

EFFECTS OF CO-DEPOSITION OF Cr_2O_3 AND MoS_2 ON CORROSION PROPERTIES OF NANOCOMPOSITE ELECTROLESS NICKEL COATING

N. Eslami Rad* and Ch. Dehghanian

* Nazli.eslamirad@gmail.com

Received: September 2010

Accepted: December 2010

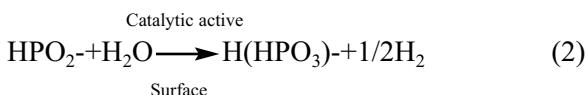
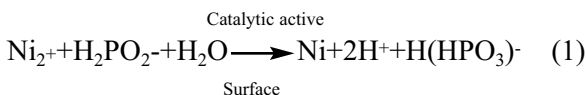
Department of Metallurgy and Materials Engineering, Faculty of Engineering, University of Tehran, Tehran, Iran

Abstract: Electroless Nickel (EN) composite coatings embedded with Cr_2O_3 and/or MoS_2 particles were deposited to combine the characters of both Cr_2O_3 and MoS_2 into one coating in this study. The effects of the co-deposited particles on corrosion behavior of the coating in 3.5% NaCl media were investigated. The results showed that both Ni-P and Ni-P composite coatings had significant improvement on corrosion resistance in comparison to the substrate. Co-deposition of Cr_2O_3 in coating improved corrosion characteristic but co-deposition of MoS_2 decreased corrosion resistance of the coating.

Keywords: Electroless nickel, composite coating, Cr_2O_3 , MoS_2 , corrosion resistance, Polarization, Impedance.

1. INTRODUCTION

Nickel electroless coatings have wide applications in industry due to the suitable corrosion properties and wear resistance [1]. Electroless plating is a chemical reduction process, which depends upon 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. Electroless nickel plating is carried out by the immersion of objects with a catalytic coating in a solution containing nickel ions and a suitable reductant, which may include hypophosphite, borohydride, aminoboranes, hydrazine, etc. at temperatures above 90 °C. The acid solutions are the most popular and well investigated. The rate of deposition is as high as 20 to 25 mm/h. The coatings obtained from acid solutions are of better quality [2]. Reactions occurring in electroless nickel deposition with hypophosphite ion as the reducing agent may be represented as:



Thus, the reaction proceeds forward due to the following factors: (1) reduction in nickel ion concentration, (2) conversion of the hypophosphite to phosphate, (3) increase in hydrogen ion concentration, and (4) adsorption of hydrogen gas by the deposit [2].

Hypophosphite reduced electroless nickel is an unusual engineering material, because of both its method of application and its unique properties. Due to the presence of phosphorous/boron, the properties of electroless nickel deposits are significantly altered. As applied, Ni-P coatings are uniform, hard, and relatively brittle. A deposited Ni-P coating can be a lubricant, which is easily solderable and highly corrosion resistant [2].

Electroless nickel coatings based on phosphorous content are divided into three general groups: Low phosphorus (1-3% Wt), medium phosphorus (3-7% wt) and High phosphorus (more than 7%wt) [3]. Phosphorus contents are function of bath composition and coating terms. Generally speaking electroless nickel coating with more than 7%wt phosphorus content, naturally is amorphous and shows good corrosion resistance [4].

Amorphous alloys are more resistant against corrosion attack compare with poly crystalline materials because there is no phase and grain boundary [5, 6]. Also because of forming glassy films on amorphous alloys surface. Electroless

coating can be categorized into three groups: 1- alloy coatings, 2- composite coating and 3- metallic coating. Composite coatings consist of a matrix and dispersed phases. Coating properties depend on coating structure. Simultaneous deposition of composite particles in electroless nickel coating can cause better corrosion resistance, friction and wear properties.

Depositing of Particles such as Poly tetra flouroethylene and MoS₂ in electroless nickel coating act as a dry lubricant and reduce the friction coefficient and increases the coating lubrication [7, 8]. Hard particles like Al₂O₃, SiC and Cr₂O₃ are used for increasing hardness and wear resistance. Among these powders, Cr₂O₃ has the same corundum crystal structure as Al₂O₃ [9]. Pure nickel shows well resistance in corrosive environments and nickel can be alloyed with elements like Cu,W,Cr for increasing corrosion resistance. Among the mentioned elements, addition of Chromium causes a significant stability and a good corrosion resistance of nickel alloys [10]. Because of Chromium structure, the hardness and corrosion resistance of the coating will increase.

