

Quantum mechanical approach for electroless plating process

S. Karthikeyan^{*1}, P. A. Jeeva², S. Narayanan², K. N. Srinivasan³ and X. Hu⁴

A high speed electroless nickel plating bath has been developed with p-tolyl thiourea and diphenyl thiourea as accelerators for electroless nickel plating process. The acceleration effect of the compounds was determined by weight gain and electrochemical method. Both compounds improved the rate of deposition to considerable extent by adsorbing strongly on the steel surface. The adsorption of the accelerators was found to obey Langmuir adsorption isotherm. The Arrhenius plot and quantum mechanical parameters further justified the impressive performance of accelerators through their effective adsorption on metal surface.

Keywords: Electroless, Thiourea, Quantum, Polarisation, Accelerators, Adsorption

Introduction

It was found on many occasions that the rate of electroless nickel deposition was below $20 \mu \text{ h}^{-1}$ and the development of high speed plating process is of great significance in both practice and industry. As pointed out by Han and Fang¹ and others,²⁻⁴ sulphur bearing organic compounds such as cystein, thioglycolic acid and some thiourea derivatives were reported as accelerators for electroless plating process.⁵⁻⁸ However, there has been no published report on the acceleration effect of p-tolyl thiourea (p-TLTU) and diphenyl thiourea (DPhTU) on electroless nickel plating. This paper explains the influence of p-TLTU and DPhTU on the rate of electroless nickel plating and energy of activation. The adsorption of the compound on metal is found to obey Langmuir adsorption isotherm. The quantum mechanical parameters such as highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), ΔE and dipole moment have been studied as a new idea to validate the adsorption of compounds on metal being responsible for acceleration of electroless nickel deposition. Tafel polarisation results indicate that the acceleration of compounds in the electroless nickel plating process follows chemical mechanism.⁹⁻¹¹

Experimental

The following compounds of analytical reagent grade were used as additives in the present study: DPhTU (Merck, Germany) and p-TLTU (Kochlight Laboratories, UK).

The bath used in the present study had the following composition: nickel sulphate hexahydrate, 0.1M; sodium hypophosphite, 0.2M; glycolic acid, 0.6M.

Experiments were performed with various additives in the concentration ranges from 0.1×10^{-3} to 10×10^{-3} mM. Each experiment was repeated for a minimum of three times to get reproducible results. The rate of deposition was calculated using the following formula: rate of deposition ($\mu \text{ h}^{-1}$) = $W \times 60 \times 10^4 / DA t$, where W is weight of the deposit (g), D is the density of the deposit (g cm^{-3}), t is the plating duration (min) and A is the surface area of the specimen (cm^2). Mild steel specimens of compositions, Fe-0.08C-0.07P-0Si-0S-0.41Mn, and of size $4 \times 1 \times 0.020$ cm were used for weight gain measurements.

The polarisation studies were carried out using 1 cm^2 area of electrolessly nickel coated specimens as the working electrodes. The measurement was made with a BAS-100A electrochemical analyser. The auxiliary electrode and the reference electrode used were of platinum plate of 4 cm^2 area and saturated calomel electrode respectively. A constant quantity of 200 mL of bath solution was taken in a 250 mL beaker. The bath temperature and pH were maintained at 88 ± 1 and $5.5 \pm 0.1^\circ\text{C}$. No agitation was provided. In order to understand the effectiveness of the mixed potential theory in clearing up the electroless nickel process, Tafel polarisation measurements were carried out in the presence and absence of accelerators in the potential range of ± 300 mV from the OCP with all the bath ingredients under the plating condition. Quantum mechanical calculations were carried using MOPAC 2000 program of CS Chemoffice packet program. The energy of HOMO, LUMO and dipole moment μ were calculated with the above given software package.

