Electroless Ni-P-TiO_2-Based Composite Coatings for Surface Engineering Applications

by S. John, K.N. Srinivasan, P.M. Kavimani, K. Hari Krishnan,[*] *J. Praveen, M.Ganesan*

Electroless nickel plating has undergone a sea change over the last decade. These coatings find wide application in the automotive and aerospace industries. As a means of overcoming problems associated with corrosion, abrasive wear and for the metallizing of nonconducting materials, this technology is rapidly expanding. Of all the electroless nickel plating processes available, the most widely used is the nickel phosphorous alloy acid bath. The main objective of our project is to codeposit TiO_2 with Ni-P at different concentrations and to study the mechanical and corrosion properties of the deposits.

Introduction and background

Conventional electroplating is accomplished when metal ions are reduced to the metallic state and deposited as such at the cathode by use of electrical energy. Electroless plating is a chemical reduction process which depends on the catalytic reduction of a metallic ion in an aqueous solution containing a reducing agent, and the subsequent deposition of the metal without the use of electrical energy.

Credit for the discovery of electroless plating goes to Brenner and Riddell,[1,2] with their work in developing a process for plating the inner walls of tubes with nickel-tungsten alloy, using an insoluble anode. This work first discussed the unusual reducing properties of the hypophosphites. This process was eventually covered by patents[3] in 1950. While the initial acceptance of the chemically deposited coating was slow, subsequent development of the process, including improvements of both bath composition and techniques, has increased its industrial utilization.

The reducing power of hypophosphorous acid and the hypophosphites has commanded considerable attention ever since the discovery of these compounds in 1819. The reduction of a nickel ion to nickel by hypophosphite was first observed by Wurtz[4] in 1845. Subsequently, other investigators studied this reaction, including Bretean,[5] Paal and Frederici,[6] Scholder and Heckel[7] and Scholder and Haken.[8]

Electroless nickel-phosphorus acid bath[9]

The acid solutions are the most popular and have been well investigated. The compositions of the chemical nickel plating solutions used by Brenner and Riddell have certain advantages over the alkaline solutions and hence are more popular. The rate of deposition is as high as 20 to 25 μm/hr (787 to 984 μ-in.). They are more stable since there is no loss of complexant by evaporation. The coatings obtained from acid solutions are of better quality. The properties can be easily controlled by controlling the amount of phosphorus in the deposit. Hence, acid solutions are generally preferred in many applications.

The reaction proceeds, yielding the following results:

- Reduced nickel ion concentration
- Hypophosphite converted to phosphite
- Increased hydrogen ion concentration
- Hydrogen gas may be adsorbed by the deposit

Amine boranes are also used as reductants instead of hypophosphite in acid electroless nickel solutions. The deposits obtained from these solutions contain boron which enhances the hardness of the coating.

Nuts & Bolts: What This Paper Means to You

In this work, the authors describe the properties of electroless nickel-phosphorus composites augmented with titania particles suspended in the solution. Based on hardness and AC impedance studies, wear and corrosion resistance were found to be enhanced.

---

[*] *Corresponding Author:*
Mr. K. Hari Krishnan
Government College of Engineering
Salem, Tamil Nadu, India
E-mail: hari_gce@yahoo.co.in

Reasons for spontaneous decomposition of electroless nickel baths

The main reasons for the spontaneous decomposition of electroless nickel baths are:[10,11]

- Local overheating,
- Too rapid an addition of sodium hypophosphite,
- High phosphite concentration,
- Too rapid an addition of alkali,
- Excessive deposits of nickel on tank walls or on heating coils,
- High pH during bath preparation (causing precipitation of nickel compounds),
- Incomplete removal of palladium after the use of a palladium activator,
- Instability of freshly prepared baths,
- Low bath loadings and
- Overuse of baths, leading to precipitation of phosphites.

