Influence of load and temperature on tribological behaviour of electroless Ni-P deposits

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Abstract. Electroless Ni-P coatings have shown tremendous potential as tribology material at room temperature. However, the performance of the same in high temperature field needs to be evaluated as investigation reveals the softening of most of the coating materials. In the current study, both as-deposited as well as heat treated samples are developed for the performance evaluation. Coatings are tested under different loads with a constant speed and at temperatures ranging from room temperature (R.T.) to 500°C. Tribological tests are carried out on a pin-on-disc tribotester by selecting a wear track diameter of 60 mm for 5 minutes. Wear is reported in the form of wear rate by following Archard’s equation. The microstructure characterization of the coating is performed using SEM (Scanning Electron Microscopy), EDX (Energy Dispersive X-Ray Analysis) and XRD (X-Ray Diffraction Analysis). Coating is developed with phosphorous weight percentages around 9% on cylindrical mild steel samples and the deposition thickness is observed to be around 50 μm. The as-deposited coating is found to be amorphous in nature and hardness of the as-deposited coating is found to be around 585HV0.1. Friction coefficient increases initially with the increase in temperature from room temperature up to 100°C but thereafter gradually decrease with the increase in temperature. Initial increase in temperature (up to 100°C) provides higher rate of wear compared to room temperature but with further increase it drops in most of the cases. Wear rate increases with the increase in temperature but as it crosses or nears the phase transformation temperature (around 340°C), the scenario gets reversed. From X-ray diffraction analysis, it is found that coating is amorphous in as-deposited condition but transforms into a crystalline structure with heat treatment.

