Performance Evaluation of Nano Additives and Surfactants on the properties of Electroless Nickel Phosphorous Coating on Aluminium – Magnesium Alloy

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Abstract: Corrosion occurs as a result of the interaction of a metal with the environment. The extent of corrosion depends on the type of the metal and the surrounding environment. This paper focuses on the investigation of the corrosion problem in Aluminum–Magnesium alloys and experimentally develops an Electroless Nickel - Phosphorous coating with different nano additives and surfactants. This paper investigates the different types of Electroless Nickel - Phosphorous coatings done to reduce corrosion in Al-Mg alloys. Two types of nano particles such as nano Al₂O₃ and nanoZnO with two types of surfactants such as SDS and CTAB were used in this investigation. Different corrosion evaluation tests such as atmospheric exposure test, and wet corrosion test were carried out on the coated samples. Coated samples were characterized with help of Scanning Electron Microscope and Energy Dispersive X-ray Spectrometry. Mechanical evaluation tests such as surface roughness and hardness were measured on the coated samples. Comparison was done between the different EN-P coatings to optimize the concentration ofnano additives and surfactants.

Key word: corrosion, coating, AL–Mg alloys, Aluminum oxide (Al₂O₃), Zinc oxide (ZnO), nickel-phosphorus(Ni-P), surfactants.

1. Introduction

1.1 Motivation
Corrosion of Al-Mg alloys one of the major problems in automobile industry. Several coatings were developed and tested previously to prevent corrosion. However, Nickel coatings have not been tested in the Omani environment. Different surfactants in the EN-P coating along with nano additives is used to optimise the best coating by changing the concentration of surfactants in EN-P coating[5].

1.2 Problem Definition
During the summer season in Oman high ambient temperature contributes to corrosion of Al-Mg alloys and is one of the major problems facing in industrialequipment’s. The effect of corrosion ranges from a simple appearance of crack to complete damage of Al-Mg alloys leading to several million riyals revenue loss [6]. Though several types of coatings are used to prevent corrosion, Electroless Ni-P is a unique surface protective coating which is not tried in Oman environment.
Electroless Ni-P is a chemical metal deposition process. In this process Nickel is deposited on the substrate by means of an auto catalytic reduction reaction [7].

2. Literature Review
Corrosion is a chemical reaction between metal and environment. Al-Mg alloy is the most chemically active of all the metals used in aircraft construction, marine constructions and many part in automobiles and is the most difficult to protect. Corrosion can be concentrated to a certain area or wide spread almost uniformly corroding the surface. Due to this problem the life time of the alloy is reduced and resulted in high replacement cost every year [1]. To overcome the existing problem of corrosion, an EN-P coating with different Nano additive and surfactant is developed. Electroless Nickel Phosphorus coating is an auto catalytic reaction used to deposit a coating of nickel on the substrate. This plating technique prevents corrosion and develops uniform coating thickness [2].The EN plating of metallic nickel from aqueous solution in presence of hypophosphate was first noted by Wurtz in 1844 [3].In this paper a new technique of protection coating is done in Electroless Nickel Phosphorus coating (EN –P) with nano Al2O3 and nano ZnO with two types of surfactants such as SDS and CTAB. In this method coating is done uniformly with uniform thickness to the entire surface [4, 5].

3. Experimental Set up
3.1 Sample preparation:
A total number of 48 samples of size 25mm x 25mm were taken for coating. Samples were polished with wet 400,600 and 2000 grit SiC paper. The surface of each sample was cleaned with distilled water, then cleaned with acetone followed by a methanol wash and dipping into acid Pickling (1%HF+3%HNO3 by volume) [6].Then take the initial weight of each sample by using digital analytical balance. The size of nano additives used for coating has a particle size of 50nm.
•Samples were coated with the following different types of coating:

- EN-P
- EN-P+nanoAl2O3
- EN-P+nanoAl2O3+SDS1%
- EN-P+nanoAl2O3+CTAB1%
- EN-P+nanoAl2O3+SDS1.5%
- ENP+nanoAl2O3+CTAB1.5%
- EN-P+nanoZNO
- EN-P+nanoZNO+SDS1%
- EN-P+nanoZNO+CTAB1%
- EN-P+nanoZNO+SDS1.5%
- ENP+nanoZNO+CTAB1.5%

3.2. Electroless Nickel Coating Bath Composition
The coating bath consists of the chemical composition as shown in the table.

| Materials & Chemicals       | Amount                     |
|-----------------------------|----------------------------|
| Nickel Chloride             | 6g*12=24g+200ml Dw         |
| Sodium hypophosphite        | 8g*4=32g+200ml Dw          |
| Sodium Tri citrate          | 5g*4=20g+200ml Dw          |
| Ammonium Chloride           | 10g*4=40g+200ml Dw         |
| Acetone                     | 200ml                      |
| Methanol                    | 200ml                      |
The various process parameters such as pH, concentration of nano additives and surfactants were varied. The pH level is maintained by the addition of ammonia. The pH value maintained is 9-10, at a temperature around 85°C. The coating process is kept for 1 hour in 200 ml of coating bath [6].

3.3. Sample preparation for Atmospheric Exposure Test
Samples were exposed to the atmospheric conditions for 60 days. The atmospheric test is carried out in the climatic condition of Oman with an average temperature of 40°C, average relative humidity of 60 to 65%.

4. Result and Discussion

4.1 Wet and dry corrosion Test
The basic idea of the test was to dip the samples in filtered sea water and dry it in atmospheric air [8]. Filtered sea water had a pH value of 7.8.