Results and discussion

Weight gain studies

The results of electroless nickel deposition rates obtained in the present study by weight gain method

¹Surface Engineering Research Laboratory, Centre for Nanobiotechnology, VIT University, Vellore 632014, India

²School of Mechanical and Building Sciences, VIT University, Vellore 632014, India

³IMF Division, CSIR-Central Electrochemical Research Institute, Karaikudi 630006, India

⁴Institute of Tribology, Heifei Institute of Technology, Heifei, China

*Corresponding author, email skarthikeyanphd@yahoo.co.in

Table 1 Effect of p-TLTU and DPhTU on rate of deposition obtained from weight gain studies

0	15:00	0	15:00
0:30	20:00	0:44	15:75
0:60	26:43	0:88	16:26
0:90	30:12	1:31	19:19
1:20	23:24	1:75	19:86
2:41	14:96	2:19	21:93
3:01	11:12	2:63	22:09
3:61	8:82	3:07	23:04
4:22	3:20	3:50	18:39
4:81	1:20	3:94	14:02
5:42	000	4:38	0:00

are presented in Table 1. Thiourea derivatives have altered the nickel deposition rate up to certain concentrations beyond which they slow down the plating process. The acceleration effect starts at 0.30×10^{-3} mM for p-TLTU and reaches a maximum deposition rate of $30.2 \mu \text{h}^{-1}$ at 0.90×10^{-3} mM. Beyond this concentration, the rate of deposition is on the declining trend and reaches zero rate at 5.41×10^{-3} mM. In the case of DPhTU, at an optimum concentration of 3.07×10^{-3} mM, the rate of deposition is found to be $23.04 \mu \text{h}^{-1}$ and at the highest concentration of 4.38×10^{-3} mM, the deposition of metal virtually stops. This may be due to the fact that beyond optimum concentrations, the additives have poisoned the rate of deposition.

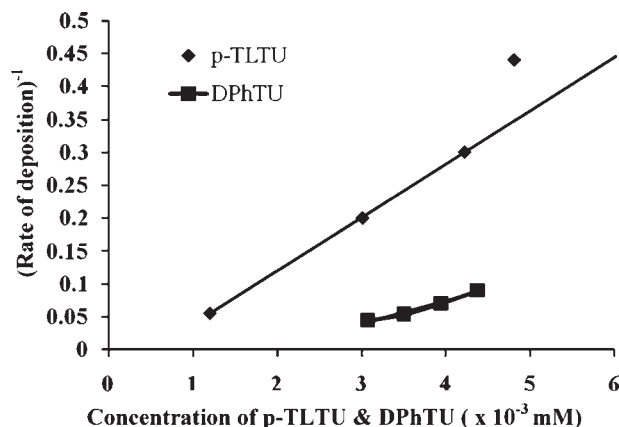
Tafel polarisation studies

In electroless nickel, the two partial reactions, namely, the reduction of Ni^{2+} ion and the oxidation of H_2PO_2^- , take place concurrently at the same rate on the metal surface at the mixed potential E_{mp} .

The plating rate and E_{mp} are obtained from E versus $\log i$ plot through the Tafel extrapolation method. This method suffers from the usual limitations associated with the theory of mixed potentials. For example, extrapolation of the polarisation curves for the decomposition of the reducing agent to the plating potential is not valid if the catalytic properties of the surface change with potential over the range of interest. It is also not suitable if the rate determining step and hence the Tafel slope for any process changes in the potential range through which the polarisation curve is extrapolated. At the mixed potential, $i_{\text{dep}} = i_{\text{m}} = i_{\text{red}}$, where i_{dep} is the deposition current, i_{m} is the current for metal ion reduction and i_{red} is the current for the oxidation of the reducing agent. Using Faraday's law, the nickel deposition current can be

Table 2 Tafel polarisation and weight gain results for rate of electroless nickel plating in presence and absence of p-TLTU and DPhTU

Accelerators and its concentration (10^{-3} mM)	E_{mp}/mV	i_{dep}/mA	Potentiostatic rate/ μh^{-1}	Weight gain method/ μh^{-1}
No accelerator	-495	1.25	1.36	15
DphTU				
1:31	-520	0.63	0.687	19:19
3:07	-710	2.82	3.074	23:04
3:50	-440	0.2	0.217	18:39
p-TLTU				
0:60	-515	0.13	0.14	26:43
0:90	-610	0.89	0.97	30:12
1:20	-410	0.06	0.07	23:24

**1** Langmuir isotherm plot for electroless nickel process in presence of different concentrations of p-TLTU and DPhTU

converted into equivalent plating rate that is obtainable from the weight gain method [$\text{rate} (\mu \text{h}^{-1}) = 1.09 i_{\text{dep}} (\text{mA cm}^{-2})$].