Composite coatings

Electrodeposited composite plating is defined as one in which a uniform dispersion of small discrete particulates is deliberately codeposited within a metallic coating.[12-15] Electroless nickel-phosphorus coatings have many properties that are superior to those of electrodeposited nickel.[16] Because of the phosphorus content, electroless nickel is harder and has better corrosion resistance.[17] Electroless nickel composites combine the unique properties of conventional electroless nickel deposits, such as uniformity of deposition over complex geometries, high hardness and good corrosion resistance with those of abrasive materials possessing high temperature resistance and tribological (wear) properties.

Electroless Ni-P-TiO_2 composite coatings

M.H. Fawzy, *et al.*[18] studied the electrodeposition of Ni-α-Al_2O_3 and Ni-TiO_2 composites from baths containing 100 g/L (13.4 oz/gal) $NiSO_4 \cdot 7H_2O$, 40 g/L (5.3 oz/gal) $NiCl_2 \cdot 6H_2O$, 25 g/L (3.3 oz/gal) H_3BO_3 and 40 g/L (5.3 oz/gal) $Na_2SO_4 \cdot 10H_2O$ with 1 to 20 g/L (0.1 to 2.7 oz/gal) α-Al_2O_3 or 1 to 20 g/L (0.1 to 2.7 oz/gal) TiO_2 particles suspended in the bath. During electrodeposition, the cathodic polarization increased with an increase of both the size and concentration of the inert particles in the bath. The current efficiency of nickel electrodeposition is relatively high (95%) and was not affected by inclusion of the inert particles. The growth morphology of the nickel deposit was affected by the inert particle content, the deposition current density and pH of the bath. The microhardness of the nickel deposit (116 kgf/mm^2) increased with an increase of the inert particle content and the current density until it reached 243 kgf/mm^2 as a maximum. The data obtained revealed that the microhardness of the deposit is a morphology-sensitive property.

Experimental

Electrode preparation

Copper, mild steel and stainless steel panels were used as substrates. The electrodes were cut to a suitable size and mechanically polished. The polished specimens were degreased with trichloroethylene. The mild steel panels were used for corrosion studies, while the copper and stainless steel panels were used for rate measurement and phosphorus analysis, respectively.

Bath development

Various formulations available in the literature were selected and their deposition rates at 80°C (176°F) were studied. Among the various solutions, baths based on sodium citrate, sodium hypophosphite and nickel sulfate were selected for further study. The bath composition was varied to arrive at a suitable composition to yield an acceptably high rate of deposition at 80°C (176°F). The following bath composition was selected:

• Nickel sulfate	50 g/L (6.7 oz/gal)
• Sodium citrate	50 g/L (6.7 oz/gal)
• Sodium hypophosphite	40 g/L (5.3 oz/gal)

Ammonia was used for pH control and TiO_2 was added to range from 0.5 to 4.0 g/L (0.07 to 0.53 oz/gal).

Bath preparation and purification

The required amounts of chemicals were weighed and dissolved in distilled water (3/4 of the total volume required). The solution was then filtered through a G4 crucible and made up to the required volume using distilled water. The solution pH was adjusted electrometrically using a pH meter, using ammonia.

Bath maintenance and control

The temperature of the bath was maintained within ±2 C° (±3.6 F°) and the pH was continuously monitored. Suitable additions of sulfuric acid or ammonia were made as warranted by the bath pH. The bath ingredients, mainly nickel sulfate and sodium hypophosphite, were suitably replenished depending on the nickel that was deposited out from the solution.

The electroless bath container was replaced periodically and the tank was cleaned with nitric acid. The bath was periodically filtered through the G4 crucible to remove any nickel metal reduced and suspended in the solution.

Analysis of the deposits

Atomic absorption spectroscopy (AAS) was used to analyze accurately the chemical composition of the deposits.