High corrosion resistance of electroless nickel-phosphorus coatings is due to a low corrosion rate and formation of passivity in most corrosive environment. In addition, Phosphorus content makes the coating sensibility to localized corrosion to be reduced. The corrosion resistance of electroless nickel-phosphorus coatings relies on the coating thickness, phosphorus content and coating bath [11, 12, 13]. The mechanism of electroless nickel-phosphorous coatings for protecting the substrate is to separate the environment from the substrate. The electroless composite coating is formed by the impingement and settling of particles on the surface of the work piece, and the subsequent envelopment of these particles by the matrix material as it is deposited. There is no molecular bonding between particles and metal matrix [14]. Because of this, the parameters like stirring and surfactant have a significant effect on particles contribution. The coating composition depends on factors related either to the particles such as size, density, composition, zeta potential and conductivity [15,16], or to the electrolyte such as composition,

pH, temperature, current density, stirring speed and surfactants. It is noted that the role of surfactant is not negligible. Surfactants can not only improve the stability of a suspension by increasing the wet ability and the surface charge of suspended particles but also enhance the electrostatic adsorption of suspended particles on a cathode surface by increasing their net positive charge [17, 18].

Several factors influence the incorporation of hard and soft particles in an electroless Ni-P matrix including, particle size and shape, relative density of the particle, particle charge, inertness of the particle, the concentration of particles in the plating bath, the method and degree of agitation, the compatibility of the particle with the matrix, and the orientation of the part being plated. The size of the particles has a definite impact on their incorporation in the electroless Ni-P matrix [16, 19]. In general, it is recommended that particles must be large and heavy enough to settle in the solution yet not so large as to make the deposit rough or make it difficult for them to be held in suspension [16]. Also, the size of the particles should be selected with reference to the thickness of the electroless nickel deposit, as attempts made to incorporate 10 μm size particles in a 7 μm thick electroless nickel deposit resulted in unsatisfactory deposit and incorporation of 10 μm size particles even in a 25 μm thick deposit physically weakened the deposit. Particle shape also plays a vital role in determining their incorporation level. It is generally believed that angular shaped particles will have a greater tendency to hold on to the surface upon impingement than round ones [16, 20].

The difference between the electroless plating process and the deposition of nickel is that the reaction used by the latter was spontaneous and complete. Since electroless plating is a chemical reduction process, the coatings obtained are of uniform thickness all over the object plated. The quality of the deposit, namely, the physical and mechanical properties, is also uniform because the composition of the coating is uniform at all thicknesses. By the proper choice of the solution composition, pH, and the operating temperatures, the rate of deposition can be seen to be as high as 20 to 25 mm/h, which is sufficiently fast for

Table 1. Composition of API 5L-X70

Element :	C	Si	Mn	P	S	Cr	Ti
%wt	0.114	0.180	1.847	0.006	0.009	0.056	0.011
Element :	Mo	Ni	Al	Cu	Nb	V	Fe
%wt	0.066	0.23	0.032	0.165	0.063	0.049	97.149

industrial applications. Recent advances in the electroless nickel system offer extremely bright deposits, which are comparable with electroplated bright nickel, while retaining the advantages of uniformity of thickness, especially for parts or products with complex geometry. The ductility of electroless nickel deposits is improved largely so that postplating operations such as crimping or forming can be easily carried out. However, the disadvantage is that the leveling ability is extremely poor [21, 16].

The purpose of this study was to investigate the role of adding Cr_2O_3 in electroless

Nickel-phosphorus bath on corrosion behavior of coat which is done for first time.

2. EXPERIMENTAL

Electroless nickel composite coating was deposited on 25×25 mm plate made of API 5L X70 steel using acidic electroless plating bath. Compositions of steel are listed in table 1. Micro-sized (average size $0.7 \mu\text{m}$) dry molybdenum sulfur and nano-sized (average size 100nm) dry Cr_2O_3 were used for composite coating.

Substrate preparation process includes magnetic grinding, Ultrasonic cleaning in acetone for three minutes and rinse with distilled water, putting in an alkaline solution for 8 minutes and the temperature $60\text{-}80^\circ\text{C}$, washing with distilled water, cleaning in ten percent of the volume of sulfuric acid solution for 5 seconds, washing with distilled water for 2 minutes, cleaning in five percent of the volume of sulfuric acid solution for 5 seconds, washing with distilled water.

