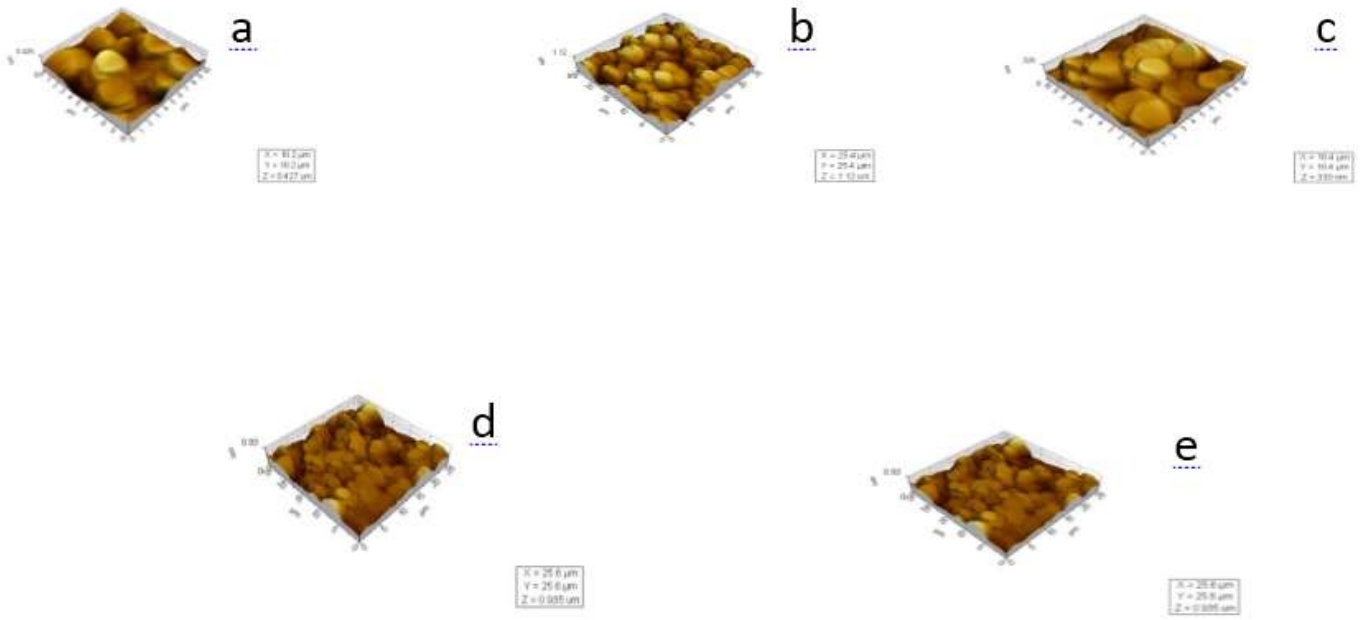

Fig. 4: AFM images of deposit obtained from bath I (a), II(b), III(c), IV(d) and V(e) at 12µm

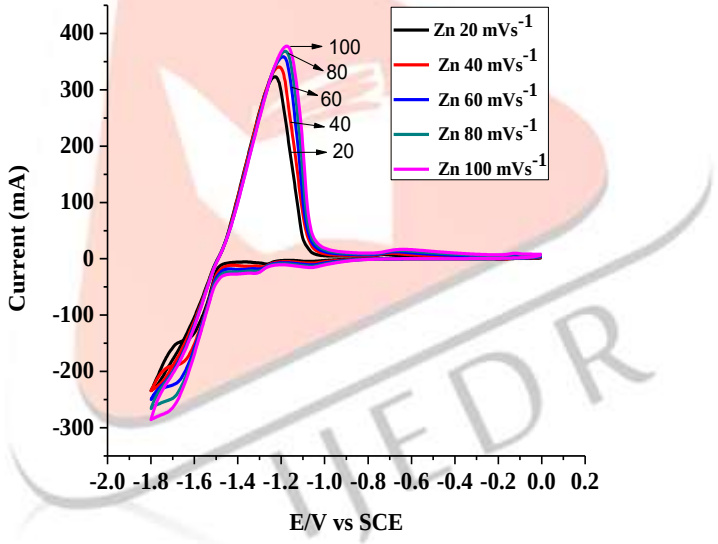

Fig .5: Voltammogram recorded on zinc bath , at Temp -30^{0}C, pH -13.

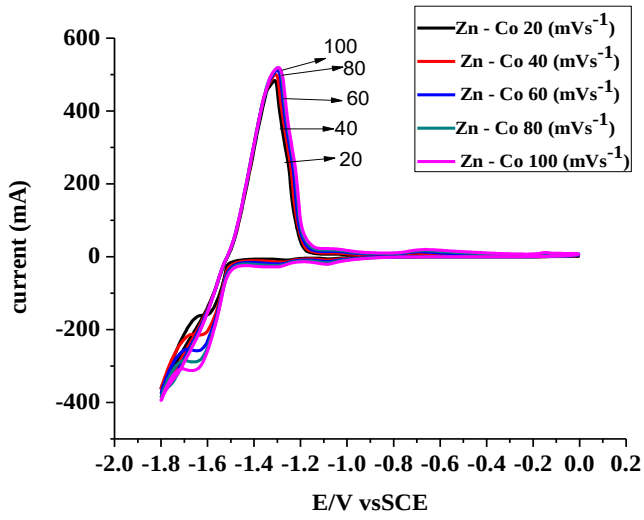

Fig .6: Voltammogram recorded on zinc- cobalt alloy bath , at Temp -30^{0}C, pH -13.

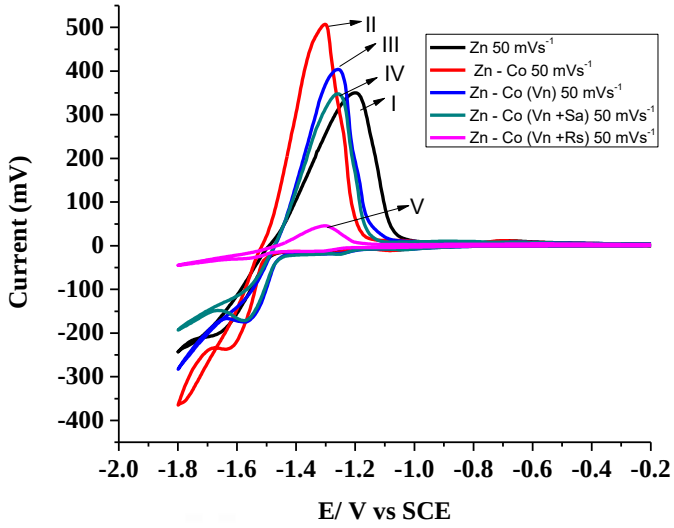

Fig .7: Voltammogram recorded on bath I to V at 50 scan rate , at Temp -30^{0}C, pH -13.