Sample preparation

Mild steel samples were cut to a size of 7.5 × 2.5 cm (approx. 3 × 2 in.) and mechanically polished. They were then degreased in trichloroethylene and etched in 20% H_2SO_4 at 60°C (140°F) for 2 min. The electroless nickel deposition was then carried out on the etched samples for different times to obtain 2-, 5- and 10-μm thicknesses. The bath temperature was maintained at 80°C (176°F) and the pH was set at values of 3.0, 4.0, 5.0 and 6.0. Experiments were carried out for each pH and the desired thickness was obtained on the mild steel specimens. These specimens were used for measuring hardness, impedance and for studying surface morphology.

Impedance testing

Polarization measurements were carried out galvanostatically by exposing a 1.0 cm^2 (0.16 in^2) area of the plated specimen using constant current. Platinum was used as an auxiliary electrode and a saturated calomel electrode was varied from 0 to 1.0 mA. The corresponding change in potential was measured versus SCE using a digital voltmeter. The electrolyte used in the study was 5% NaCl. Polarization measurements were also carried out for bare mild steel specimens. The AC impedance spectra obtained for the electroless nickel deposits were carried out before and after heat treatment of the deposits. In this experiment the AC voltage was superimposed on the rest potential of an electroless deposited electrode immersed in 5% NaCl. Using the Nyquist plot, the charge transfer resistance was calculated as the X intercept of the semicircle where the X axis represents the real part of the impedance.

Results and discussion

Figure 1 shows the effect of bath temperature on the deposition rate in the presence of 3.0 g/L (0.4 oz/gal) TiO_2 particles.

Figure 2 shows the variation of deposition rate with time. The rate is seen to increase, achieving a near-constant value after 30 min. Though not shown in the figure, a very high rate was observed in the first few seconds. This may be related to the deposition of electroless nickel on freshly activated mild steel surface. With time, the reduction takes place on an electroless nickel surface which has a different catalytic property. In addition, phosphorus is codeposited with the nickel.

Figure 3 shows the variation of the deposition rate with pH. The solution pH was varied between 4.0 to 7.0. Increasing the bath pH increased the deposition rate.

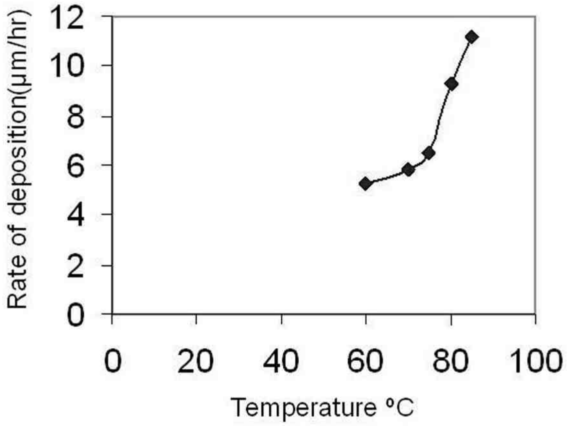

Figure 1—Effect of temperature on the deposition rate in the presence of TiO_2 particles (3.0 g/L at pH 4.0).

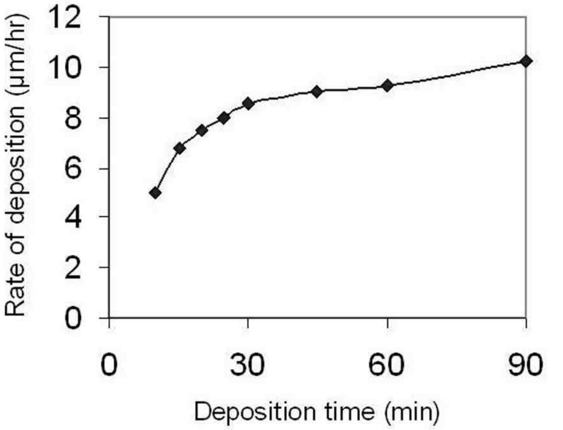

Figure 2—Effect of deposition rate with respect to deposition time in the presence of TiO_2 particles (3.0 g/L at pH 4.0 and a constant temperature of 80°C (176°F)).