1. Introduction
To meet the challenging needs of a variety of industrial applications, Brenner and Riddell [1, 2] discovered electroless nickel (EN) technology in 1946. EN coatings have got wide range of industrial applications because of their excellent mechanical, electrical, physical, corrosion, hardness, friction and wear resistance properties [3]. Electroless Ni-P coating is an autocatalytic deposition of a Ni-P alloy from an aqueous solution unto a substrate without the application of electric current. The substrate develops a potential when it is dipped in electroless solution called bath The electroless bath usually consisting of metal ions, reducing agents, complexing agents and stabilizers. Due to the developed potential, both positive and negative ions are attracted towards the substrate surface and release their energy through charge transfer process The process relies on the presence of a reducing agent, for example sodium hypophosphite in case of Ni-P which reacts with the metal ions to deposit metal. The bath used to operate at a particular level of metal ion and reducing agents concentration,
temperature, pH ranges and proper ranges of complexing agent. The performance of developed coatings is highly dependent on each of the factors such as metal ion, reducing agent, stabilizer, temperature, pH etc. The thickness corresponds to coatings is solely depends on the deposition rate which again depends on the process parameters. Each process parameter is responsible for the efficiency and crystallinity of electroless Ni-P deposits [4]. The stabilizer content does not have much influence on the coating efficiency although it promotes the formation of amorphous phase. Increase in concentration of reducing agent increases the deposition up to a certain value and further increase in concentration decreases the deposition. Temperature also affects the deposition significantly and for lower bath loading deposition is significantly high [5]. Coating thickness is not an affecting parameter for surface roughness of electroless nickel coatings [6], however roughness characteristic of electroless Ni-P coating is depends on nickel source [7]. Heat treatment is a key operation that marks the arrangement of atoms, depth, resistance against load and surface morphology of electroless nickel coating. The hardness increase when as-plated electroless nickel alloys are heated at 400°C for a suitable time period, the structure recrystallizes to mixture of nickel phosphorous solid solution and nickel phosphide because the recrystallization temperature of Ni-P is 340°C [8]. Generally, the optimal heat treatment regime is 400°C for 1 h or 260°C for 10 h as it results maximal hardness of electroless Ni-P coatings [9]. The properties and microstructures of electroless nickel coatings depend on the amount of phosphorous alloyed in the deposit [10]. Different optimization techniques [11] are developed to choose the most suitable approach for electroless nickel coatings to increase its efficiency. To obtain better chemical, mechanical, physical, magnetic, and other properties from the same coatings sometimes further metal elements are added into the chemical deposition process. To meet the challenges for the development of material with enhanced characteristics such as high temperature sustainability, higher hardness, lubricity, wear and corrosion resistant etc. is the main cause behind the merger of particles. Many soft particles such as WS₂, MoS₂, PTFE (poly tetra fluoro ethylene), graphite as well as hard particles as like WC, SiC, Al₂O₃, B₄C, diamond etc are there which generally used as additional particles. Each of the particles has a unique characteristic and because of that fact it provides effects on the overall properties and performance of the developed coating. The hardness of the as deposited sample also can be increased (nearly 50 %) by adding surfactants like SDS (sodium dodecyl-sulfate) and CTAB (cetyl trimethyl ammonium bromide) to the chemically deposited Ni-P coatings. It may because of the fact of change in structure from amorphous for Ni-P to crystalline-amorphous for surfactant added Ni-P [12]. Surface roughness of autocatalytic Ni-P is affected by the concentrations of surfactant in the deposition. Higher concentration (>0.6 g/l) of surfactant helps to reduce the average roughness value of the chemically deposited Ni-P coatings. Beside the bath constituents including additional particles, the friction characteristics of electroless nickel coatings are also dependent on the condition of the friction-wear testing and the counter face material used. Friction coefficient of electroless nickel coating is increased due to missing of natural lubricity because of the addition of hard particles viz., B₄C and SiC in the deposits [13, 14, and 15]. Whereas addition of softer particles viz. PTFE, Graphite and MoS₂ in the electroless deposition provides a drastic reduction in the friction coefficient value [15, 16, 17]. Wear resistance and hardness of a coated surface are correlated, though wear properties of the coatings are affected by many other factors such as the nature of the applied stress and the surface morphology. Phosphorus content and heat treatment are the two main parameters that affect wear resistance a lot. An attractive force is generated in between nickel atoms and the counterface material during the rubbing activity that causes the wear of electroless nickel phosphorus coating. Sometimes wear depth curve moves in negative direction that may because of the formation of buildup oxide debris in between the coated sample and counterface material [18]. Load is an important parameter that affects wear heavily as there exists an direct relationship and it does not bother with the condition of electroless Ni-P, whether as deposited or heat treated [19]. The optimization of the coating parameters [20] reported that the role of annealing temperature and bath temperature on wear performance of chemically deposited Ni-P is significant. For elevated temperature tribological tests, formation of continuous oxide film on contacting surfaces of the sample and the counter face helps to increase wear resistance and decreases friction coefficient
of the Ni-10% P coating [21]. High temperature application is responsible for shorter life of the coating component [22] may because of the becoming soft and worsening in the wear resistant activity. Wear and friction coefficient are both directly proportional to the applied normal load and inversely proportional to sliding speed in high temperature test. High temperature tests yield a lower value of coefficient of friction compared to room temperature tests which may be because of the oxide layer provides a lubricating effect resulting in lowering of the friction coefficient [23]. Wear rate corresponds to high temperature is found to be about 10 times more than room temperature wear for Ni-P coating, but this value decreases by about two folds when it mixed with Ag nano particles [24]. Tribological properties of Al₂O₃ and Ag based Ni-P composite coating were similar to each other [25]. Composite coating with silver in nano form can be reflected as a ‘chameleon’ coating, due to the development of self-lubricating thin film of Ag at sliding contact conditions at high temperature applications [26].

Electroless Ni-P coatings are proven at room temperature from tribological point of view but the same is yet not justified in high temperature environment. Load is also an important parameter that affects tribo-behaviour a lot. The present study attempts to bring out the friction and wear trends of the chemically deposited Ni-P coatings subjected to different load in high temperature environments.