A Commercial electroless nickel bath (SLOTONIP 70A from Schlottter) was used to obtain the coating. This bath provides NiP deposit with high phosphorous content, 9-10%wt. Plating conditions are listed in Table 2. The powders were added to the solution and stirred by magnetic stirrer and ultrasonic for 20 and 10 min, respectively. Then it was added to the main bath and the sample was placed in the bath when the solution temperature was reached to 88°C . PEG2000, a nonionic polymeric surfactant, was also used [15]. The arrangement of various composite particles in electroless nickel coating structure was observed by SEM. Coating

Table 2. Composition of EN-composite bath and plating condition

Additives	EN	EN- Cr_2O_3	EN- MoS_2	EN- $\text{MoS}_2\text{-Cr}_2\text{O}_3$
$\text{Cr}_2\text{O}_3(\text{g/l})$	-	1	-	1/5
$\text{MoS}_2(\text{g/l})$	-	-	1	0/5
Surfactant(g/l)	-	0/1	0/1	0/15
pH	4/5	4/5	4/5	4/5
Temperature($^\circ\text{C}$)	88 ± 1	88 ± 1	88 ± 1	88 ± 1

composition was determined by energy-dispersive X-ray spectroscopy (EDS). The corrosion tests were conducted using EG&G 273A potansioatat/galvanostat. In polarization tests, the open Circuit potential (OCP) of steel in 3.5% NaCl solution was read after adjusting instrument parameters. Scan rate was chosen to be 2mv/sec. For ac-impedance test, the frequency range was set from 0.1 to 100,000 Hz. The impedance data was analyzed and plotted by Zview software.

3. RESULTS AND DISCUSSION

Figures 1-3 shows the surface morphology of NiP and NiP composite coatings. The surface morphology of the coating with Cr_2O_3 and MoS_2 is different from NiP matrix. Figure 1 shows that electroless NiP coating has a uniform and semispherical morphology. Adding Cr_2O_3 to the bath caused semispherical coating morphology to be finer as shown in figure 2. This may be due to the fact that the co-deposition of Cr_2O_3 in coating structure reduces growth rate of semispherical grain in width directions. It should be mentioned that surfactant has an important role on co-deposition of particles. Adding surfactants increase participating of particles in Ni-P matrix. The mechanism of PEG2000 (which was used in

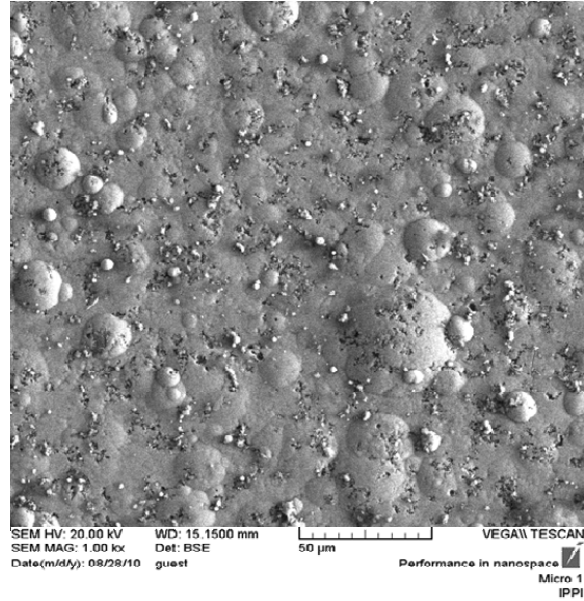


Fig.2. Surface morphology of NiP- Cr_2O_3

this research) is to make esteric forces. As a matter of fact, one part of PEG molecules attracted to powders particles surface and the other part, which is in solution, surrounds particle in a layer form. As a result, when powders particles come close to each other, repulsive force obstructed them therefore particles did not attract each other so there will be a uniform coat without porosity. The surface morphology of Ni-P- MoS_2 - Cr_2O_3 is shown in figure 3. The presence of molybdenum sulfur in coating structure caused the growth and nucleation

