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Quantum mechanical and acceleration studies of autocatalytic coating process

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Abstract: It is perceived on several studies that the rate of electroless nickel without hypophosphite or borohydrides or amine boranes as the reducing agents is below 15 μ/hr and so for a feasible industrial needs high speed electroless nickelis a subject of recent study. In this paper, authors have attempted the role of Sulfamethoxazole (SMX) as an accelerator to achieve high plating rate. Experimental results such asanodic, cathodic polarization, A.C impedance and quantum mechanical descriptors had validated that the present accelerator could enhance the rate of electroless nickel deposition.

1. Introduction

It is known that the additives have an important role in the plating process for they can act as accelerator – inhibitors, partial accelerators and accelerators only besides their complexing ability for the metal ion. Sulphur bearing organic compounds are some of the potential additives often tried in plating, battery electrolyte and pickling baths[1-8]. From the detailed literature survey it is obvious that very few publications are available for derivatives of thiourea such as methyl, diphenyl, N,N'-Ethylene , p-tolyl and acetyl have been tried as a accelerators for EN plating [9-13]. However, no concrete reports are available using Sulfamethoxazole as accelerator/Accelerator in auto catalytic plating of nickel.Hence there is good scope to study the structural aspects of this additive related to its performance as the accelerator. Also the mode of action of Sulfamethoxazole (SMX) has been studied employing anodic and cathodic Tafel polarization, cyclic voltammetric studies and quantum mechanical analysis.

2. Methods and Materials

The bath used in the present study had the following composition which was optimized by trial and error methods[14-16].

NickelSulpahte hexahydrate	0.13M
Hydazine	0.22M
Tri ethanolamine	0.52M
Ammonium sulphate	0.04M
Proprieatrybrightner	0.01M
pH	5.8-6.0
Temperature	87 ± 0.1°C

The rate of deposition was a calculated using the following formula.

Rate of deposition (μ hr^{-1}) = W x 60 x 10^4 / DAt, (1)

where W = weight of the deposit (g); D = density of the deposit (g cm^{-3}); t= plating duration (min); A = surface area of the specimen (cm^2).

Mild steel specimens of compositions, C = 0.08%, P = 0.07%, Si = 0%, S = 0%, Mn = 0.41% and Fe remainder, and of size 4 x 1 x 0.020 cm were used for weight gain measurements. The required quantity of accelerator viz., Sulfamethoxazole [Mol.wt = 253.28] was dissolved in small quantity of alkalineethanolic solution and diluted with de ionized water for a litre.

The polarization studies were carried out using 1cm^2 area of electrolesslynickel deposited specimens as the working electrodes. The measurement was made with BAS –100A, Electrochemical analyzer. The auxiliary electrode and the reference electrode used were of platinum plate of 4cm^2 area and saturated calomel electrode respectively. A constant quantity of 150ml of bath solution was taken in a 250ml beaker. No agitation was provided. In order to understand the effectiveness of the compounds on the stability of the bath, anodic and cathodic polarisation measurements were carried out both in the presence and absence of nickel metal and hydrazine in the potential range of 0 to 1000mV which is a wide potential window adapted in order to follow the oxidation of reducer and reduction of nickel metal under the plating condition.Quantum mechanical descriptors were calculated using Gaussian 03 software package. The energy of highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and Dipole moment (μ) were studied with the above given software package.

3. Results and Discussion

3.1 Weight gain studies

The results of electrolessnickel deposition rates obtained in the present study by weight gain method are presented in table 1. This table also includes the deposition rate of nickel obtained in the absence of the additives. It can be seen from these tables that Sulfamethoxazole is found to enhance the nickel deposition rate up to certain dosage in plating bath beyond which they start retarding the plating process.

Table 1. Effect of Sulfamethoxazole (SMX) on rate of deposition by weight gain studies pH 5.7 Temp. 92^{o}C

Dosage of accelerator x10^{-4} M	Rate of deposition (μ/hr)
0	7.00
0.70	8.31
1.42	13.87
2.15	14.64
3.45	17.27
4.46	19.31
5.82	23.22
6.61	33.63
7.62	21.07

Table 1 indicates the values of electroless nickel deposition rate in the presence of several dosage of SMX in plating formulation. It is seen from the table that the accelerator effects start even at 0.75 x 10^{-4} M of SMX compound. At the dosage level at 7.75 x 10^{-4} M of SMX, the accelerator reduces the coating rate. The maximum plating rate of 32 μ/hr is achieved with even trace amounts of (6.60x 10^{-4} M) of SMX. This is a remarkable feature of the compound used in this study. This accelerator can be categorized as accelerator-inhibitor groups as reported earlier for thioureas[17-18].