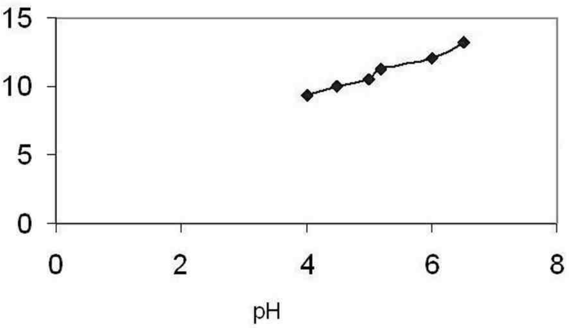

Figure 3—Effect of pH on the deposition rate in the presence of TiO_2 particles (3.0 g/L).

As shown in Fig. 4, the hardness decreased as the TiO_2 content in the bath was increased. This would be expected owing to the incorporation of additional particles in the deposit. Similar observations were made by Balaraju, *et al*.[19] in the case of graphite composites and by Nishira, *et al*.[20] in the case of Ni-P-PTFE composites. After heat treatment at 200°C (392°F), the TiO_2 particles may become sintered, leaving TiO_2 films on the surface of the deposit, which would account for the dry lubrication characteristic, a desirable feature of this composite. As the heat treatment process proceeds and exudes more TiO_2 particles onto the surface from the bulk of the deposit, it may also increase the hardness.

The four plots of Figure 5 give the impedance measurement results. For the Ni-P-TiO_2 coating, the charge transfer resistance, R_{ct}, was 6.0 kΩ while the value for the Ni-P coating was 1.6 kΩ. The results of the impedance studies with and with out TiO_2 additions are shown in Table 1. From this table we can observe that the charge transfer resistance increased with the TiO_2 additions. We can conclude that Ni-P-TiO_2 coated specimens were more corrosion resistant than Ni-P deposits.

Table 2 shows the effect of the TiO_2 particle concentration in the bath on the percentage of Ni, P and TiO_2 in the deposit. Increased TiO_2 in the bath increased the incorporation of TiO_2 in the deposit. Beyond 3.0 g/L (0.4 oz/gal) however, no further increase in TiO_2 content was observed. Hence the maximum concentration of TiO_2 particles in the bath was fixed at 3.0 g/L (0.4 oz/gal). Further experiments were carried out at this level.

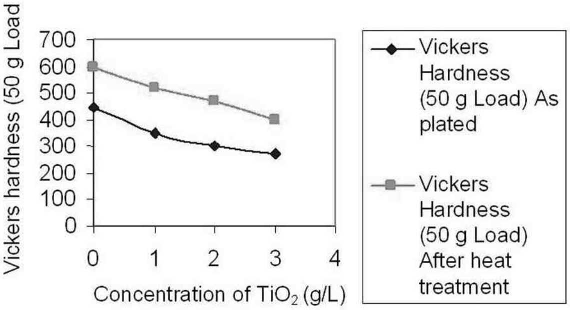

Figure 4—Effect of TiO_2 particle concentration on the coating hardness with respect to heat treatment.

Table 1
Effect of TiO_2 particle concentration (g/L) in impedance testing to determine corrosion resistance

Sample Number	Specimen Condition	Open Circuit Potential, V	Charge Transfer Resistance, kΩ
1	Heat treated without TiO_2	-0.511	0.380
2	Heat treated with 1.0 g/L TiO_2	-0.420	1.6
3	Heat treated with 2.0 g/L TiO_2	-0.405	6.0
4	Heat treated with 3.0 g/L TiO_2	-0.338	8.0