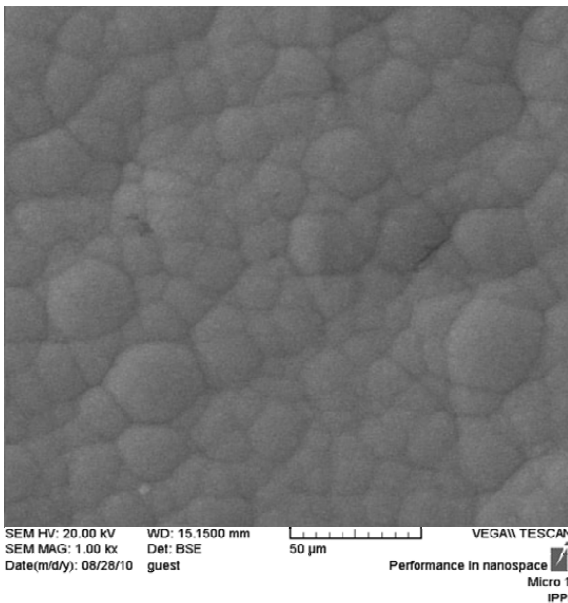


Fig.1. surface morphology of NiP

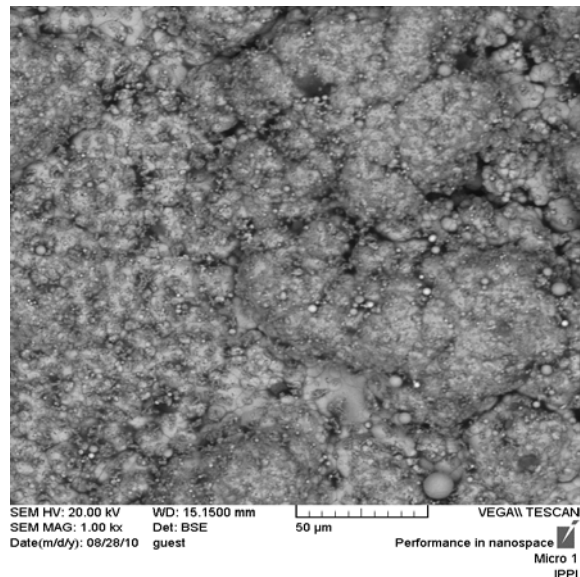


Fig. 3. surface morphology of NiP- MoS_2 - Cr_2O_3

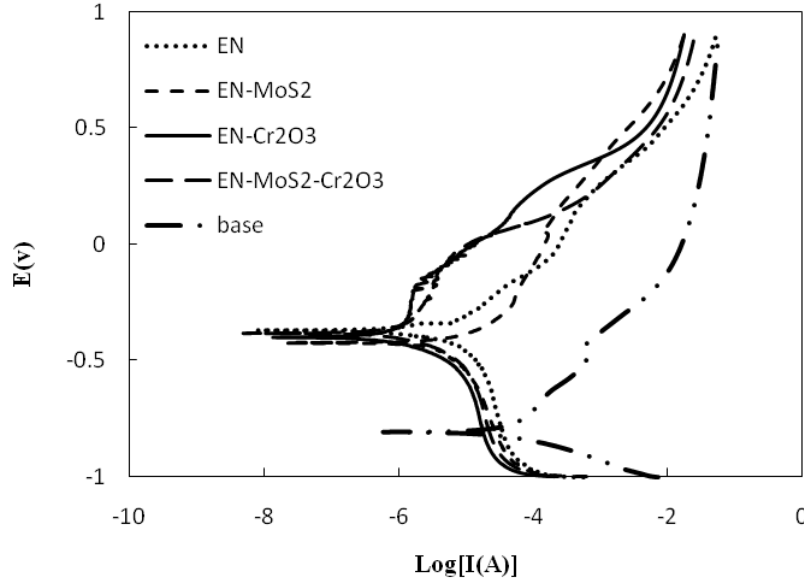


Fig. 4. The polarization of EN and EN composite coatings

disorder and reduced the uniformity of electroless nickel coating. Relative compression and non uniform distribution of particles in the coating caused a reduction in coating growth for the limited zones while the coating growth was steady in the other zones. This caused a non uniformity in coating surface.

Figure 4 is a plot of polarization curves for the coated samples. The results presented by this figure indicated an increase in corrosion

resistance of samples. Among all coated samples, Ni-P-Cr₂O₃ coating had a lower corrosion current. XRD analyzes of this sample, showed an amorphous coating structure. Figure 2 shows that there is no porosity on the surface. Therefore, it can be concluded that the presence of Cr₂O₃ increases the corrosion resistance due to the stabilizing nickel. Cr₂O₃ also acts as an effective barrier against corrosive ions.