2. Materials and experimental details

2.1 Materials

Cylindrical mild steel (AISI 1040) specimens with an average roughness value around 0.70 $R_a$ and a hardness of 202 HV₀.₁ are used as substrates for the deposition of the electroless Ni-P coating. Specimens are having a diameter of 6 mm and length of 30 mm is prepared using turning, drilling and surface ground operation.

![Figure 1. Experimental setup of electroless deposition](image)

| Bath composition | Working conditions |
|------------------|--------------------|
| Nickel chloride and Nickel sulphate (1:1) | 30 g/L | pH 4.5 |
| Sodium hypophosphite | 10 g/L | Time 4 h |
| Sodium succinate | 12 g/L | Deposition temperature 80°C |

Table 1. Bath composition and working conditions
2.2 Coating deposition
Soap water is used for initial cleaning of mild steel substrates, then given a pickling treatment with 50% hydrochloride acid for one minute. Finally, the cleaned samples are activated in palladium chloride solution at 55ºC temperature and placed in the electroless bath. Bath composition and operating conditions [27] are shown in Table 1. A double bath deposition is employed for all the substrates to enhance the coating thickness as desired in friction and wear tests.

Deposition time and bath volume is kept same for all specimens so that the coating thickness and bath loads are remains almost same. Thickness of the coating reaches nearly 50 µm. Distilled water is used to wash the samples after taken out of the electroless nickel bath. Heat treatment is provided to few coated specimens in the box furnace at 400ºC for 1 hour and then cooled naturally. Experimental set up of electroless deposition for Ni-P coating is shown in Figure 1.

2.3 Hardness
Vicker’s hardness of the samples are found out in as-deposited and heat treated condition at an indentation load of 100 g, dwell time of 15 s and a velocity of 25 µm/s. The Vicker’s method is based on a combination of mechanical and optical system. A square base pyramid shaped diamond is employed for producing the indentation. The size of the indentation (length of the diagonals) is measured with the help of an optical microscope which is then converted to a hardness value using appropriate formula. Three readings are taken on each of the opposite faces of the pin and the average value of hardness of each sample is evaluated. The average hardness value of the samples is found to be approximately 585 HV\(_{0.1}\) in as-deposited condition and 1005 HV\(_{0.1}\) for heat treated case.

2.4 Tribological performance
Pin-on-disc type tribotester is being used to evaluate friction and wear characteristics of the EN coated specimens under high temperature following ASTM G99-05 (2010) standard [28]. The effects of loads under dry, non-lubricated conditions on tribological performance in different test temperature are being studied. Both as deposited and heat treated coated samples are slide by selecting a track diameter of 60 mm against a counter face made of hardened steel. The loading of the pin is done precisely through a stepper motor and load cell arrangement. The rotating counter face disc is heated inductively to the desired temperature and the test is conducted in a closed chamber. Wear is evaluated by the conventional weight loss method and reported in the form of wear rate by following Archard’s equation. A button type load cell (10-100 N) is used to measured frictional force. For the present study, considering the low thickness of the coating, sliding speed and duration of the tests are fixed at 70 rpm and 5 minutes respectively.

Table 2. Testing equipment

| Number | Name                                              | Model               |
|--------|---------------------------------------------------|---------------------|
| 1      | Digital electronic balance                        | Afcoset             |
| 2      | Magnetic Stirrer                                  | Ika RCT basic       |
| 3      | Vicker’s micro hardness tester                    | UHL VMHT            |
| 4      | Tribo tester                                      | DUCOM, INDIA        |
| 5      | Field-emission Scanning Electron Microscope       | FEG Quanta 250      |
| 6      | X-ray diffractiometer                             | Rigaku, Ultima III |

2.5 Microstructure
Characterization tests are conducted after deposition of the coating to ensure about the proper development of the coating as well as after the tribological test to observe the nature of failure. In the present study, surface morphology study of the electroless Ni-P coatings is done by scanning electron
microscopy (SEM) in order to observe the microstructure of the coatings. Energy dispersive X-ray analysis (EDX) is done to evaluate the percentages of nickel and phosphorous (by weight) of Ni-P coatings. X-ray diffraction (XRD) analysis is used to identify different precipitated phases, so that the effects of heat treatment can be visualized.