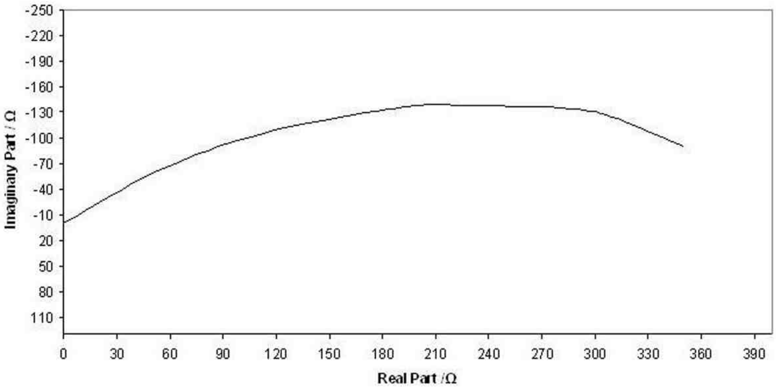

Figure 5(a)—Impedance curve (Nyquist plot) for an electroless-deposited specimen without heat treatment and TiO$_2$ (Test conditions: potential: -0.511 V; current: 21.07 µA; temperature: -22.8°C ± 5.1C° (-9.1°F ± 9.2F°).

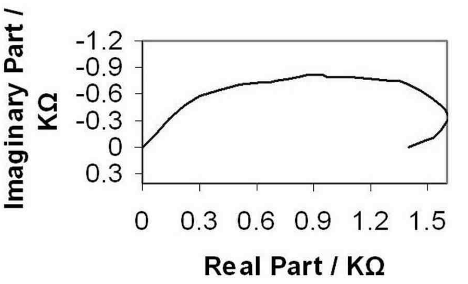

Figure 5(b)—Impedance curve (Nyquist plot) for an electroless-deposited specimen with heat treatment and 1.0 g/L TiO$_2$ (Test conditions: potential: -0.42 V; current: 16.48 µA; temperature: -24.1°C ± 5.5C° (-11.5°F ± 9.9F°).

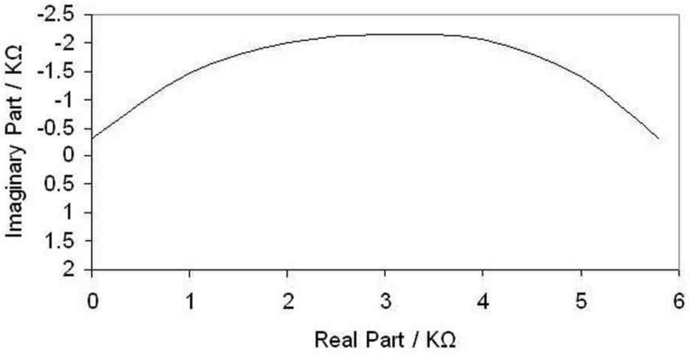

Figure 5(c)—Impedance curve (Nyquist plot) for an electroless-deposited specimen with heat treatment and 2.0 g/L TiO$_2$ (Test conditions: potential: -0.405 V; current: 15.796 µA; temperature: -24.4°C ± 5.4C° (-12.0°F ± 9.7F°).

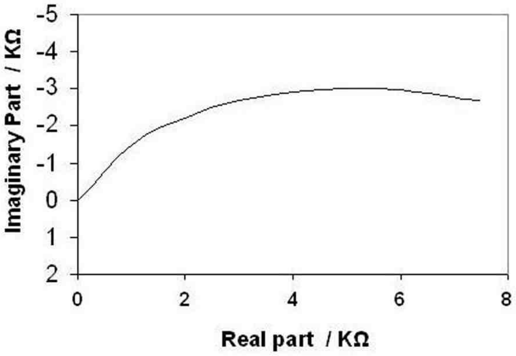

Figure 5(d)—Impedance curve (Nyquist plot) for an electroless-deposited specimen with heat treatment and 3.0 g/L TiO$_2$ (Test conditions: potential: -0.338 V; current: 384.35 µA; temperature: -25°C ± 5.7C° (-13.1°F ± 10.3F°).