Figure 5 shows Nyquist plots of EN and their

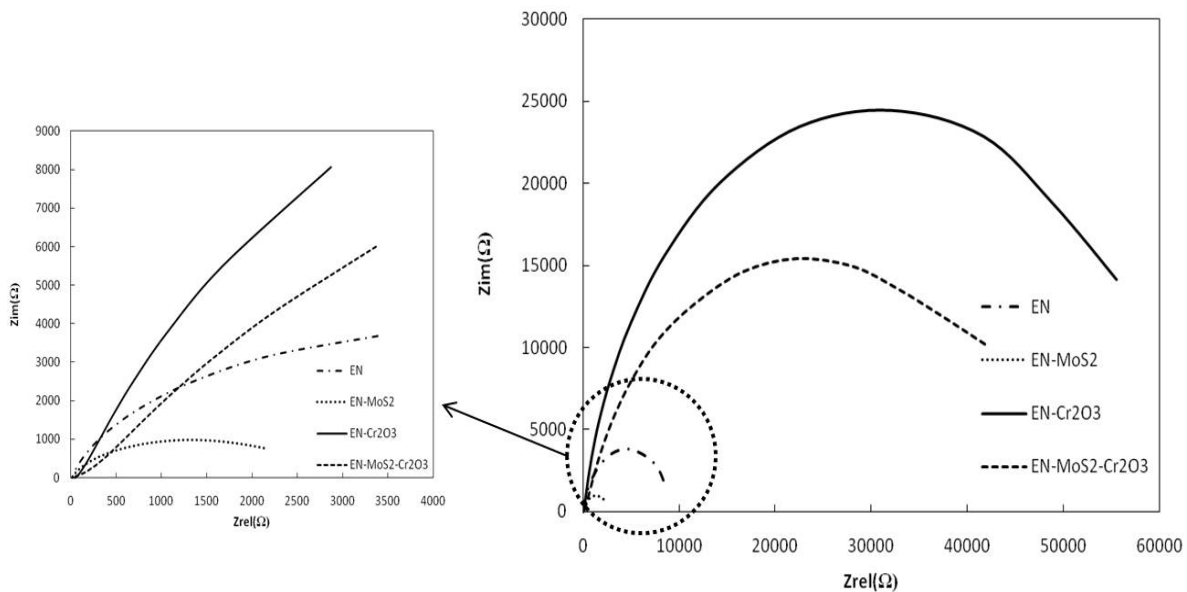


Fig. 5. The impedance of EN and EN composite coatings

composite coatings. All the plots are simple semi circles, therefore there is one time constant for each coating. As it is shown in Fig. 5, coating containing Cr_2O_3 has a better corrosion resistance comparing to the Ni-P and Ni-P-MoS₂ coating. MoS₂ particles have an electric conductivity of ($2.09 \times 10^{-4} \Omega^{-1}\text{cm}^{-2}$) [10], which when they are trapped in nickel coating, they act as zones with different potential with respect to nickel. Therefore a galvanic cell will be developed. Nickel acts as an anode and molybdenum sulfur acts as a cathode. Therefore this maybe a reason for decrease in corrosion resistance of electroless nickel-phosphorus coating in the presence of molybdenum sulfur.

Addition of Cr_2O_3 and MoS₂ into the bath reduces the corrosion resistance of the coating. Co-existence of molybdenum sulfur and Cr_2O_3 particles in the coating decreases the interfacial contact of Cr_2O_3 with solution. In addition, MoS₂ has electrical conductivity which reduces the corrosion rate of Ni-P-MoS₂- Cr_2O_3 coating in comparison to that of Ni-P- Cr_2O_3 coating. Also the cause of porosity with molybdenum sulfur increase is that, because MoS₂ particles have polygon and disordered shape, they can decrease combined force between nickel matrix and phosphorus. As a result it can decrease corrosion resistance of coating.

4. CONCLUSIONS

Based on this research the following conclusions can be drawn:

1. Both EN and EN composite coatings demonstrated significant improvement in corrosion resistance in salty atmosphere;
2. Co-deposition of Cr_2O_3 particles increased the corrosion resistance of steel in 3.5% NaCl solution;
3. Co-deposition of MoS₂ and Cr_2O_3 particles decreased corrosion resistance in comparison to co-deposition of Cr_2O_3 particles alone;
4. Ni-P-MoS₂ coating demonstrated lower corrosion resistance for steel in comparison to Ni-P- Cr_2O_3 coating.