The testing equipment used in the experiments included digital electronic balance (ER-182A), magnetic stirrer cum heater machine (Figure 1), Vicker’s micro hardness tester (VMHT MOT, Sl. No. 1002001), high temperature tribo tester (TR-20-M56), scanning electron microscopy machine and X-ray diffraction analyzer, as listed in Table 2.

3. Results and discussion

3.1 Tribological behaviour

In the current study, friction and wear behaviour of electroless Ni-P coatings are investigated at a sliding velocity of 0.220 m/s by varying the testing parameters viz. normal load and test temperature. The effects of each parameter on the friction and wear of the coating is deliberated in details. The experiments are arranged in an incremental manner by varying one factor at a time. Coefficient of friction and wear rate of as-deposited sample are expressed as a function of elevated temperature under different applied loads in Figure 2a and 2b respectively. Initial increase in friction coefficient is noticed with the increase in temperature from room temperature up to 100ºC but thereafter the same gradually decrease with the increase in temperature. High operating temperature results the softening of the material. Moreover, oxide layer formed during high temperature test provides a lubricating effect resulting in lowering of the friction coefficient [22-23]. The initial increase in the friction coefficient up to 100ºC may be due to the combined effect of the exposure to low temperature as well as the heat generated at the contact due to the tribological interaction between the coating and the counter face. This may be resulting in the change of shear rate of the coating material which turn affects the friction performance. A positive relation exists between load and coefficient of friction for room as well as high temperature condition. With the increases in load there is an increase in friction coefficient for any test temperature condition. Wear is evaluated by finding the wear volume and expressed in the form of wear rate by following Archard’s equation. It is found that wear rate escalations with intensification in applied load [19]. With the increase in temperature, the wear rate is also increased. Though at a temperature of 500ºC, wear rate decreases by quite an extent. It may be because of the in-situ heat treatment of the as deposited sample by crossing recrystallization temperature of 340ºC [8] that lead to increase in hardness as well as reduced wear rate.
Figure 3. (a) Variation of coefficient of friction and (b) wear rate of heat treated chemically deposited Ni-P against sliding velocity of 0.220 m/s by increase in temperature at different applied load

Figure 3 illustrates the coefficient of friction and wear rate trend for heat treated electroless Ni-P coatings at different operating temperatures and under various loads for a particular sliding velocity. Friction coefficient increases with increase in load similar to as deposited trend. An initial increase in coefficient of friction value is observed though with further increase in temperature it drops. Hence, coating softening phenomenon is also believed to occur for heat treated samples also as evident from the results. For room temperature tests, as deposited coatings shows a higher friction coefficient compare to heat treated samples which may be attributed to the fact that as-deposited Ni-P coatings exhibit lower hardness compared to heat treated samples [3]. Due to the softness and ductility, as-deposited coatings are easily deformable which results in an increase in the area of contact between the coating and the hard counterface. As a result, more friction force is required for shearing of the contact points formed [21]. Initial increase in temperature (up to 100ºC) provides higher rate of wear compared to room temperature but with further increase it drops in most of the cases.

Figure 4. Wear rate using fixed sliding velocity (0.220 m/s) by varying temperature for as deposited and heat treated samples under (a) load of 10 N (b) load of 30 N and (c) load of 50 N

Figure 4 compares the wear performance of as deposited coatings with heat treated ones at different operating temperatures for various normal loads. It is clear from Figure 4 that wear rate increases with the increase in temperature but as it crosses or nears the recrystallization temperature (around 340ºC), the scenario gets reversed. The percentage increase in wear resistivity at 500ºC w.r.t that at 300ºC...
operating temperature is higher for as deposited samples compared to heat treated samples. This is also proved from the post-test hardness results of as deposited Ni-P coatings which shows higher increment compared to that of heat treated samples.