The above mentioned bath with or without the presence of different concentrations of the accelerators was used for the polarisation measurements under the same conditions mentioned earlier. The results are presented in Table 2.

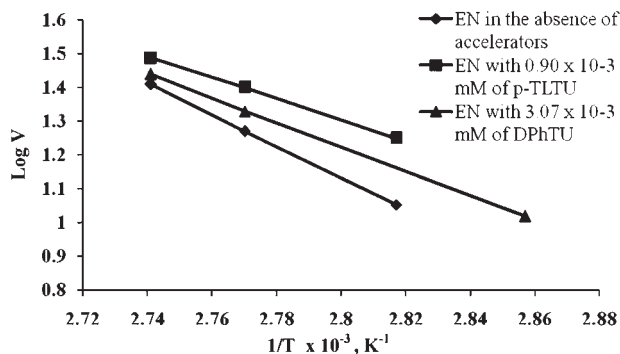
The results of the deposition current i_{dep} indicate that the role of accelerators is not at all reflected. Further shift of the mixed potential E_{mp} is also not in a regular way. Therefore, this technique appears not to serve any useful purpose in the evaluation of the accelerators. Similar findings have been put forth by Mital *et al.*¹² in their studies with electroless nickel plating in the presence of sodium hypophosphite as the reducing agent. However, with dimethylamine borane (DMAB) or a mixture of sodium hypophosphite and sodium borohydride as the reducing agent, a good correlation exists between the rate of deposition obtained through this method and weight gain method. The reason cited is that in the case of sodium hypophosphite, the chemical mechanism dominates over the electrochemical mechanism. With the Ni-P-B system, the very powerful reducing action of DMAB over hypophosphite has been quoted as the reason. It is also practically noted that the action of 1 g of DMAB is equivalent to 11 g of sodium hypophosphite. Thus, it is confirmed that the Tafel polarisation technique in electroless nickel plating with sodium hypophosphite as a reducing agent may not be helpful in getting the plating rate as the chemical mechanism predominates.

Application of adsorption isotherms

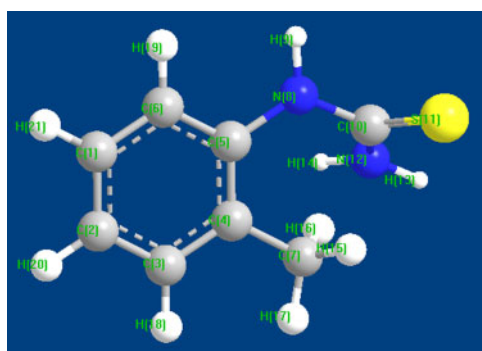
In the present study, the values of fractional surface coverage θ were obtained using values of rates of deposition in the presence and absence of additives r_0 from weight gain method. The Langmuir isotherm was tested by plotting $1/r_t$ versus C_0 for all the compounds. A straight line relationship was obtained in all the cases, thereby confirming that the adsorption process obeys Langmuir adsorption isotherm. The results are presented in Fig. 1.

Activation energy

The relationship between the rate of reaction and the temperature on electroless nickel plating can be expressed through the Arrhenius equation



2 Log v versus $1/T$ curves of electroless nickel in presence and absence of accelerators



3 Optimised structure of TLTU

$$y = Ae^{-E_a/RT} \quad (1)$$

$$E_a = \text{slope} \times 2.303 \times R \quad (2)$$

where R is the gas constant. Figure 2 signifies the Arrhenius plots for the electroless nickel process in the presence and absence of the accelerators at their optimum concentration. This study cleared that all the accelerators in trace quantities are able to bring down the activation energy of electroless nickel process. Lower activation energy indicates (Table 3) higher acceleration process by the compounds. The order of performance of the compounds is well revealed in their activation energy values.