3.2 Anodic polarization measurements

Anodic polarization was carried out over a wide range of potential for the plain bath (with outnickel metal) and the working electrode is 1cm^2 area of nickel coated steel surface at a fixed scan rate of 1mV/s. The results are given in table 2. This study was carried out at various dosages of Sulfamethoxazole chemical in the plating formulation. The oxidation current of hydrazine is found to increase in the presence of Sulfamethoxazole additive.It is visualized that as the oxidation current is higher than the plain plating formulation, SMX accelerate the reaction as well as stabilize the bath. Upon increasing the dosages of Sulfamethoxazole, oxidation current is decreased taking the role of stabilizers. Hence the additive may be classified as accelerator -stabilizer class, but primarily as accelerator for electroless nickel plating process

Table 2.Anodic polarization results for the electroless plating of nickel in the presence and absence of the accelerators

S.No	Accelerator and Dosage x 10^{-4} M	Oxidation current of hydrazine (in mA)
1	No Accelerator	10.05
2	Sulfamethoxazole (SMX)	
	0.70	11.97
	1.42	17.32
	2.15	22.41
	3.45	25.18
	4.46	33.58
	5.82	40.86
	6.61	48.69
	7.62	30.04

3.3 Cathodic polarization studies

Table 3.Cathodic polarization results for the electroless plating of Nickel metal in the presence and absence of the accelerator

S.No	Accelerator and Dosage x 10^{-4} M	Oxidation current of hydrazine (in mA)
1	No Accelerator	13.00
2	Sulfamethoxazole (SMX)	
	0.70	12.42
	1.42	12.12
	2.15	12.04
	3.45	11.72
	4.46	11.42
	5.82	11.08
	6.61	11.07
	7.62	11.01

Cathodic partial polarization was carried out to realize the influence of Sulfamethoxazole (accelerators / stabilizers) on the reduction of Ni^{2+} ions. Table 3 shown the additive at all its dosages have not influenced the reduction of Ni^{2+} ions unswervingly in the absence of hydrazine. A similar remark has been made by Han et al[19] for the autocatalytic deposition of nickel.

3.4 Impedance studies

The impedance studies for electroless plating of nickel in the presence and absence of Sulfamethoxazole are presented in Table 4. The charge transfer resistance value is very less for the bath well-known that the solution is highly conducting due to presence of Sulfamethoxazole using the Nyquist plots the charge transfer resistance values of the reduction reaction of nickel ions are calculated as the X intercept of the semicircle where the x-axis represented the real part of the impedance.

Table 4. Values of charge transfer resistance and double layer capacitance obtained from the impedance measurements of electroless Nickel –hydrazine bath in the without and with Sulfamethoxazole additive

S.No	Accelerator and Dosage x 10^{-4} M	R_t(ohm/cm^2)	C_{dl}(µF/cm^2)
1	No Accelerator	8.4	9.1
2	Sulfamethoxazole (SMX)		
	0.70	7.5	9.7
	1.42	7.2	9.9
	2.15	6.7	10.7
	3.45	.5.9	10.9
	4.46	5.4	11.9
	5.82	5.0	12.7
	6.61	4.2	15.8
	7.62	4.3	14.2

Perfect semicircles are encountered, in case where the electrochemical reaction of interest is under charge transfer control. Where the reactions are partially under charge transfer and mass transport control there is a drag noted in the semicircular plot. When the reaction is under diffusion control a rising portion is noted in the low frequency end of the plot. Also any looping at the tail – end of the plot is attributed to the role of the Warburg impedance. R_t values are fetched down and C_{dl} values are enhanced due to the acceleration of Ni^{2+} reduction process[20-21]. These results were in good covenant with weight gain results.

3.5 Quantum mechanical studies

The computed quantum chemical parameters like energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), LUMO- HOMO, energy gap (ΔE), dipole moment (µ), are summarized in Figure 1.and 2.

The energy gap value for the space filled negative clouds of SMX molecule is found as 8.2985 e.V and dipole moment value is 4.5Debyes. It has been reported that, larger values of dipole moment (> 3.5) will favour the adsorption of compounds on metal surface[22]. The dipole moment (µ) of SMX is high signifying that the compound adsorbs resolutely on mild steel surface and enhance the rate of nickel deposition to considerable extent as compared with thioureas[22-23].

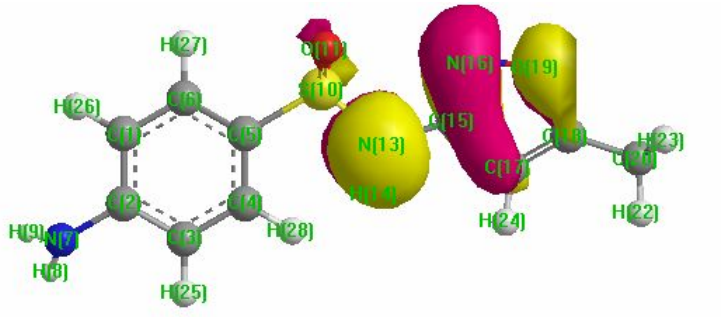

Fig.1. HOMO space filling structure of Sulfamethoxazole

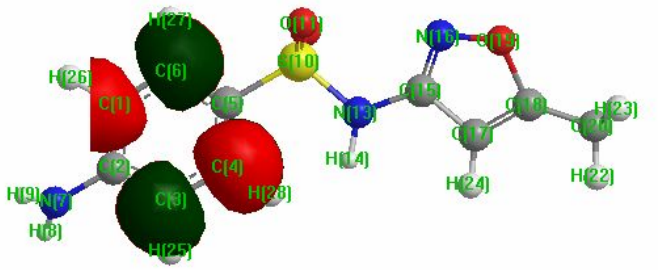

Fig.2. LUMO space filling structure of Sulfamethoxazole

4. Conclusions

The acceleration performances of environment friendly, Sulfamethoxazole compound (SMX) on the auto catalytic deposition of nickel has been analyzed methodically and it is implicated that SMX performed as accelerator in plating process through its effective adsorption on mild steel surface. The quantum mechanical descriptors confirmed the mere adsorption of compound on metal surface being responsible for acceleration of the autocatalytic nickelplating process.

5. References

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