Figure 5 indicates the descriptive curves aimed at coefficient of friction for chemically deposited Ni-P (both as deposited and heat treated condition) under an elevated temperature of 500°C at sliding velocity of 0.220 m/s with different applied loads. There is no such major change is detected in the friction coefficient value with the sliding duration after the early ephemeral run-in time. The value indicating friction coefficient are much closer to each other and no notable alteration is observed still after running through 60 seconds time period. Higher value of coefficient of friction is perceived for greater normal load and lowest at a load of 10 N. Increased normal load results in bigger area of contact between the two interacting surfaces. Hence, more tangential force is required to break the formed contacts which in turn show up in the form of increased friction coefficient [19].

Figure 5. Evaluation of coefficient of friction with time at typical temperature of 500°C and sliding velocity of 0.220 m/s at different normal load for (a) as deposited and (b) heat treated condition

Figure 6. SEM images of chemically deposited Ni-P coatings: (a) as deposited and (b) heat treated

3.2 Microstructure study
The difference in as deposited and heat treated coated surface are presented via SEM images as shown in Figure 6. Numerous globules are present on the surface of the developed coatings, few are larger in size nearly around 10-15 µm. There is no voids are visible in between the globules on the surface structure. The effect of heat treatment is represented by the coarse grain structure which is arising due to the propagation of globules size. SEM micrograph (Figure 7) shows the coating surface of as deposited and heat treated samples after wear testing at a temperature of 500º C with 10 N load and 0.220 m/s sliding velocity. It is observed through the SEM images that the worn surface is composed of few irregular grooves mixed with some agglomerates, peeling pit and delamination all over the Ni-P surface. This is revealing of the existence of both abrasive and adhesive wear phenomenon.

![Figure 7. SEM images of autocatalytic Nickel-Phosphorous coatings: (a) as deposited and (b) heat treated after high temperature wear friction test (10 N load, 0.220 m/s sliding velocity)](image)

### 3.3 Compositional analysis

Energy dispersed X-ray analyzer (EDX) together with SEM is used to find out the percentages of nickel and phosphorous of the chemically deposited Ni-P coatings. Both for as-deposited as well as heat-treated samples is carried out EDX analysis separately before and after the high temperature test and outcomes are given in Table 3.

**Table 3.** EDX results of Ni-P coatings for as deposited and heat treated sample before and after test

| Coatings and its condition | Ni (% wt.) | P (% wt.) | Total |
|---------------------------|------------|-----------|-------|
| As deposited              | 91.42      | 8.58      | 100   |
| Heat treated              | 91.56      | 8.44      | 100   |
| As deposited (tested at 500ºC) | 92.79      | 7.21      | 100   |
| Heat treated (tested at 500ºC) | 92.73      | 7.27      | 100   |

### 3.4 Phase structure analysis

Figure 8 shows the XRD plots found for substrate mild steel, as-deposited and heat treated electroless Ni-P coatings. Cu Ka radiation is used in XRD analysis to identify the key phases in the coatings both before and after heat treatment. X-ray diffraction results show that as-deposited Ni-P coating is almost
amorphous in nature with a series of small peaks very close to each other. Precipitation of nickel phosphide phases occurs with the heat treated (400°C, 1 hr), that helps to turns the coating as crystalline.

![Figure 8](image)

**Figure 8.** XRD plots of mild steel substrate, as-deposited and heat treated electroless Ni-P coatings

### 4. Conclusion

The effect of elevated temperature on friction-wear behaviour of autocatalytic Ni-P coating is deliberate under application of different normal loads. The coefficient of friction for chemically deposited Ni-P coating practices chief increment with rise in load under elevated temperature at constant velocity of 0.220 m/s. Coating is found to be amorphous in as-deposited condition but transforms into a crystalline structure with heat treatment. In high temperature tests it is observed that wear rate and friction coefficient is almost directly proportional to the applied load under a constant value of speed. Friction coefficient increases initially with the increase in temperature from room temperature up to 100°C but thereafter gradually decrease with the increase in temperature. The decrement wear for a temperature of 500°C is observed mostly for as-deposited sample as it exhibits a higher increase in hardness after the tests compared to already heat treated coatings. Scanning electron microscope images of the damaged surface of the coating reveals that mixed abrasive and adhesive wear phenomenon is present as mechanism behind wear for elevated temperature.