REFERENCES

1. Huang, Y. S. and Cui, F. Z. "Effect of complexing agent on the morphology and microstructure of electroless deposited Ni-P alloy", *Surface & Coatings Technology*, 2007, 201, 5416–5418.
2. Hari Krishnan, K., John, S., Srinivasan, K. N., Praveen, J., Ganesan, M. and KaviMani, P. M. "An overall aspect of electroless Ni-P depositions-A review article", *Metallurgical and materials transactions*, 2006, 37A, 1917-1926.
3. Cui, G., Li, N., Li, D., Zheng, J. and Wu, Q. "The physical and Electrochemical properties of electroless deposited nickel-phosphorus black coatings", *Surface & Coatings Technology*, 2006, 200, 6808–6814.
4. Crobu, M., Scorciapino, A., Elsener, B., Rossi, A. "The corrosion resistance of electroless deposited nano-crystalline Ni-P alloys", *Electrochimica Acta*, 2008, 53, 3364-3370.
5. Yoon, J.W., Park, J.H., Shur, Ch.Ch. and Jung, S.B. "Characteristic evaluation of electroless nickel-phosphorus deposits with different Phosphorus contents", 2007, 84, 2552-2557.
6. Huang, Y. S., Zeng, X. T., Hu, X. F. and Liu, F. M. "Corrosion properties of electroless nickel composite coatings", *Electrochimica Acta*, 2004, 49, 4313-4319.
7. Ger, M.D. and Hwang, B.J. "Effect of surfactant on codeposition of PTFE particle with electroless Ni-P coating", *Material chemistry and physics*, 76, 2002, 38-45.
8. Moonir-Vaghefi, S. M. and Saatchi, A. "Deposition and properties of electroless nickel-phosphorus-Molybdenum disulfide Composites", *Metal finishing*, 1997, 46-52.
9. Lin, H.T., Wang, Sh.Ch., Huang, J.L. and Chang, Sh.-Y. "Processing of hot pressed Al_2O_3 - Cr_2O_3 /Cr-carbide nanocomposite prepared by MOCVD in fluidized bed", *Journal of the European Ceramic Society*, 27, 2007, 4759–4765.
10. *Metals handbook*, edition, vol.13, Corrosion, ASM International, Materials park, OH, 1994, pp.641.
11. *Metals handbook*, 9th edition, vol.5, Surface cleaning, finishing and Coating, ASM International, Materials park, OH, 1994,

- pp.641.
12. Balaraju, J. N., Sankara Narayanan, T. S. N., Seshadri, S. K. "Evaluation of the corrosion resistance of electroless Ni-P and Ni-P composite coatings by electrochemical impedance spectroscopy", *J solid state Electrochem*, 2001, 5, 334-338.
 13. Mimani, T., Mayanna, S. M. "The effect of microstructure on the corrosion behaviour of electroless Ni-P alloys in acidic media", *surface and coatings Technology*, 1996, 79, 246-251.
 14. Yoon, J. W., Koo, J. M., Kim, J. W., Ha, S. S., Noh, B. I., Lee, Ch.-Y., Park, J. H., Shure, Ch. Ch. and Jung, S. B. "Effect of boron content in electroless Ni-B Layer on plating Layer properties and soldering Characteristics with Sn-Ag Solder", *Journal of Alloys and compounds*, 2008, 4, 73-79.
 15. Myers, D. "Surfactants science and technology", Third edition, 2006.
 16. Balaraju, J. N., Sankara Narayanan T. S. N. and Seshadri, S. K. "Electroless Ni-P composite coatings", *Journal of applied electrochemistry*, 2003, 33, 807-816.
 17. Wang, L. M. "Effect of surfactant BAS on MoS₂ co-deposition behavior", *J Appl Electrochem*, 2008, 38, 245-249.
 18. Liu, D., Yna, Y., Lee, K. and Yu, J. "Effect of surfactant on the alumina dispersion and corrosion behaviour of electroless Ni-P-Al₂O₃ composite coatings", *Materials and corrosion*, 2009, 60, 690-694.
 19. Sampath Kumar, P. and kesavan Nair, P. "Studies on Crystallization of electroless Ni-P deposits", *Jornal of material processing technology*, 1996, 56, 511-520.
 20. Sarret, M., Muller, C., Amell, A. "Electroless NiP micro- and nano-composite coatings", *Surface & Coating Technology*, 2006, 201, 389-395.