IMPROVE WEAR RESISTANCE BY NANO COMPOSITE ELECTRO LESS COATING FOR LOW ALLOY STEEL (NI-P-GRAFENHE)

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Abstract
Several experiments were carried out for the electroless coating process. Sodium hypophosphate with (10, 14 and 24)g/l were added to achieve low, medium and high phosphorous in electroless coating for low alloy steel, the coating time (45, .75 and 105)min and use different heat treatment temperatures (200, 300, and 400)ºC. Wear resistance was tested by ASTM G99 to evaluate the best result of creating a nano composite coating, in order to add Nano graphene, the graphene was added by (0.1, 0.3, 0.5 and 0.7) g/l to coating bath. The FESEM (Field emission scanning electron) was conduct, X-ray diffraction to figure out the alloy compound on the layer coating, EDS energy dispersive spectroscopy to calculate the wt% P for low, medium and high, the pin on disk type were accomplished to evaluate the coating best result against the wear resistance. The results of the experiments showed that the coating with different weight% P, different coating time and different heat treatment temperature leads to improved wear resistance due to increased hardness and reduced friction coefficient by the addition of graphene.

Keywords: FESEM, X-ray diffraction, electro less, Nano composite, volume loss, graphene.

Introduction
Electro less is a chemical process can be applied without electrical power on a metal surface [1]. The coating layer thickness increases linearly if the coating chemical concentration of the solution is kept stable. The diversity in properties is the need in the engineering parts that we create new surfaces for metals and alloys because the lack of strength, corrosion attacks and wear damage. Some of these problems can be overcome by make new surface [2]. Nickel-Phosphorous electro less is the new surface coating to make continuous and uniform coating layer [1]. Nickel-Phosphorous electro less coatings it is very important industry fields cause the properties can provide hardness, corrosion resistance and wear resistance. Three types of these coating classified on the Phosphor content low phosphor with (1 - 4 wt%) , medium phosphor with (4 - 7 wt%) and the high phosphor (7 - 13 wt%) [3-4]. The bath of coating can be Alkaline or acidic. Depending on the reducing agent, alkaline coatings can not be used for some metals, especially some aluminum alloys [5-6]. During the electro less process the PH will change and to control the PH cause it very important for coating NaOH can be added to the bath solution . [7-8]. The heat treatment is very important to performed on the electro less coatings, as a result of heat treatment the properties such as hardness, adhesiveness, corrosion resistance and wear resistance are increased. The increase is due to structural changes that occur in coatings layers when heated over 200-400ºC temperature range. The amorphous precipitates get crystallized above 320ºC. Corrosion resistance and wear resistance increased due to The formation of Ni₃P [9-10]. The temperature is important and should be the same in the whole bath that can be done by agitation of the solution, the temperature range acidic baths, is between 80ºC and 95ºC. [11-12]. Nano composite coating is used the same method of electro less and in addition the are Nano particles to achieve the Nano composite that lead to a new level of properties, like these Nano composite Nickel-Boron –CNT [13]. Table(1) shown the symbols of variables.

| Symbols | wt% of sodium hypophosphate | Time(min) | Temperature(ºC) |
|---------|----------------------------|-----------|-----------------|
| A       | 10                         | 45        | 200             |
| B       | 14                         | 75        | 300             |
| C       | 24                         | 105       | 400             |

Table1: Symbols of variables

MATERIALS AND EXPERIMENTAL PROCEDURE
Materials
the samples are from rack shaft of steering car system the sample 20 mm diameter and 10 mm thickness each sample grinded using grinding sand paper (SiC) start from the 180 – 3000 grid after that the polishing with diamond paste. Each sample was cleaned in several stages as shown in figure (1).
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Chemical composition of the sample:
The chemical composition list in the table (2) are a result test that conducted by Spectrometer in The state company for inspection & engineering rehabilitation (SIER) formerly (the specialized institute for engineering industries) as in figure (2).

![Spectro Max](image)

**Fig. 2 The Spectro Max**

Coating process:
The samples are ready for the coating after the cleaning process that has been showed in Figure 1, in mean while the coating bath on the magnetic stirrer, the chemical concentration, temperature all showed in table 3.

**Table 2: Chemical composition for sample**

| Element | C% | Si% | Mn% | P% | S% | Cr% | Mo% | Ni% | V% | Cu% | Al% | Fe% |
|---------|----|-----|-----|----|----|-----|-----|-----|----|-----|-----|-----|
| sample  | 0.40 | 0.22 | 1.59 | 0.029 | 0.068 | 0.12 | 0.006 | 0.053 | 0.000 | 0.15 | 0.009 | Bal. |

The Chemical composition for sample indicate for the low alloy steel AISI 1340.