### References

[1] Brenner A and Riddell G E 1946 *J. Res. Nat. Bur. Stand.* **37** 31
[2] Brenner A and Riddell G E 1946 *J. Res. Nat. Bur. Stand.* **39** 385
[3] Sahoo P and Das S K 2011 *Mater. Design.* **32** 1760
[4] Jappes J T W, Ramamoorthy B and Nair P K 2005 *J. Mater. Process. Tech.* **169** 308
[5] Oraon B, Majumder G and Ghosh B 2006 *Mater. Design.* **27** 1035
[6] Taheri R, Oguocha I N A and Yannacopoulos S 2001 *Wear* **249** 389
[7] Sahoo P 2008 *Tribology Online*, **3** 6
[8] Elsener B, Atzei D, Krolkowski A, Rossi Albertini V, Sadun C and R. Caminiti 2004 *Chem. Mater.* **16** 4216
[9] Ashassi-Sorkhabi H and Rafizadeh S H 2004 *Surf. Coat. Tech.* **176** 318
[10] Allen R M. and Vandersande J B 1982 *Scripta. Metall.* **16** 1161
[11] Kundu S, Das S K and Sahoo P 2014 *IJMMME* **4** 1 (doi: 10.4018/ijmmme.2014100101)
[12] Elansezhian R, Ramamoorthy B and Nair P K 2008 *Surf. Coat. Tech.* **203** 709
[13] Ebrahimian-Hosseinabadi M, Azari-Dorcheh K and Vaghefi S M M 2006 *Wear* **260** 123
[14] Araghi A and Paydar M H 2010 *Mater. Design.* **31** 3095
[15] Wu Y, Liu H, Shen B, Liu L and Hu, W 2006 *Tribol. Int.* **39** 553
[16] Wu Y, Liu H Z, Shen B, Liu L and Hu W B 2006 Surf. Coat. Tech. 201 441
[17] Zou T Z, Tu J P, Zhang S C, Chen L M, Wang Q, Zhang L L and He D N 2006 Mater. Sci. Eng. A 426 162
[18] Palaniappa M and Seshadri S K 2008 Wear 265 735
[19] Krishnaveni K, Sankara Narayanan T S N and Seshadri S K 2005 Surf. Coat. Tech. 190 115
[20] Sahoo P 2009 Mater. Design. 30 1341
[21] Masoumi F, Ghasemi H R, Ziaei A A, and Shahriari D 2012 Int. J. Adv. Manuf. Tech. 62 1063
[22] Kundu S, Das S K and Sahoo P 2014 Procedia. Eng. 97 1698
[23] Kundu S, Das S K and Sahoo P 2015 BLB-International Journal of Science and Technology, Special Issue, ISSN 0976-3074 (Print) 84
[24] Alirezaei S, Monirvaghefi S M, Saatchi A, Ürgen M, and Motallebzadeh A 2013 T. I. Met. Finish. 91 207
[25] Alirezaei S, Monirvaghefi S M, Saatchi A, Ürgen M, and Motallebzadeh A 2013 Surface. Eng. 29 306
[26] Voevodin A A and Zabinski J S 2005 Compos. Sci. Technol. 65 741
[27] Sahoo P and Pal S K 2007 Tribol. Lett. 28 191
[28] ASTM Standard G99-05 2010, Standard Test Method for Wear Testing with a Pin-on-Disk Apparatus (West Conshohocken, PA: ASTM International) DOI: 10.1520/G0099-05R10