4.1.1 Weight loss Test
In this weight loss technique the samples were coated with different types of chemicals. The initial weight before exposure to test was taken. After 8 weeks the samples were taken out and cleaned and final weight was taken. The difference gives the weight loss. The weight loss for different coated samples are recorded in figure 1.

![Figure 1. Weight loss in samples coating using dry/wet test.](image)

4.1.2 Corrosion Rate
The rate can also be calculated as follows: \( C_{rate} = 87.6 \times (W/ADT) \) where:

- \( W \) = total weight lost
- \( T \) = time taken for the loss of metal
- \( A \) = the surface area of the exposed metal
- \( D \) = the metal density in g/cm³

Calculation of area of the Sample:

\[
\text{Samplesize} = 25 \times 25 = 625 \text{ mm}^2, \quad \text{Thickness} = 0.4 \text{ mm}
\]
\[
\text{Area} = (25 \times 25) \times 2 + (25 \times 0.4) \times 4 = 1290 \text{ mm}^2 = 12.9 \text{ cm}^2
\]
4.2 Atmospheric Exposure Test

Atmospheric test was conducted for a period of 60 days with ambient conditions as stated above.

4.2.1 Weight loss Test

Figure 2. Corrosion rate by wet/dry test

From Figure 2 shows that sample without coating has highest value of corrosion rate due to its less corrosion resistance. However, EN-P in the presence of nano\(\text{Al}_2\text{O}_3\) and nano\(\text{ZnO}\) and concentration of surfactant (SDS1.5% and CTAB1.5%) have lowest corrosion rate because of high corrosion resistance.

Figure 3. Weight loss in samples coating using atmospheric test.
4.2.2 Corrosion Rate

The above figure shows the results in terms of corrosion rate for the atmospheric test. The sample without coating has highest corrosion rate with a rate of 1.54 mm/y. The best coating was EN-P coated with Nano-Al₂O₃ and concentration of surfactant (SDS 1.5% and CTAB1.5%) because corrosion rate was between (0.2 mm/y-0.26 mm/y) for atmospheric exposure test.

4.3 Mechanical Properties
4.3.1 Rockwell hardness Test

![Hardness Test](chart.png)

**Figure 5.** Hardness test.
The hardness test was used to measure the hardness of the Al-Mg alloy for different coating, where the sample without coated has lowest value of hardness when compared with others samples [7]. The samples coated with EN-P and nano-additives (Al₂O₃&ZnO) have approximately similar value. The samples coated with EN-P + nano additives and surfactant have good result in hardness [7]. The best result was for EN-P coated with Nano-additive(Al₂O₃, ZnO) and concentration of surfactant (SDS 1.5%,CTAB1.5%) because it is has the highest value of hardness when compared with others samples.

4.3.2 Coating Thickness Test
For further evaluation the samples coating thickness were measured using thickness gauge.

![Coating Thickness Chart]

**Figure 6.** Coating thickness.

As we see in the above figure, the samples coated with EN-P +nano-additive (Al₂O₃, ZnO)and concentration of surfactant(SDS 1.5%,CTAB1.5%)have highest coating thickness when compared with another samples.

4.4 Characterization Testing
Surface morphology and composition of the EN P coatings were analyzed by scanning electron microscope(SEM) and X-ray diffraction (XRD) as shown below [8].
Figure 7. Characterization test in sample (EN-P+nanoAl$_2$O$_3$+SDS 1%) coating.

Figure 8. Characterization test in sample (EN-P+nanoAl$_2$O$_3$+CTAB 1%) coating.

Figure 9. Characterization test in sample (EN-P+nanoAl$_2$O$_3$+SDS 1.5%) coating.

Figure 10. Characterization test in sample (EN-P+nanoAl$_2$O$_3$+CTAB 1.5%) coating.

Figure 11. Characterization test in sample (EN-P+nanoZnO+ SDS 1%) coating.

Figure 12. Characterization test in sample (EN-P+nanoZnO + CTAB 1%) coating.
Moreover the surface area of the sample without any coating can be completely corroded [12].

5. Conclusion
Corrosion is a natural phenomenon and needs to be handled with all techniques to protect the Al-Mg alloys. The degradation of a material's properties as a result of it interacting with the operating environment, plays a critical role in determining the life –cycle performance, safety and cost [9]. Investigations done to study the behavior of the corrosion in different conditions was promising as it met the project objectives. Corrosion cannot be terminated from the metals, but it can be isolated by applying good coating [10]. Corrosion rate for different coating is tested by conducting atmospheric exposure test and dry/wet test and results are concluded in terms of corrosion rate. Characterization tests like SEM and XRD was also done.

The purpose of this paper is to provide a study about corrosion analysis of different coating on Al-Mg alloy. The metal coatings and their thickness play a vital role against corrosion [11]. From the various corrosion tests it is concluded that, EN-P in presence of nanoAl2O3 and nanoZnO and concentration of surfactant (SDS1.5% and CTAB1.5%) have lowest corrosion rate because of high corrosion resistance. However, when surfactant like (SDS & CTAB) where added with less concentration to the EN-P bath, less number of cracks were observed on the deposits. The main reason for improved corrosion resistance in presence of surfactant is due to structural change from crystalline to amorphous nature. At higher concentration of surfactant the coated samples exhibit more amorphous fraction than crystalline. This improved the corrosion resistance.

6. Recommendation and Future Work
The recommendation is to use surfactants like (SDS & CTAB) but with high concentration (1.5%, 2%, 2.5% and 3%) and it can be observed that there are no cracks formed on the deposits.

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