Table 2
Effect of TiO$_2$ particle concentration in the bath on the percentage of Ni, P and TiO$_2$ in the deposits

Sample Number	TiO$_2$ Concentration in the Bath, g/L	Deposit Composition, wt%		
		Nickel	Phosphorus	TiO$_2$
1	0.0	89.80	10.20	---
2	1.0	88.79	10.01	1.20
3	2.0	87.79	10.25	1.96
4	2.5	88.50	9.60	2.40
5	3.0	86.90	10.10	3.00
6	4.0	86.80	10.20	3.00

These measurements indicate that the composite will be more corrosion resistant than Ni-P coatings in marine environments. The greater corrosion resistance is attributable to the uniform dispersion of TiO$_2$ particles and to the reduced porosity in the coating.

Surface morphology

Photographs of the heat treated Ni-P coatings and the Ni-P-TiO$_2$ coatings containing 1.0 and 3.0 wt% TiO$_2$. These are shown in Figs. 6, 7 and 8, respectively. It is clearly evident from the figures that there was an increase in incorporated TiO$_2$ particles in the deposit from the increased particle concentration from 1.0 to 3.0 g/L (0.13 to 0.40 oz/gal) in the bath.

Figure 6—Microstructure of electroless-plated specimen from a bath without TiO$_2$ (50X).

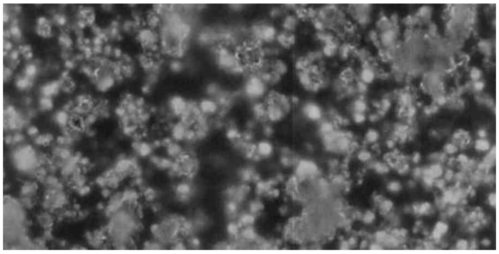

Figure 7—Microstructure of electroless-plated specimen from a bath with 1.0 g/L TiO$_2$ (50X).

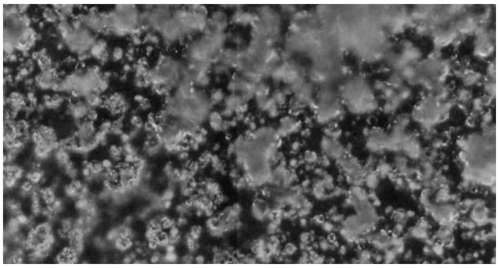

Figure 8—Microstructure of electroless-plated specimen from a bath with 3.0 g/L TiO$_2$ (50X).

Conclusion

A new bath has been developed for producing Ni-P-TiO_2 composite coatings. The optimum concentration and operating conditions are as follows:

Nickel sulfate	50 g/L (6.7 oz/gal)
Sodium citrate	50 g/L (6.7 oz/gal)
Sodium hypophosphite	40 g/L (5.3 oz/gal)
TiO_2	3.0 g/L (0.4 oz/gal)
pH	4.0
Temperature	80°C (176°F)

Under these conditions, the deposit was found to contain 86.9 wt% Ni, 10.1 wt% P and 3.0 wt% TiO_2. There was a decrease in hardness with the incorporation of TiO_2, due to the soft nature of the TiO_2 particles. The wear and corrosion resistance were very much improved with the presence of TiO_2 particles. Therefore, the coating can be used for engineering applications where high wear resistance and lubricity are required.

Acknowledgement

The authors would like to express their deepest thanks to their scientists in IMF-1, CECRI, Karaikudi and staffs in GCE, Salem, India, who gave us considerable help in completing this research work and also the authors would like to express their sincere thanks to Dr. James Lindsay, Technical Editor**,** AESF, for the useful discussions to modify this manuscript.