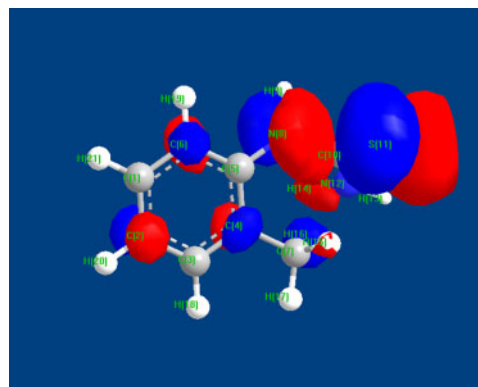
The $-M$ effect of the phenyl ring is moderately offset with the presence of methyl group in the para position in the case of p-TLTU, and this accounts for its improved

Table 3 Energy of activation calculated for electroless nickel plating in presence and absence of accelerators

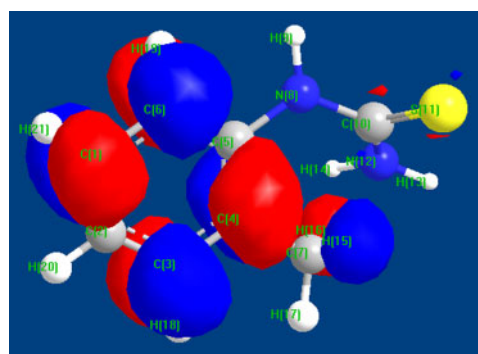
Accelerator	Activation energy $E_a/K \text{ J mol}^{-1}$
No accelerator	-59.16
p-TLTU	-79.56
DPhTU	-76.33

Table 4 Quantum mechanical parameters for thiourea derivatives

Compound	LUMO/eV	HOMO/eV	$\Delta E/\text{cal. mol}^{-1}$	Dipole moment/D
p-TLTU	-0.27989	-8.41832	8.13843	5.8799
DPhTU	-0.509037	-7.73773	7.228693	4.7493



4 Highly occupied molecular orbital of p-TLTU

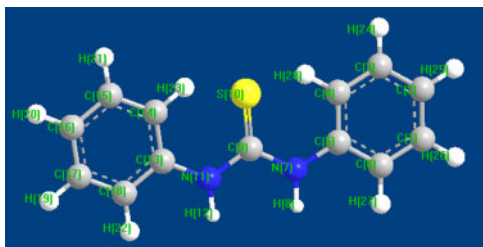


5 Lowest unoccupied molecular orbital of p-TLTU

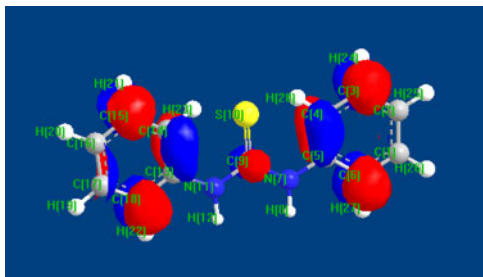
position compared to DPhTU. The inferior performance of DPhTU is due to the $-M$ effect of the two phenyls, which totally deactivates the sulphur atom in the compound.

Quantum mechanical studies

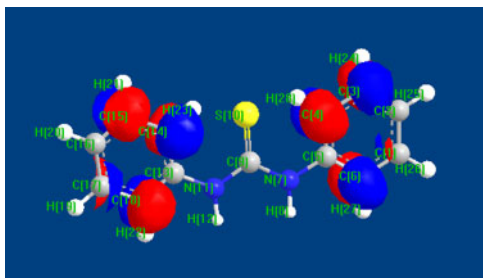
The computed quantum chemical parameters like energy of HOMO E_{HOMO} , energy of LUMO E_{LUMO} , LUMO-HOMO, energy gap ΔE and dipole moment μ are summarised in Table 4. From Figs. 3-5, it can be observed that HOMO and LUMO energy orbitals were loftily localised on tolyl moiety and almost nil on thiourea, indicating that the tolyl moiety possesses good adsorption centres,^{13,14} consolidating the opinion of several researchers that p-electrons and hetero-atoms are responsible for the adsorption process.^{15,16} In the case of DPhTU (Figs. 6-8), HOMO and LUMO were effectively localised on one of the phenyl moiety, whereas another phenyl ring is partly confined with HOMO and LUMO. This indicates that DPhTU has not effectively adsorbed on the metal surface and in turn diminished the acceleration of electroless deposition. The gap between HOMO and LUMO energy levels of molecules was another important parameter that needs to be considered. The smaller is the value of ΔE of a compound, the higher is the inhibition of reaction. The higher value of energy gap ΔE for p-TLTU indicates that the compound has not inhibited the deposition