**Table 3: Chemical Concentration of coating Path**

| No. | Substance          | Concentrations(g/l) | Conditions     |
|-----|--------------------|---------------------|----------------|
| 1   | Nickel sulfate     | 30                  | PH 4.5-5.8     |
| 2   | Sodium hypophosphate | 10-14-24          | Temp. 85±2     |
| 3   | Sodium citrate     | 40                  | NaOH Adjust ph |
| 4   | Graphene           | 0.1-0.3-0.5-0.7    | Time 45-75-105 |

Each sample ready for the coating with as listed in table 1. The coating process in simplify way can be clear in the equations below.

\[
\begin{align*}
\text{Ni}^{2+} + 2\text{H}^+ & \rightarrow \text{Ni} + 2\text{H}^+ & \quad (2) \\
\text{(H}_2\text{PO}_4)^+ + \text{H}_2 \O & \rightarrow \text{H}^+ + \text{P} + \text{H}_2\text{O} + \text{OH}^{-} & \quad (3)
\end{align*}
\]

After the coating finish the sample dried and next steps the vacuumed tube furnace to complete the heat tretment 200, 300 and 400 Cº for 1 hour only, then the sample are ready for the Wear (volume loss) for each type low, medium and high containing Phosphours.
RESULTS AND DISCUSSION

Scanning Electron Microscopy and XRD

In this research, the three types of coating were identified starting from 10, 14 and 24 g/l sodium hypophosphate. Therefore, the three low, medium and high types were included, where the EDS (Energy Dispersive spectroscopy) equipped with SEM Scan Electron Microscopy was used to prove the existence of each one of the three types, as shown in figure 3. (A) For the low weight% P, (B) for the average wt% of P and (C) for the high percentage wt% of P. SEM was performed to evaluate the percentage P% of weight.

![Images of SEM samples](A B C)

The XRD for the same sample and the base were used to search for the alloy compounds on the surface for each type as shown in the figure 4.

![XRD images](A B)

**Figure 4 (A)** shows the base sample with existence of Fe and FeC, the (B) with high strong signal.

**The Hardness Test (Vikors)**

The coating layer has a reputation in hardness. The results of hardness showed the base with hardness (271.5) it was away from the lowest reading with coating, the samples groups showed various reading starting with the lowest 428.82 for the sample (A/B/A) and the reading began to increase until the sample (C/C/C) with 1126.86 which is 4 times the base. The increment in the hardness very clear it been effected by the heat treatment temperature and the 400°C has the highest value.

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The Wear Test Results:

ASTM G-99 are the leading way for this test. The G-99 are demanding the volume loss method for the test and it considered in this research as appear in the equation (4).

\[
\text{Volume loss (mm}^3) = \frac{\text{mass loss (g)}}{\text{density (g/cm}^3)} \times 1000 \quad (4)
\]

The wear test device (shown in figure 3) need a few parameters like the load 10N, 250 RPM and radius = 5 mm, several period of time 5, 10, 20 and 30 min, the weight of each sample were scaled in very sensitive scale for each period of time and right back for the device to next round.

The coating process create the Low, medium and high Phosphorus coating on different sample and been tested for hardness, each group tested. the results (as shown in figures 6 and 7) showed the group of 24 g/l sodium hypophosphosphate which represent the high content of P in this research, this coated sample were less wear rate than other. The best result was sample (C-C-C), because it has the highest hardness and that related to the presences of NiP, Ni$_3$P and Ni$_2$P as shown in fig. 4.

The sample (C-C-C) has been chosen for the Nano composite coating with different amount of graphene three groups.
Nano composite result
the graphene type was UGRAY, India 3 to 5 wall layer, the addition as listed in the table 3 (0.1, 0.3, 0.5, and 0.7 g/l) in the coating bath. The Sodium dodecyl sulfate has been added 0.1 g/l to stabilize the Nano in the coating solution with the help of ultrasonic cleaner for 1 hour [14].

first test is FESEM carried to prove the Nano graphene exists in coating as show in the figure 8. The figure shows the wt% of graphene addition and the measuring for the Nano is clear, the agglomerated graphene increased as the graphene wt% increased as shown in the fig.8.
Fig. 8: FESEM Images A, B for 0.1 wt% graphene, C, D for 0.3 wt% graphene, E, F for 0.5 wt% graphene, G, H for 0.7 wt% graphene.

Hardness and wear tested again for each sample are coated by Nano composite.

The hardness results as shown in the table (5). Figure (9) illustrates the relation between the Hardness and the wt% of graphene, where it was observed the increasing the wt% graphene will reduce the hardness.

Table 5: The result for Nano composite coating hardness

| No. | Sample   | Micro Hardness HV 25 |
|-----|----------|-----------------------|
| 1   | C-C-C-0.1| 994.61                |
| 2   | C-C-C-0.3| 894.1                 |
| 3   | C-C-C-0.5| 698.51                |
| 4   | C-C-C-0.7| 675.21                |

Fig. 9: Show the change in hardness with wt% graphene.

From the table 5 and figure 9 it is clear that the increment of wt% graphene lead to decreasing the hardness and that are cause the Nano agglomerate as showed in the figure 8 and these region will act as weakness.

The wear test for these samples are conducted under the same conditions for four samples (C-C-C-0.1), (C-C-C-0.3), (C-C-C-0.5) and (C-C-C-0.7)

As shown in the figure 10 the (C-C-C-0.1) has less volume loss of the four samples, the Nano graphene is famous with friction coefficient and that lead to decrease the wear but when the graphene increased the volume loss increased too that because the agglomerate which lead to increase the roughness on the surface.

Fig. 10: The wear rate and the graphene addition.
CONCLUSION
From the previous results and their discussions conclusions may be listed as follow:
1- The electro less coating nickel – phosphorus very helpful against the corrosion and wear attacks.
2- The increase in wt% of sodium hypophosphate causes the wear volume loss increase.
3- The increase in the time coating reduces the wear volume loss.
4- The 400 °C heat treatment temperature has best effect on the hardness as well the wear resistance.
5- The best addition of graphene for hardness and wear resistance are 0.1 gram per litter.
6- Nano composite electroless coating is the effective method according to the cost.

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