References

1. A. Brenner & G.E. Riddell, *Proc. AES*, **33**, 23 (1946).
2. A. Brenner & G.E. Riddell, *Proc. AES*, **34**, 156 (1947).
3. A. Brenner & G.E. Riddell, US Patent (1950).
4. A. Wurtz, *Comptes rendus de 1' academic des sciences*, **18,** 702 (1844).
5. P. Bretean, *Bulletin des societés chimiques*, **9**, 515 (1911).
6. C. Paal & L. Frederici, *Berichte der deutschen Chemischen Gesellschaft*, **64B**, 1766 (1931).
7. R. Scholder & H. Heckal, *Zeitschrift fur unorganische allgemeine chemie*, **198**, 329 (1931).
8. R. Scholder & H.I. Haken, *Berichte der deutschen Chemischen Gesellschaft*, **64B**, 2870 (1931).
9. *ASTM Technical Publication No.265*, ASTM, Philadelphia, PA, 1959.
10. R.N. Rhoda, *J. Electrochem. Soc.*, **108,** 707 (1961).
11. E.L. Gostin & S.D. Swan, US Patent (1962).
12. E.C. Ked Ward, *Electroplating & Metal Finishing*, **20**, 25 (1972).
13. M. Pushpavanam, S. Gowri, S. Krishnamoorthy, R. Thangappan & B.A. Shenoi, *Electroplating & Metal Finishing*, **27**, 24 (1972).
14. F.J. Honey, V. Wride & E.C. Ked Ward, *Plating & Surface Finishing*, **42**, 73 (1986).
15. R.A. Jeanmenne, *Products Finishing*, **84**, 1 (1990).
16. F.A. Lowenheim, *Modern Electroplating*, John Wiley & Sons, New York, NY, 1974; p.591.
17. I. Rajagopal, *Bulletin of Electrochemistry*, B, 384 (1992).
18. M.H. Fawzy, *et al.*, *Trans. IMF*, **74**, 2 (1996).
19. J.N. Balaraju, T.S.N. Sankara Narayanan & S.K. Seshadri , *J. Appl. Electrochem.*, **33**, 807 (2003).
20. M. Nishira & O. Takano, *Plating & Surface Finishing*, **81**, 48 (January 1994).

About the Authors

Sri. S. John is a Scientist and Deputy Director at the Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India. He is affiliated with the Industrial Metal Finishing Division, and holds a B.E. in Metallurgical Engineering from the National Institute of Technology - Thrichy, Tamil Nadu, India. His research interests are in electroplating, metal finishing, electroforming and solar thermal energy conversion systems.

Dr. K.N. Srinivasan is a Scientist at the Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India. He is affiliated with the Industrial Metal Finishing Division, and holds a B.Sc. and M.Sc. in Metallurgical Engineering from the University of Madras, Chennai, India. He was the recipient of the Sampath Award from the Electrochemical Society of India, in 2003. His research interests are in electroless plating, electroforming and cathodic protection.

Professor P.M. Kavimani, ME, MIIM, is Head of the Metallurgical and Materials Engineering Department at the Government College of Engineering, Salem, Tamil Nadu, India. He earned his B.E from Government College of Engineering and his M.E. from the National Institute of Technology Surathkal in extractive metallurgy. His research is involved in corrosion, and his teaching subjects are in corrosion and iron and steel making technology. He is a member of the Indian Institute of Metals and the All India Council for Technical Education (AICTE).

Mr. K. Hari Krishnan is in his final year toward earning his M.Tech. Degree in Physical Metallurgy from the Indian Institute of Technology, in Roorkee, India. He holds a B.Eng. from the Government College of Engineering, Salem, Tamil Nadu, India. He is a member of the Society for Advancement in Metallurgical Engineering (SFAME).

Mr. J. Praveen is in his final year toward earning his M.Eng. in welding engineering in the Metallurgical and Materials Engineering Department, at the National Institute of Technology Thrichy, Tamil Nadu, India. He earned his B.Eng. from Government College of Engineering, Salem, India. He is a member of the Society for Advancement in Metallurgical Engineering (SFAME).

Mr. M. Ganesan is in his final year toward earning his M.Eng. in welding engineering in the Metallurgical and Materials Engineering Department, at the National Institute of Technology Thrichy, Tamil Nadu, India. He earned his B.Eng. from Government College of Engineering, Salem, India. He is a member of the Society for Advancement in Metallurgical Engineering (SFAME).