6 Optimised structure of DPhTU



7 Highly occupied molecular orbital of DPhTU



8 Lowest unoccupied molecular orbital of DPhTU

process. However, the ΔE value for DPhTU is lower than p-TLTU, demonstrating that the former may not accelerate the electroless deposition of nickel. It has been reported that larger values of dipole moment will favour the adsorption of compounds on metal surface.^{17–20} The dipole moment μ of p-TLTU is higher than that of

DPhTU, indicating that p-TLTU adsorbs strongly on metal surface and enhances the plating process to considerable extent as compared with DPhTU.

Conclusion

Thiourea derivatives enhanced the rate of electroless nickel deposition through their effective adsorption on metal surface, and the reduction of nickel with hypophosphite as a reducing agent follows chemical mechanism. The energy activation and quantum mechanical parameters established the mere adsorption of compounds on metal surface.

References

1. K. P. Han and J. L. Fang: *J. Appl. Electrochem.*, 1996, **26**, 1273–1277.
2. J. L. Fang, Y. Lu and K. P. Han: *Plat. Surf. Finish.*, 1997, **84**, 91–94.
3. K. P. Han and J. L. Fang: *Met. Finish.*, 1997, **95**, 73–75.
4. K. N. Srinivasan, S. Karthikeyan, T. Vasudevan and S. John: *Electroplat. Finish.*, 2004, **23**, 1–6.
5. S. Karthikeyan, K. N. Srinivasan, T. Vasudevan and S. John: *Port. Electrochim. Acta*, 2006, **24**, 405–413.
6. E. Rudnik and M. Mucha: *Surf. Eng.*, 2012, **27**, 683–689.
7. K. Zangeneh-Madar and A. Jafari: *Surf. Eng.*, 2012, **28**, 393–399.
8. M. Selvam: *Surf. Eng.*, 2012, **27**, 711–718.
9. H. Zhang and R. L. Liu: *Surf. Eng.*, 2012, **27**, 5–10.
10. A. R. Rahimi, H. Modarress and S. Amjad Iranagh: *Surf. Eng.*, 2012, **27**, 26–31.
11. S. Karthikeyan: *Electroplat. Finish.*, 2008, **10**, 1–5.
12. C. K. Mital, P. B. Srivastava and R. G. Dhaneswar: *Met. Finish.*, 1987, **85**, 87.
13. S. E. Nataraja, T. V. Venkatesha and H. C. Tandon: *Corros. Sci.*, 2012, **60**, 214–223.
14. S. E. Nataraja, T. V. Venkatesha, K. Manjunatha, B. Poojary, M. K. Pavithra and H. C. Tandon: *Corros. Sci.*, 2011, **58**, 2651–2659.
15. N. Soltani, M. Behpour, S. M. Ghoreishi and H. Naeimi: *Corros. Sci.*, 2010, **52**, 1351–1361.
16. K. F. Khaled, S. A. Fadi-Allah and B. Hammouti: *Mater. Chem. Phys.*, 2009, **17**, 148–151.
17. Y. Tang, X. Y. Yang, W. Z. Yang, R. Wan, Y. Z. Chen and X. S. Yin: *Corros. Sci.*, 2010, **52**, 1801–1808.
18. H. Ma, S. Chen, Z. Liu and Y. Sun: *J. Mol. Struct. (Theochem)*, 2006, **74**, 19–22.
19. G. Gao and C. Liang: *Electrochim. Acta*, 2007, **52**, 4554–4559.
20. M. Lebrini, M. Lagrénée, M. Traisnel, L. Gengembre, H. Vezin and F. Bentiss: *Appl. Surf. Sci.*, 2007, **253**, 9267–9276.